Title
THE EFFECTS OF ION HYDRATION IN SOLVENT EXTRACTION AND ION EXCHANGE

Author
Whitney, David C.

Publication Date
1962-10-12

UCRL-10505

University of California

Ernest O. Lawrence Radiation Laboratory

THE EFFECTS OF ION HYDRATION IN SOLVENT EXTRACTION AND ION EXCHANGE

Berkeley, California

DISCLAIMER

Research and Development

UCRL-10505
UC-4 Chemistry
TID-4500(18th Ed.)

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

THE EFFECTS OF ION HYDRATION IN SOLVENT EXTRACTION AND ION EXCHANGE

David C. Whitney
(Ph.D. Thesis)

October 12, 1962

Printed in USA. Price $2.75. Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D.C.

THE EFFECTS OF ION HYDRATION IN SOLVENT EXTRACTION AND ION EXCHANGE

Contents

C. Results and Discussion

III. Conculsion

THE EFFECTS OF ION HYDRATION IN SOLVENT EXTRACTION AND ION EXCHANGE

David C. Whitney
(Ph.D. Thesis)

Lawrence Radiation Laboratory
University of California
Berkeley, California

October 12, 1962

ABSTRACT

The extraction of $HClO_4$, $HReO_4$, HBr, HNO_3, $HAuCl_4$, and $HAuBr_4$ into dilute solutions of tributyl phosphate (TBP) in inert diluents has been studied, and the extracting species and extraction mechanism have been determined. It has been found for all the acids except HNO_3 that so long as the TBP concentration is $\leqslant 0.1$ M and the stoichiometric ratio TBP/H^+ is $\geqslant 3$ the only extracting species are the molecular adduct $TBP \cdot H_2O$ and the solvated hydronium ion $3TBP \cdot H_3O^+ \cdot mH_2O \ldots X^-$, an ion pair, where $0 \leqslant m \leqslant 1$. For $1 < TBP/H^+ < 3$ there are several possible species, whereas at $TBP/H^+ = 1$ the only species present in the organic phase is the salt $TBPH^+ \ldots X^-$. HNO_3 is found to extract as an anhydrous molecular adduct at all TBP and HNO_3 concentrations such that TBP/HNO_3 is > 1; the HNO_3 that extracts in excess of 1:1 with TBP is partially hydrated. These results are interpreted in terms of a proposed general model for such strong-acid-basic-solvent extraction systems.

Anion-exchange studies on the salts of the fatty acids have been carried out by using a quarternary ammonium (strong-base) resin. The selectivity of these resins in contact with very dilute external solutions (negligible resin invasion by nonexchange electrolyte) is considered due in large part to changes in the solvation of the ions, resulting from differences in the properties of the resin-phase solution and the external dilute aqueous solution. The resin-phase solution is a concentrated electrolyte solution with three significant differences from a dilute electrolyte solution: (a) the cationic species is fixed on the resin matrix; (b) electrostatic forces are stronger; (c) the water molecules in the resin phase have less cooperative structure. The tendency of large univalent ions to be forced out of the dilute solution into the resin phase because of their small degree of hydration and considerable water-structure-breaking character is considered, as well as the effects of specific group hydration.

The elution of tracer alkali metal and trivalent cations from cation-exchange resin columns by several uni-univalent salts and acids has been investigated. The elution order in dilute solution is explained as resulting from the water-water, ion-water, and ion-resin interactions in the system. Changes in this order and deviations of the elution behavior from the simple mass-action laws as the salt or acid concentration is increased are interpreted as being due to changes in these interactions. On the basis of the elution behavior in concentrated solutions, a model for the prediction of resin selectivities is proposed.

PREFACE

Ion exchange and solvent extraction are two of the tools used by inorganic chemists to study the behavior of substances in aqueous solution. In the past, much of the knowledge of the processes involved in the use of these tools has been of the empirical or semi-empirical type. It is the purpose of this study to present some basic foundations toward an understanding of ion-exchange and solvent-extraction processes and to provide some idea of the considerations involved in the formulation of any general theory for such processes.

Although there are many similarities between ion exchange and solvent extraction, since they both involve the transfer of a substance from a completely aqueous to a nonaqueous, or at least less aqueous, solution, they are treated separately in this study, except for a short summation statement in the conclusion. The evaluation of the results of the various experiments performed is more qualitative than quantitative, owing mostly to the great lack of knowledge of the thermodynamic properties of such complex systems. It is felt, however, that the results given herein will be of value in describing these systems; and it is hoped that studies such as this will eventually lead to the ability to derive accurate, quantitative data concerning both the processes themselves and the substances involved in them. This report is presented toward the end of achieving these goals.

I. SOLVENT EXTRACTION

A. Introduction

Solvent extraction has long been established as a fundamental technique for chemical separation and purification of organic compounds, but only within the last two decades has any great interest been shown in the application of solvent extraction to inorganic separations. The impetus to develop solvent-extraction methods was provided by the large-scale investigation of atomic energy and the subsequent need for simple, rapid, and specific separation of fissionable materials from both radioactive fission products and non-radioactive chemical impurities. About the same time, it was discovered by analytical chemists that not only was solvent valuable for separation of one component from a mixture, but also by changing conditions it was possible to carry out a whole series of clean separations of all the components in the mixture, which greatly simplified what heretofore had been very complex analyses. A comprehensive review of the early work is given by Morrison and Freiser[1] in their book on solvent extraction; more recent work is covered biennially in excellent reviews by the same authors.[2-4] Several other, more limited, reviews are also available.[5-7] A comprehensive discussion and analysis of the state of the art from the standpoint of mechanisms and general extraction behavior has been given recently by Diamond and Tuck.[8]

Quite aside from the role it plays in industrial and analytical separations, solvent extraction, particularly of inorganic substances, is of value to the physical chemist for the insight it gives into the nature of species in solution. Through its ability to isolate ions and molecules from aqueous solutions, the solvent is able to give some indication of hydration and solvation energies and the chemical behavior of water in aqueous and nonaqueous solutions.

1. Extraction of Inorganic Compounds

A solvent-extraction system may be characterized by the interactions among its various components. These interactions can be divided into three types--solvent-solvent, solvent-solute, and solute-solute--where "solvent" refers to either the organic liquid (or liquids, in the case of an extractant dissolved in an inert organic compound) or water, and "solute" refers to the inorganic compound. In general, solvent-extraction systems are chosen such that the two phases are essentially immiscible, so that the interactions can be considered separately for each phase (an exception to this is the case in which the organic phase is composed of two organic compounds, one of which is quite hydrophilic; in such a system water itself becomes a solute in the organic phase).

When the solute is in dilute concentration in the aqueous phase, it is possible to make several statements about the interactions listed above. Solvent-solvent interactions are similar to those found in the pure solvent. Solute-solute interactions are negligible, owing to the dispersion of the solute, while solvent-solute interactions are at their greatest. Since all inorganic solutes have an attraction for water, even if only of an induced dipole-dipole type, extraction occurs only if some means are available to counteract this attraction, thus making energetically feasible the transfer of the inorganic substance out of the aqueous phase and into the organic phase.

Such a condition can be effected either through the different characteristics of the solvent-solvent interactions in the two phases or through some specific solvent-solute interaction in the organic phase. These effects give rise to two broad classes into which solvent extraction of inorganic compounds may be divided—the first based primarily on the disruption of the physical and chemical structure of the solvent by the solute in each phase, the second based primarily on the specific chemical bonding which can occur between the solvent and solute in the organic phase. Since both these interactions are opposing the water-solute interaction (hydration), the general rule for either class is that the weaker the hydration, the better the extraction. A detailed discussion of these interactions, and examples of the subgroups contained in each class are given in the following paragraphs.

Considering first the solvent-solvent interactions: in pure water, at room temperature, each water molecule is hydrogen-bonded, on the average, about three other water molecules in a pseudotetrahedral short-range structure, each hydrogen bond involving 3 to 5kcal of energy.[9] (In the absence of quantitative data concerning entropy and ehthalpy for most of the reactions discussed herein, energy will be understood to mean the free energy, ΔF, of the reaction.) In order for a substance to dissolve in water, it must break a number of these hydrogen bonds, with a corresponding loss in bonding energy. This energy can be regained, however, if the dissolved substance is able to hydrate, i.e., to coördinate the water molecules around itself in some kind of solvation sphere, with the ensuing hydration energy making up for the loss of energy due to the breaking of the water-water bonds.

In most organic solvents, on the other hand, such intermolecular bonding forces are much weaker. The solvent does not offer much resistance toward the dissolution of a substance in it; however, neither does it have the ability to appreciably aid the dissolution by solvation of the substance, since the organic solvent is, in general, capable of only very weak intermolecular interactions.

Thus it is seen that the relative solubility of a given substance in each phase is governed by the degree to which it tends to solvate. In particular, a large, covalently bonded molecule, owing to its structure-breaking characteristics, prefers the organic solvent, while a small, ionic molecule, owing to its high hydration, prefers the aqueous phase. These considerations give rise to what can be termed a molecular extraction, one of the best and most thoroughly studied examples of which is I_2 extracting into CCl_4,[10] where the disruption of the water structure by large I_2 molecule causes the aqueous phase to eject the iodine into the CCl_4. Thus the energy lost when the water-water bonds were broken is regained, except for the small amount of energy needed to break the weak, intermolecular bonds in the organic phase.

A more quantitative measure of the effects of water-structure disruption by large molecules in the extraction of fatty acids, which proceeds in the order valeric > butyric > propionic > acetic.[11,12] Here the hydration energy derived from the carboxylate group, which is the same for all the acids, is being conterbalanced by longer and longer hydrocarbon chains which are protruding farther and farther into the water structure, with the result that the higher homologues are being ejected more and more strongly by the aqueous phase. The rise in the distribution ratio is roughly a factor of 2 per $-CH_2-$ group, which gives an idea of the effect of chain length on extraction.

Disruption of water structure is not limited to neutral molecules. Large, monovalent ions which show extraction behavior, such as tetraethylammonium,[13] tetraphenyl arsonium,[14] and tetraphenyl boron,[15] break a great number of hydrogen bonds when they dissolve in aqueous solutions; but the energy lost in these ruptures is more than regained by solvation of the counter ion. However, if both a large cation and a large anion are present in the same solution, this solvation is greatly decreased and both cation and anion tend to be ejected out of the aqueous phase. This transfer of ions results in a loss of electrostatic energy in the aqueous phase, but if an organic phase with a fairly high dielectric constant is available, a fair portion of this energy is regained and the water-water interactions are again maximized.

Finally a system that involves ion hydration and water structure is chelate extraction.[16,17] This type of extraction actually falls under both classifications, since two solvents are used. The first is a chelating agent--an organic ion that is able to satisfy two or more co-ordination sites of a polyvalent ion while at the same time neutralizing part or all of its charge. Several chelates may be attached to a cation so that it is co-ordinately saturated. The final result is a large, pseudo-organic species with very little or no charge, which behave very similarly to those described in the preceding paragraph and extract quite well into a second, inert organic solvent.

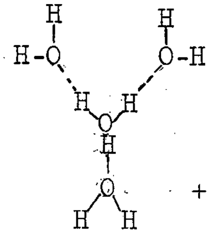
The second major class of extractions involves solvents that have the ability to co-ordinate to charged species, i.e., they are able to replace water as solvators. These solvents are all basic organic compounds that contain a nonbonded electron pair available for co-ordination with a co-ordinately unsaturated species; the most prominent examples involve a basic oxygen or nitrogen atom. The extraction is essentially a neutralization between a Lewis acid or electron acceptor and a Lewis base or electron donor; three types of Lewis acids that undergo extraction fairly readily are the (hydrated) proton,[18,19] associated acids,[12-18, 20-23] and large, covalently unsaturated species such as MO_2^{++}, M^{+++}, or M^{+4} nitrates.[24-26]

It is with this second class, and most particularly with proton extraction, that this work is concerned. The hydrogen ion, as present in strong acids, is unique in its role as the only small, univalent cation to extract appreciably in basic organic solvents; and the relatively large distribution ratios for the strongest acids imply that a very specific interaction is taking place between the proton and the solvent, an interaction that does not occur to nearly the same extent for any other cation of comparable (hydrated) size.

2. Extraction of Acids

The proton, being a positive charge concentrated in a very small volume, cannot exist alone in solution, but must coordinate with some electron donor.[27] In any system such as that last described, the electron donors are the acid anion, water, and basic organic solvent, and the extraction depends on the outcome of the competition for the proton among these three solvators.

Consider first a proton in a large volume of water. Because of its size and charge, it co-ordinates very strongly to one of the nonbonded electron pairs of the oxygen atom to form a hydronium ion, H_3O^+. This ion, because of the partial positive charge on each of the hydrogen atoms, is then able to form very strong hydrogen bonds to three other water molecules, yielding a species with the formula $H_9O_4^+$ and the structure



This species can be compared to an alkali metal cation plus its primary hydration shell, with the important exception that the three waters of hydration are held by specific bonds in specific directions in space, as opposed to the more general electrostatic attraction between alkalies and water molecules.

The foregoing ideas of proton hydration have been under intensive investigation during the last decade, and a large amount of experimental evidence has been accumulated in their support. The hydronium ion in the solid state (as, e.g., $H_3O^+ClO_4^-$) has been characterized by X-ray,[28,29] nuclear magnetic resonance,[30] infrared,[31] and Raman studies,[32] and infrared methods have detected it in strong acid solutions.[33] In aqueous acid solutions, numerous methods have been used to determine the hydration number of the proton, among them activity coefficients,[34-36] isopiestic measurements over ion-exchange resins,[37-39] acidity functions,[40,41] specific heats of solution,[42,43] and ion exchange of acetic acid,[44] all of which yield values that fall within a few tenths of 4.0. Theoretical calculations have been made by Grahn for H_3O^+ [45,46] and $H_9O_4^+$.[47] In addition, several reviews of the hydronium ion and its hydration have been published.[8,18,27,48,49]

Two techniques for determining hydration number deserve special mention, since they are more straightforward than those mentioned above. The first is a study of the masses of the singly ionized species observed when ions which are volatilized from pure water by a field-emission source are recorded by use of a mass spectrometer.[50] It was found that only four species were present, and the relative amounts of each were in the order $H_3O^+ > H_5O_2^+ > H_7O_3^+ > H_9O_4^+$. As the field strength was decreased, thus diminishing the disruptive forces on the ions, the proportion of higher-mass species increased at the expense of the lower-mass one with the proportion of $H_9O_4^+$ increasing most rapidly. This suggests that in the limit of no field at all, $H_9O_4^+$ would be an important--and possibly even the principal--species.

The other special technique for determining proton hydration is solvent extraction. As mentioned in the introduction, solvent extraction is particularly useful for the isolation of species that may be present in aqueous solution, especially those involving H_2O in their structure. With this in mind, several workers have utilized basic solvents to extract the hydrated proton and then have determined analytically the amount of water per hydrogen ion. Some systems and their H_2O/H^+ extraction ratios are as follows:

System	Ratio	Reference
diisoprophl ether – $HFeCl_4$	4 to 5	51
several ethers – $HFeCl_4$	3 to 4	52
dibutyl Cellosolve – $HClO_4$	4.1 to 4.5	18
tributyl phosphate (TBP) – $HClO_4$	3.6 to 4.6	18, 19, 53-55
TBP – HCl	3.9 to 4.3	18, 19, 56, 57
TBP – HBr	4.0 to 4.7	18, 19, 58
TBP – H_2SO_4	4.5	53
TBP – H_3PO_4	4.5	53
diisopropyl ketane – $HClO_4$	4.5	18
bis-(2-chloroethyl) ether – $HClO_4$	4.2	59

One other system of interest is that involving the more basic extractant tri-octyl-phosphine oxide (TOPO) and $HClO_4$. The H_2O/H^+ ratio appears to be 1.0, whereas the $TOPO/H^+$ ratio is 3.0,[60] implying the trisolvation of a hydronium ion by three TOPO molecules; this possibility is discussed more thoroughly in the section on TBP-acid-water.

Returning to the problem of solvator competition for the proton, consider now the extraction of a strong acid, such as perchloric acid, in which the anion is such a poor electron donor that it is unable to compete with either the water or the basic solvent for the proton and is present merely to preserve electrical neutrality. The extent of extraction depends on the ability of the organic base to attract the proton away from the very favorable water environment that surrounds it, and this ability is related to the strength of the (hydrogen) bond formed between the acid and base, the steric availability of the basic group, and the extent to which the organic phase accepts charged species and any possible accompanying hydration spheres.

A typical list of extractants for which data are available, in order of base strength, is trialkyl amines > trialkyl phosphine oxides > trialkyl phosphates > ketones and ethers. The distribution ratios for strong acids also decrease in the same order, indicating that the most important factor is the strength of the hydrogen bond. This decrease is not nearly as rapid, however, as would be expected from the differences in the base strengths of the organic solvents, as determined by their ability to compete with water for protons. This phenomenon occurs through a new mode of extraction, whereby the hydrogen ion extracts not as a bare proton, as in the amine case, but as a hydrated species, such as H_3O^+ or $H_9O_4^+$. Since it requires much less energy to free $H_9O_4^+$ from an aqueous solution than H_3O^+, which in turn requires less energy than H^+, solvents that can accommodate the hydrated species are able to extract acids much better than would be expected from their base strengths alone. Since the bonding to the hydrated proton must necessarily be weaker, the extraction is much less than for those solvents which extract the proton directly.

With these considerations in mind, the experimentally observed extraction orders and extracting species for the various solvents are readily explained. The most basic amines extract the anhydrous proton (and its accompanying anion) directly and completely to form a non-hydrated trialkylammonium salt. The less basic phosphine oxides are not able to remove the proton from its fundamental aqueous form, H_3O^+. Instead acids must extract as the trisolvated hydronium ion, with a corresponding decrease in the total amount of extraction due to the distribution of the positive charge among three protons, which form correspondingly weaker hydrogen bonds with the extractant. Farther down the scale, the phosphates are unable to displace even the first hydration shell of the hydronium ion, so the H_2O/H^+ ratio is on the order of 4, corresponding to the extraction of $H_9O_4^+$. It is interesting to note that for the even more weakly basic ketones and ethers, the ratio is still about four, although the extraction has become much poorer, implying that any secondary hydration shell of $H_9O_4^+$ is much more weakly bonded, so that the aqueous-phase hydrogen bonding does not permit it to extract.

So far in this discussion the effect of the anion on acid extraction has been ignored. For strong, completely ionized acids, it has been assumed that the anion is unable to participate in the competition for the proton, and thus its only function is to maintain electrical neutrality. However, since the transfer of the anion from the aqueous phase to the organic phase is subject to the same solvent-solvent and solute-solvent interactions as any other solvent extraction process (as discussed in the introduction), the anion has a definite influence on the extent of the extraction. In particular, the larger, lower-charged, and more hydrophobic the anion, the better the extraction will be. Thus those acids mentioned above, and especially the larger $HClO_4$ and $HFeCl_4$ with their singly charged, water-structure-breaking anions, are those which extract best.

If the anion is a strong enough base to enter into the competition for the proton--i.e., the acid is not completely dissociated in aqueous solution--an entirely different extraction system is formed This system is similar to that previously described for the extraction of fatty acids into inert solvents, with the added possibility of hydrogen bonding in the organic phase. In this case, the extraction takes place through the formation of a hydrogen bond between the organic base and the molecular acid, and since the extracting species is essentially a neutral molecule, so that no transfer of charge between phases occurs, the distribution ratios are quite high. Examples of this system are TBP-HNO_3,[21,22] TBP-trichloroacetic acid,[18] and dibutyl-ether--HCOOH.[8]

3. Presentation of the Problem

In spite of the relative wealth of data collected on the extraction of acids by TBP, a great deal of doubt, and a fair amount of disagreement, remains concerning the extracting species and extraction mechanisms. Most of the difficulty resides in the fact that by far the larger amount of the data has been taken using either pure TBP or concentrated solutions ($> 0.5\underline{M}$) of TBP in an inert solvent. It has been shown by McKay et al.[20] that the activity coefficients of TBP fall very rapidly as the TBP concentration (in kerosene) rises, being only 0.4 at 0.5 $\underline{M}$, and thus TBP solutions and TBP itself exhibit far from ideal behavior. These authors have subsequently pointed out that because of this behavior one must be very cautious in drawing conclusions from calculations involving organic-phase concentrations, rather than activities, as an inaccurate picture of the extraction may result.[61]

In the absence of activity coefficients for the various species present in the extraction of acids by TBP, the best solution to the problem of nonideality is to limit the concentration of the extractant to less than a few tenths molar in some inert organic diluent and to choose the experimental conditions such that only a few percent of the extractant molecules are involved in the extracting complex. Thus the organic phase will retain essentially the properties of the inert diluent, and changing the concentration of the extractant, acid, or water in that phase will presumably have only a slight effect on the activity coefficients of these various species. Furthermore, the equilibrium expressions are written so that they involve ratios of the activity coefficients instead of using the coefficients directly; since activity coefficients for different species generally change in the same manner with changes in conditions, taking their ratio tends to reduce the effects of the change.

Although the total concentration of the several species in the organic phase remains low, it is still possible to observe the effect that varying their concentrations will have on the extraction. In particular, by allowing only one component to vary, holding the others constant, it is possible to establish the dependence of the extracting species on that component and hence its part in the complex. After determining in this manner the nature of the extracting species in the dilute extractant, one may extend the study to more concentrated (and more nonideal) solutions, and variations in the extraction can be interpreted on the basis of changes in activity coefficients and more complex interactions in the organic phase.

Another advantage to using dilute solutions is that the solubility of water in the organic phase is greatly reduced, permitting a much more accurate appraisal of the role of water in the extracting complex. Also, since the distribution ratios are greatly reduced in dilute solutions as compared with pure TBP, it is possible to use very high aqueous-phase acid concentrations, with their correspondingly low water activities, and observe the variation in the extraction caused by reducing the effective concentration and coordinating ability of the water.

B. Experimental Method

1. Reagents

All chemicals were reagent grade and, with the exceptions noted below, were used as purchased. Acids were diluted with distilled water; neutral or basic solutions were diluted with conductivity water ($> 7 \times 10^7$ ohm). Standard analytical methods were used in all aqueous concentration determinations. Several of the chemicals required purification; the methods used are described in the following paragraph.

The tributyl phosphate (TBP) was washed several times with 0.04 M NaOH to remove acid impurities and rinsed with distilled water (pH ≈ 5) until the rinse water was of pH 6 or less. The TBP was then dried under vacuum and stored in the dark over Drierite ($CaSO_4$). The HBr was saturated with H_2S gas to reduce any Br_2 to HBr. Then the solution was distilled and the fraction boiling between 121 and 129°C (constant-boiling HBr, 47%) was collected. All HBr solutions were made from this constant-boiling HBr and all were kept in sealed amber-glass bottles to prevent decomposition. The methanol used in the Karl Fischer titrations was dried with molecular sieves.

$HReO_4$ was not commercially available and had to be made from $KReO_4$. The method was as follows: 50 g $KReO_4$ was dissolved in 6 liters of H_2O and passed through 100 ml of Dowex AG-50 × 12 cation-exchange resin, which had been previously treated with 500 ml 3 M $HClO_4$ and 1000 ml H_2O. The resulting $HReO_4$ was evaporated to 100 ml and analyzed; the analysis showed the concentration to be 1.74 M $HReO_4$ with < 1% $KReO_4$ present.

$HAuCl_4$ solutions in HCl were made by dissolving weighed quantities of Au foil in HCl + HNO_3, evaporating down to dryness three times with HCl and taking up the resultant $HAuCl_4$ in HCl solutions of known concentration. These solutions were kept in the dark to prevent decomposition.

Radioactive tracers were produced by irradiation of naturally occurring isotopes in the Livermore pool-type reactor or the General Electric test reactor. $KReO_4$, after irradiation, was allowed to stand for five days in order to let short-lived products (mainly K^{42}, $t_{1/2}$ = 12.4 h and Re^{188}, $t_{1/2}$ = 17 h)[62] decay, then dissolved in H_2O to form a solution approx 10^{-6} M in $KReO_4$ with a specific activity of 10^5 counts/min/μl. Au foil was dissolved immediately after irradiation in HCl + HNO_3, evaporated down to dryness three times with HCl, and taken up in 0.5 M HCl to form a solution approx 10^{-5} M $HAuCl_4$ with a specific activity of 10^5 counts/min/μl.

2. Procedure

a. Tracer Experiments

Between 5 and 10 μl of tracer solution was injected with a micropipet into a two-phase mixture consisting of equal volumes of acid solution and extractant solution(generally 5.00 ml of each phase) in 60-ml glass-stoppered bottle. The samples were shaken on a mechanical wrist-type shaker for 15 to 30 min, transferred to 12-ml centrifuge cones, and centrifuged for three min. Duplicate 2.00-ml aliquots were taken from the upper phase, and one 2.00-ml aliquot was taken from the lower phase, the aliquots being placed in 1-dram screw-cap vials. The vials were counted with a well-type NA(Tl)I scintillation counter and single-channel pulse-height analyzer; the ratio of the counts/min in each phase (after correction for background) was taken to be equal to the distribution ratio for the tracer acid.

A few comments concerning some of the steps given above are in order. The distribution of a tracer acid between an aqueous acid and an organic extractant should be independent of the concentration of the tracer, so long as that concentration is negligible with respect to both of the macro-concentrations and the same species is extracting at all concentrations. In the extraction of $HReO_4$ this must, of necessity, be true in the aqueous phase, since the macro-acid and tracer acid are identical and the conditions of the extraction were such that the organic phase had only a few percent of its extractant molecules used in the extraction in almost every case. This concentration independence should also hold for $HAuCl_4$ extracting from HCl whenever the HAuCl concentration is < 1% of both the extractant and HCl concentrations. It was found, however, that curves of D vs initial aqueous $HAuCl_4$ concentration pass through a minimum between 10^{-6} and 10^{-4} M $HAuCl_4$, the exact value depending on the HCl concentration and the nature (but not the concentration) of the extractant and inert diluent (similar nonconsistancy, but no minimum, has been observed by other workers).[63] Although the difference between the minimum and maximum of the curve was a factor of two or less, it occurred reproducibly and necessitated that the initial aqueous $HAuCl_4$ concentration be kept constant. This was done either by using known $HAuCl_4$ in HCl solutions (generally 10^{-5} M) to which was added a negligible amount of tracer $HAuCl_4$, or by carefully adding precisely 10 μl of a tracer solution of known concentration (generally 5×10^{-4} M $HAuCl_4$) to the $HAuCl_4$-free sample, so that the major portion of the data is for aqueous $HAuCl_4$ either 10^{-5} or 10^{-6} M initially.

The time required for the samples to come to equilibrium is presumably on the order of a few minutes or less, since variations of the shaking time over the range of .5 to 120 minutes did not produce significant differences in distribution ratios. The normal range of 15 to 30 minutes used in these experiments was chosen arbitrarily. The centrifugation time was also arbitrarily chosen, since longer times showed no changes in the distribution ratios and tended to promote evaporation of the organic phase.

Since the distribution ratios ranged from 10^{-4} to 10^{4}, extreme care was required to prevent upper-phase contamination of the aliquots of the lower phase for counting. The best technique found was to pass a steady stream of air through the pipet tip while inserting the pipet through the upper phase, draw an excess amount of the lower phase into the pipet, and allow this excess to flow slowly through the tip while the pipet was being withdrawn from the centrifuge cone, at the same time wiping the outside of the pipet with an absorbent tissue. By use of this technique it was consistently possible to remove 2.00-ml aliquots of the lower phase that contained < 1 part in 10^5 of the upper phase.

The well crystal was 1-3/4-in. in diameter by 2 in. high, with a well 3/4-in. in diameter by 1-1/2 in. deep, and gave a very high geometry. The response time of the counting apparatus was approx 5 μsec, which meant that aliquots of up to about 2×10^5 dis/min could be counted with < 2% loss in counts. Aliquots were counted for a minimum of 10^4 counts or 10 minutes, whichever occurred first, but under no circumstances for < 1 minute.

In some cases the inert diluent was found to have an appreciable distribution ratio, even with no extractant present. This could be due either to basic impurities in the solvent or to mechanical occlusion of the aqueous phase. In either case it had to be considered as a correction factor, and the ratios so obtained were subtracted from those with extractant present to yield the true distribution ratios.

b. Organic-phase analyses

Equal volumes of acid solution and extractant solution were shaken for one hour in a glass-stoppered bottle. The samples were transferred to centrifuge cones and centrifuged for 2 to 3 minutes, and the organic phase transferred to a 60-ml glass-stoppered bottle. Aliquots were taken of the organic phase for acid, water, and infrared analysis.

In these experiments the organic phase was always a dilute solution of TBP in CCl_4. No study was made of extraction vs time, except that shaking for four hours showed no change in the distribution ratio. Centrifugation time was not critical except when the two phases had approximately equal densities, when three minutes or more was sometimes required. Since the distribution ratios were in the range 10^{-2} to 10^{-5} and the organic phase was the lower phase in almost every case, the same precautions as in part A were required for clean phase separations. Owing to the unstable nature of concentrated HBr solutions, it was necessary to carry out experimental observations on them immediately after separation; the H_2O, HNO_3, $HClO_4$, and $HAuCl_4$ solutions showed little change even after several weeks of standing.

The acid content of the organic phase was determined by addition of a known (excess) amount of 0.01000 M NaOH to a two-phase mixture of the organic aliquot and 10 ml conductivity water, adding three drops of 0.1% phenol red (pK = 7) and titrating to the end point with 0.01000 M HCl.[64] A blank was run using a dry solution of TBP in CCl_4 of the same concentration, and the amount of NaOH used for a blank was subtracted from that used for the samples. The accuracy of this method was ± 1% or ± 0.0001 M, whichever was larger, as determined by injecting known amounts of acid into TBP solutions and titrating as described above.

The water content of the organic phase was determined by the Karl Fischer method.[65] A blank solution of 2 to 3 ml dried methanol and 0.1 to 1.0 ml pyridine was first titrated by use of the visual end point, then the organic-phase aliquot was added to the blank and a new end point determined, the difference between the end points being a measure of the organic-phase water content. The Karl Fischer reagent was standardized by the same method, using known water-in-methanol and water-in-TBP solutions which had been prepared by careful injection of accurately known volumes of water into dried methanol and TBP. The accuracy of this method was ± 3% or ± 0.001 M, whichever was larger.

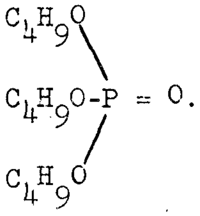
Infrared measurements were made on a Beckman IR-5 double-beam recording spectrophotometer, with dry CCl_4 or a dry TBP solution of the same concentration as the sample used as a reference. Both sample and reference were contained in matched 2.0- or 1.0-mm cells with CaF_2 windows, 0.5-mm cells with AgCl windows, or 0.1-mm cells with Irtran-2 windows. The cells were calibrated for quantitative use by comparison of the absorbance values of the water peaks in spectra of H_2O-TBP solutions prepared by both injection and saturation with the values given by Karl Fischer titration and from injected concentrations. The Absorbance values for water in CCl_4 were also determined in order that corrections could be made to the total absorbance and a measure of TBP-bonded water alone could be ascertained. Water concentrations determined in this manner were accurate to ± 4% or 0.0003 M. No attempt was made to do quanitative analysis for acid concentrations, because of the complexity of the spectrum and the relatively low resolution of the instrument.

All experimental work was done at room temperature, 23 ± 2°C, with no apparent changes in extraction occurring over this range.

C. Results and Discussion

1. Tributyl Phosphate-Water

The extractant used for the major portion of this study, tri-n-butyl phosphate (TBP), is less basic than the amines and is known to extract strong acids with the accompaniment of water. TBP is an ester of phosphoric acid and butyl alcohol, and has the structure



There are four basic sites in the molecule, corresponding to the four oxygen atoms, but the terminal oxygen atom of the P = o bond far exceeds the other oxygen atoms in base strength and can thus be considered to be the principal coordinating site for acidic species (possible exceptions to this for very high acid concentrations are presented in the section on concentrated solutions). Since TBP and the acid anion are both bases—that is, they both contain electron-donor groups—no significant amount of coordination would be expected between them and it is assumed that none exists.

It has been observed by several authors that water has an appreciable solubility in TBP. Since the presence of water in the organic phase would have an effect on the extraction of acids, both in terms of the relative suitability of the organic phase for charged species and in terms of the availability of the TBP for proton solvation (since TBP that is bonded to H_2O cannot be used for acid extraction), it was necessary that the extraction of water alone by dilute TBP in CCl_4 be investigated.

The equation for the reaction can be written

$$n\overline{\mathrm{TBP}} + H_2O = \overline{n\mathrm{TBP}\cdot H_2O} \qquad (1)$$

the superscript bar indicating the organic phase. The corresponding equilibrium constant is

$$K_{H_2O} = (\overline{nTBP\cdot H_2O})/(H_2O)(\overline{TBP})^n = [\overline{nTBP\cdot H_2O}]\gamma_{\overline{nTBP\cdot H_2O}}/[H_2O]\gamma_{H_2O}[TBP]^n\gamma^n_{\overline{TBP}}\ , \tag{2}$$

where parentheses signify activities and brackets concentrations. Two assumptions may be made:

(a) $(H_2O) = [H_2O]\ \gamma_{H_2O} \approx 1$, since the solubility of TBP in H_2O is negligibly small;

(b) the ratio $\gamma_{\overline{nTBP\cdot H_2O}}/\gamma^n_{\overline{TBP}}$ is a constant, since the two species are in dilute solution in CCl_4.

The equation then becomes

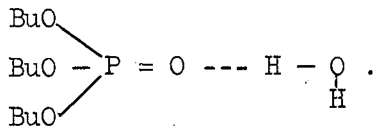
$$K'_{H_2O} = [\overline{nTBP\cdot H_2O}]/[TBP]^n\ ; \tag{3}$$

taking logarithms and rearranging yields

$$\log\ [\overline{nTBP\cdot H_2O}] = n\ \log\ [\overline{TBP}] + \log\ K'_{H_2O}. \tag{4}$$

Thus if there is some species $nTBP\cdot H_2O$ present in the organic phase, a plot of the logarithm of the organic-phase H_2O concentration vs the logarithm of the equilibrium TBP concentration (that is, the total TBP concentration minus n times the organic-phase H_2O concentration) results in a straight line of slope n, where n is the number of TBP molecules per water molecule in the extracting species.

Organic-phase water concentrations were determined by the Karl Fischer method for water-saturated TBP solutions that range from 0.1 to 60% by volume (0.00316 to 2.20 $\underline{M}$) in CCl_4 (Table I) and the results plotted (after subtraction of the H_2O dissolved in CCl_4), as described above, in Fig. 1. It is seen that a straight line of slope n = 1.0 is obtained from 0.003 to 0.1 M equilibrium TBP, implying the existence of the species $TBP \cdot H_2O$ throughout, and presumably below, this region. From the polar nature of the two species involved, the bonding presumably takes place through one of the protons of the water molecule to form a moderately strong hydrogen bond, giving a structure such as



In TBP concentrations of > 0.1 M, outside the region that may properly be called "dilute", the line curves upward, indicating a greater relative uptake of H_2O by the more concentrated solutions. This change in slope suggests either the presence of some new, more highly hydrated species or some other breakdown of assumption (b) in that the ratio of the organic-phase activity coefficients is no longer constant. The behavior of water in these more concentrated solutions is suggested in a subsequent portion of this section, where the infrared spectra of such solutions are discussed.

In the region below 0.1 M (corresponding to < 3% by volume TBP), Eq. (3) is completely applicable for n = 1, and $K'_{H_2O} = 0.15$. In making the subtraction for the solubility of H_2O in CCl_4, it was assumed that the water dissolving in CCl_4 was completely independent of the water dissolving in TBP, so that the correction was merely the solubility of water in pure CCl_4 (0.0099 M) times the mole fraction of CCl.

In an effort to determine the reasons for the deviation from the straight line at higher TBP concentrations, and also to aid in the interpretation of the acid-extraction data, a method was developed for determination of H_2O concentration in the organic phase by infrared

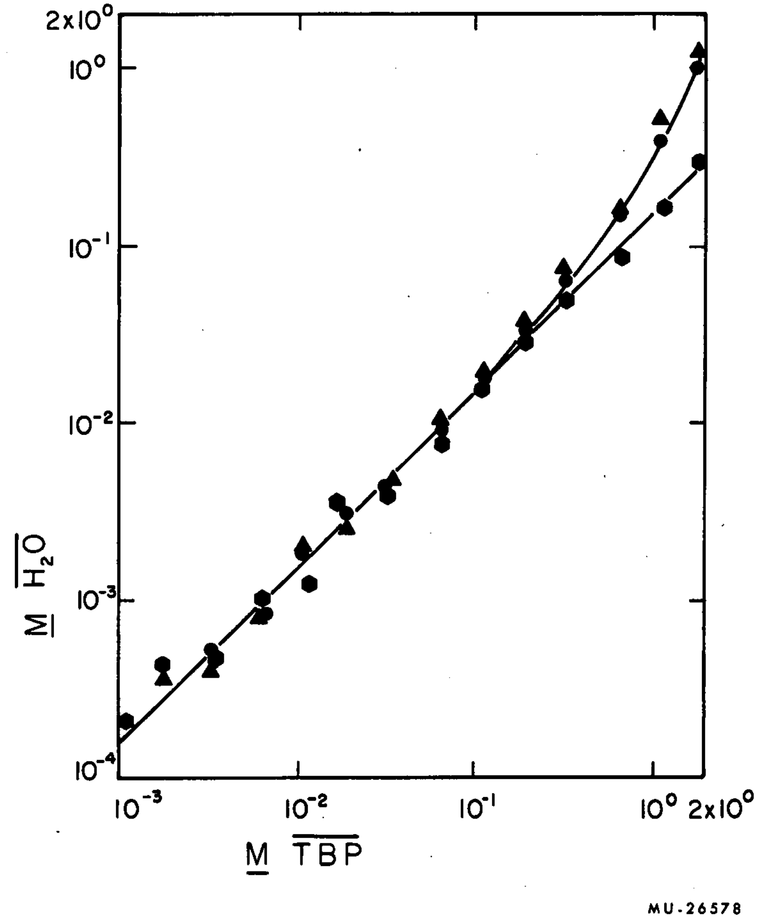
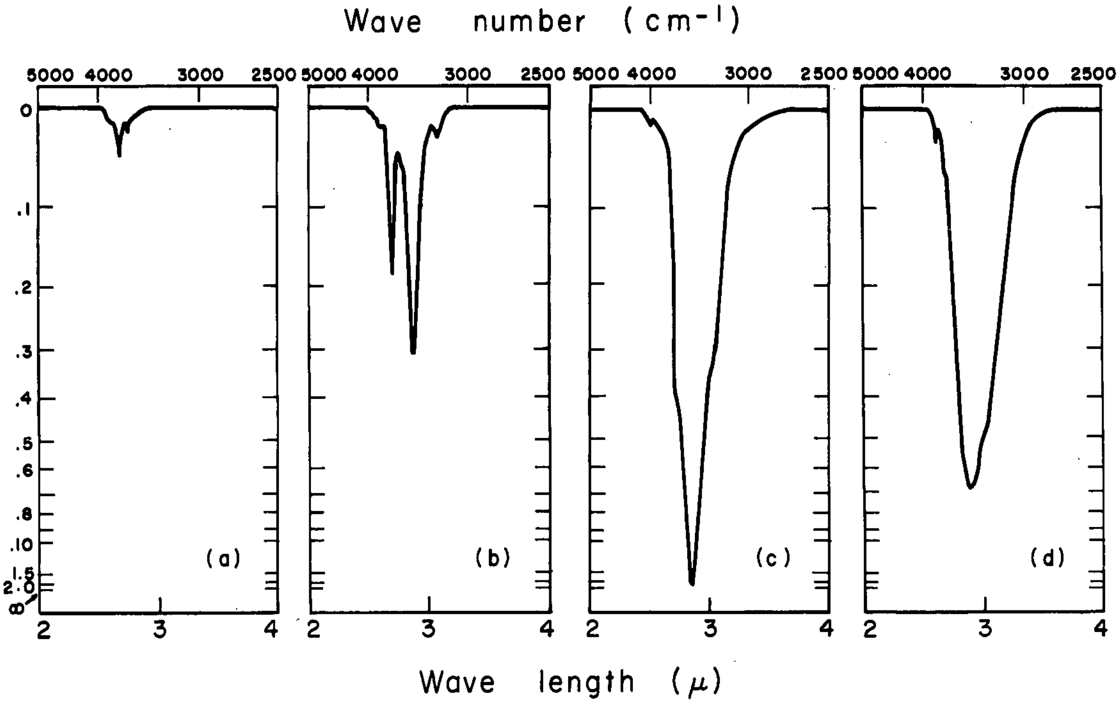


Fig. 1. Variation of water content of organic phase (CCl_4 diluent) with TBP concentration, corrected for solubility of H_2O in CCl_4: ●, Karl Fischer; ⬢, 2.72-μ peak; ▲, 2.90-μ peak.

analysis. The wave lengths of the absorption peaks of water in the range 2 to 16μ are shown in Table II for H_2O in several different physical states. Of those wavelengths listed for H_2O in TBP-CCl_4 solutions, only those at 2.72 and 2.90μ were suitable for quantitative study, the others being either too small, or, in the case of the 6.17-μ peak, too susceptible to interference from CCl_4, TBP, or hydrogen-bonding absorbances; discussion of the changes in the peaks is limited to those given.

It will first be noted that the locations and absorbance ratios of the two peaks are nearly identical for gaseous H_2O and H_2O dissolved in CCl_4, indicating for both cases that only the monomer is present and there is no hydrogen bonding. When H_2O is extracted into dilute (< 0.1 *M*) TBP in CCl_4, however, there is a shift to higher wavelength, or lower energy, in both peaks, and the peak-height ratios have changed from 2.70:2.75 $\approx$ 4 for the ratio of 0.5 for 2.72:2.90 (Fig. 2). Both the shift and change in ratio can be ascribed to the formation of the hydrogen bond (see structure p. 20) which weakens both O-H bonds and also enhances the symmetric stretch at the expense of the asymmetric. In order to ascertain whether all the peaks observed in the TBP-H_2O spectrum and ascribed to H_2O were actually due to H_2O, spectra were taken of HDO- and D_2O-saturated TBP. The new peaks were shifted in wavelength from those given for the monomeric HDO and D_2O by the same factors as the H_2O-TBP peaks were shifted from the monomeric H_2O.[66,67]

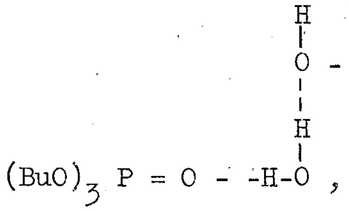
The absorption spectra were taken of the previously described 0.1 to 60% TBP in CCl_4 solutions and the quantitative results for H_2O concentration from both the 2.72- and 2.90-μ peaks are shown in Fig. 1. It is seen that both peaks and the Karl Fischer analysis agreed quite well so long as the TBP concentration remained below 0.1 *M*. However, the values given by the two peaks diverged above 0.1 *M*, the 2.90-μ peak value going as the Karl Fischer value (i.e., showing total water), while the 2.72-μ peak values continued along the line of slope $n = 1$.



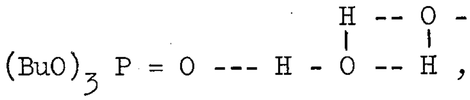
MU-26575

Fig. 2. Infrared spectra of (a) H_2O-saturated CCl_4, (b) H_2O-saturated 0.128 M TBP in CCl_4, (c) H_2O-saturated 2.11 M TBP in CCl_4, (d) liquid H_2O film.

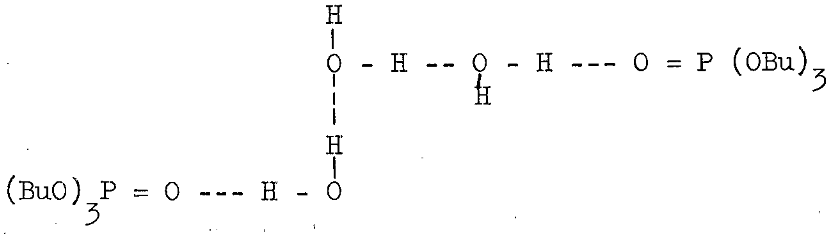
From the various considerations given above, it can be concluded that the 2.72-µ peak represents the -O-H stretch for a non-hydrogen-bonded proton, since it is higher in energy, does not account for the total water content in concentrated TBP-H_2O solutions, and is less affected by hydrogen bond formation. Also, as will be seen in a subsequent section, it is unaffected by the presence of acid in the organic phase. On the other hand, it was concluded that the 2.90-µ peak represents the hydrogen-bonded -O-H stretch, since it is at a lower energy, reflects the total water content at all TBP concentrations, and is greatly affected by the formation of hydrogen bonds. Also, it is very responsive to acid in the organic phase. Similar conclusions have been reached by other workers for intramolecular hydrogen bonding in diols.[68,69] On application of these conclusions to the concentrated TBP-H_2O solutions, it appears that above 0.1 M TBP water is able to form complexes containing more than one H_2O molecule, such as



$$(\mathrm{BuO})_3\,\mathrm{P} = \mathrm{O}\ \text{- -}\mathrm{H}\text{-}\overset{\substack{\mathrm{H}\\ | \\ \mathrm{O}-\mathrm{H}\\ \vdots \\ \mathrm{H}\\ |}}{\mathrm{O}}\ ,$$



$$(\mathrm{BuO})_3\,\mathrm{P} = \mathrm{O}\ \text{---}\ \mathrm{H} - \overset{\substack{\mathrm{H}\ \text{--}\ \mathrm{O} - \mathrm{H}\\ |\qquad\quad |}}{\mathrm{O}\ \text{--}\ \mathrm{H}}\ ,\ \text{or}$$



$$\begin{array}{l} \qquad\qquad\quad \mathrm{H}\\ \qquad\qquad\quad |\\ \qquad\qquad\quad \mathrm{O} - \mathrm{H}\ \text{--}\ \underset{\mathrm{H}}{\mathrm{O}} - \mathrm{H}\ \text{---}\ \mathrm{O} = \mathrm{P}\ (\mathrm{OBu})_3 \\ \qquad\qquad\quad \vdots \\ \qquad\qquad\quad \mathrm{H} \\ \qquad\qquad\quad | \\ (\mathrm{BuO})_3\mathrm{P} = \mathrm{O}\ \text{---}\ \mathrm{H} - \mathrm{O}\end{array}$$

The main conclusions that can be drawn from the behavior of H_2O-TBP solutions is that in order for the advantages of dilute solutions to be retained the TBP concentration must remain below a few tenths molar, and most desirably below 0.1 M. In all the acid-extraction studies in subsequent sections of this work the TBP concentration was 10% by volume or less, corresponding to equilibrium concentrations of 0.3 M or less.

Although it was realized that the higher concentrations of this range are not ideal solutions, it was felt that the large increase in extraction afforded by the greater TBP concentration more than overbalanced the slight loss in ideality. In all cases, enough points were taken inside the ideal range to allow good extrapolations up to 0.3 M TBP, and no appreciable differences between extrapolated and actual points were noted.

2. Tributyl Phosphate—Acids

The general equations for the extraction of a strong acid HX by TBP can be written as

$$H^+ + X^- + mH_2O + n\overline{TBP} = \overline{nTBP \cdot HX \cdot mH_2O} \qquad (5a)$$

if the organic species is molecular or

$$H^+ + X^- + mH_2O + n\overline{TBP} = \overline{nTBP \cdot H^+ \cdot mH_2O \ldots . X^-} \qquad (5b)$$

if the organic species is ion-paired, or

$$H^+ + X^- + mH_2O + n\overline{TBP} = \overline{nTBP \cdot H^+ \cdot H_2O} + \overline{X^-} \qquad (5c)$$

if the organic species is completely ionized, where for all three equations the superscript bar indicates a species in the organic phase and aqueous ion hydration has been omitted. The corresponding equilibrium constants are

$$K_{HX} = \frac{(\overline{nTBP \cdot HX \cdot mH_2O})}{(HX)\ (H_2O)^m (TBP)^n} = \frac{[nTBP \cdot HX \cdot mH_2O]\gamma_{\overline{nTBP \cdot HX \cdot mH_2O}}}{[H^+][X^-]\gamma_{HX}[H_2O]^m \gamma^m_{H_2O}[TBP]^n \gamma^n_{TBP}}, \qquad (6a)$$

$$K_{HX} = \frac{\overline{(nTBP \cdot H^+ \cdot mH_2O \ldots X^-)}}{(HX)\ (H_2O)^m\ (TBP)^n} = \frac{\overline{[nTBP \cdot H^+ \cdot mH_2O \ldots X^-]}\gamma_{\overline{nTBP \cdot H^+ \cdot mH_2O \ldots X^-}}}{[H^+][X^-]\gamma_{HX}[H_2O]^m\gamma^m_{H_2O}[\overline{TBP}]^n\gamma^n_{\overline{TBP}}}, \quad (6b)$$

$$K_{HX} = \frac{\overline{(nTBP \cdot H^+ \cdot mH_2O \ldots X^-)}}{(HX)\ (H_2O)^m(TBP)^n} = \frac{\overline{[nTBP \cdot H^+ \cdot H_2O]}\,\overline{[X^-]}\gamma_{\overline{nTBP \cdot H^+ \cdot mH_2O \cdot X^-}}}{[H^+][X^-]\gamma_{HX}[H_2O]^m\gamma^m_{H_2O}[TBP]^n\gamma^n_{\overline{TBP}}}, \quad (6c)$$

where parentheses indicate activities and brackets concentration.

Several simplifications may be made in the above expressions. Since the only species present in the aqueous phase are the acid HX and the water, $(HX)(H_2O)^m = [H^+][X^-]\gamma_{HX}[H_2O]^m\gamma^m_{H_2O}$ may be written as $\underline{a}'_{HX}$, the corrected aqueous phase activity, which can be determined by using the aqueous-phase concentrations, the H_2O/H^+ ratio (m) in the organic phase, and standard tables of activity coefficients. Since the number of the organic-phase species containing X^- is the same as the number of species containing H^+, it is possible to set each of the expressions

$\overline{[nTBP \cdot HX \cdot mH_2O]}$, $\overline{[nTBP \cdot H^+ \cdot mH_2O \ldots X^-]}$, $\overline{[nTBP \cdot H^+ \cdot mH_2O]}$, and $\overline{[X^-]}$ equal to

a quantity $[\overline{H}^+]$, the amount of acid in the organic phase, which can be experimentally determined. There is also one assumption that must be made. Very little is known concerning activity coefficients in organic solvents, especially for extracted inorganic species. The best approximation that can be made is to assume that for dilute organic phases the ratio of activity coefficients of the two species present, i.e., $\gamma_{\overline{nTBP \cdot HX \cdot mH_2O}}/\gamma^n_{\overline{TBP}}$, $\gamma_{\overline{nTBP \cdot H^+ \cdot mH_2O \ldots X^-}}/\gamma^n_{\overline{TBP}}$, or $\gamma_{\overline{nTBP \cdot H^+ \cdot mH_2O \cdot X^-}}/\gamma^n_{\overline{TBP}}$, is a constant.

Two other assumptions are implicit in the derivation of these equations. The first is that the extracting anion in Eqs. (6b) and (6c) is unhydrated and unsolvated, which is almost certainly true for nonprotonated anions, as shown in the introduction for the extraction of ionic species. The second is that the extraction of water by TBP, as discussed in the previous section, takes place concurrently with and independently of the extraction of acid. Evidence that this is true is presented in a subsequent portion of this section.

By using the simplifications and assumptions given above, it is possible to rewrite Eqs. (6) as

$$K'_{HX} = \frac{[\overline{H}^{+}]^{y}}{[\overline{TBP}]^{n}\ \underline{a}'_{HX}}, \qquad (7)$$

where y has a value of 1 for a molecular or ion-paired extracting species and two for a dissociated species. By holding $[\overline{TBP}]$ constant and determining the dependence of $[\overline{H}^{+}]$ on $\underline{a}'_{HX}$, it is possible to evaluate y. Taking logarithms of both sides of Eq. (7), rearranging, and combining constants results in

$$y \log [\overline{H}^{+}] = \log \underline{a}'_{HX} + \log K''_{HX}; \qquad (8)$$

and a plot of $\log [\overline{H}^{+}]$ vs $\log \underline{a}'_{HX}$ should yield a straight line of slope 1/y.

The above procedure has been carried out for the three acids $HClO_4$, HBr, and HNO_3 extracting into various concentrations of TBP in CCl_4 (Tables III-IX), and it can be seen in Figs. 3, 4, and 5 that all three yield a straight line of slope 1.0, which gives y in Eq. (7) a value of 1. This indicates that the extracting acids are either unionized or are ion-paired, an altogether reasonable conclusion, since the low dielectric constant of the CCl_4 solutions would tend to repress and dissociation in the organic phase. These results are also in agreement with those obtained by Hesford and McKay[70] for $HClO_4$, the strongest

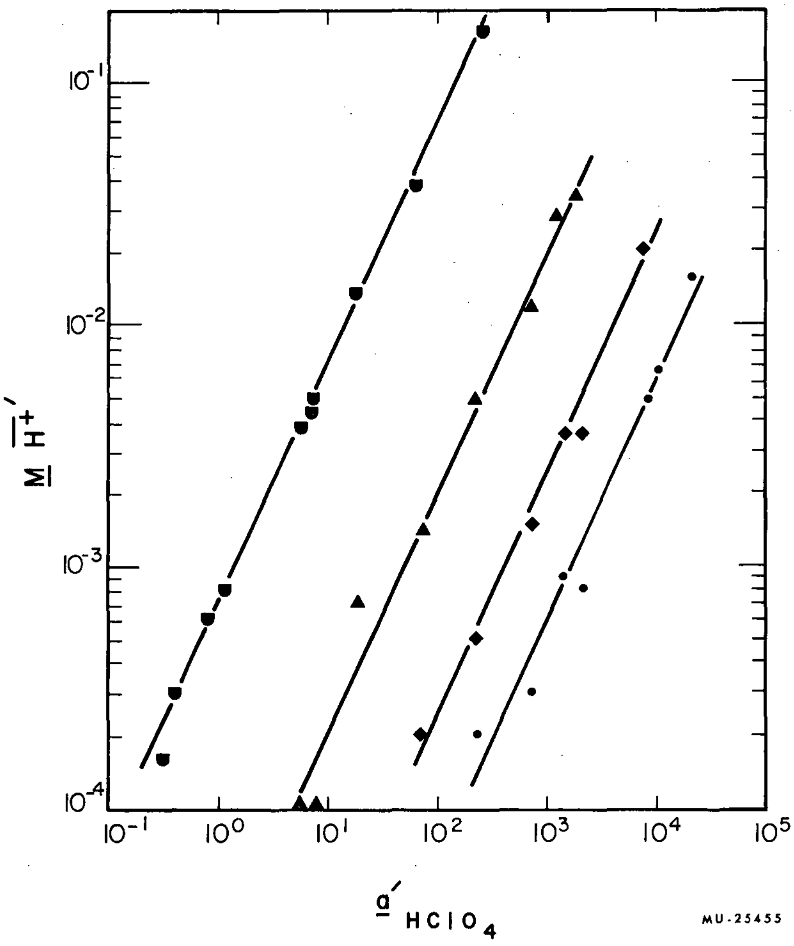


Fig. 3. Variation of acid content of organic phase (CCl_4 diluent) with $\underline{a}'_{HClO_4}$ (see page 26) for equilibrium TBP concentrations of: ●, 0.0345 $\underline{M}$; ◆ , 0.0535 $\underline{M}$; ▲ , 0.109 $\underline{M}$; ⬤, 0.307 $\underline{M}$. All lines drawn with slope 1.0.

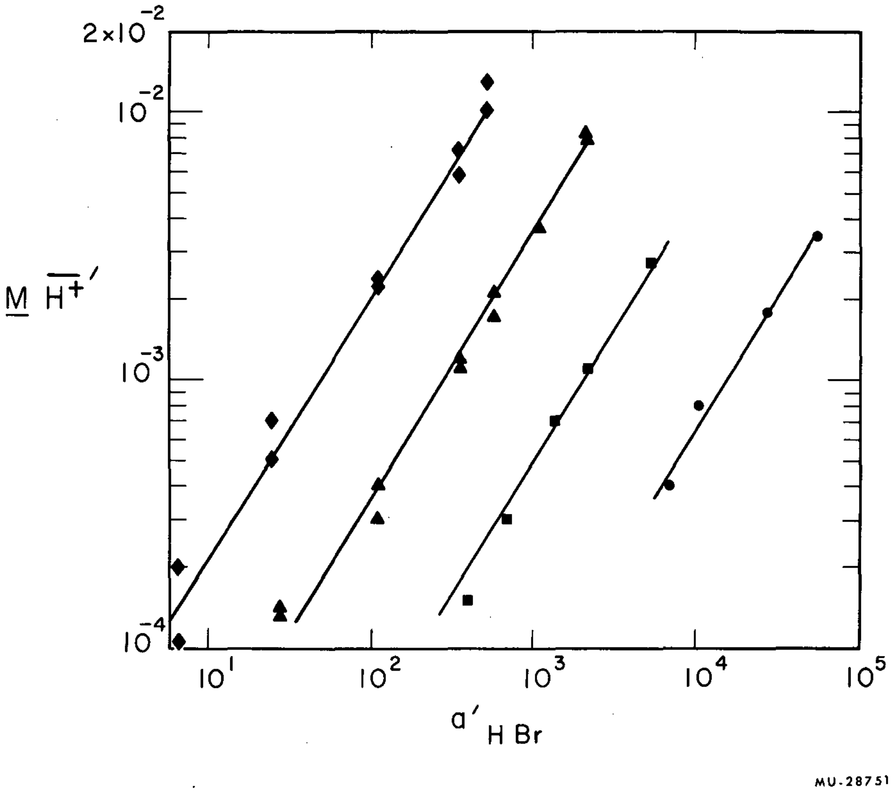
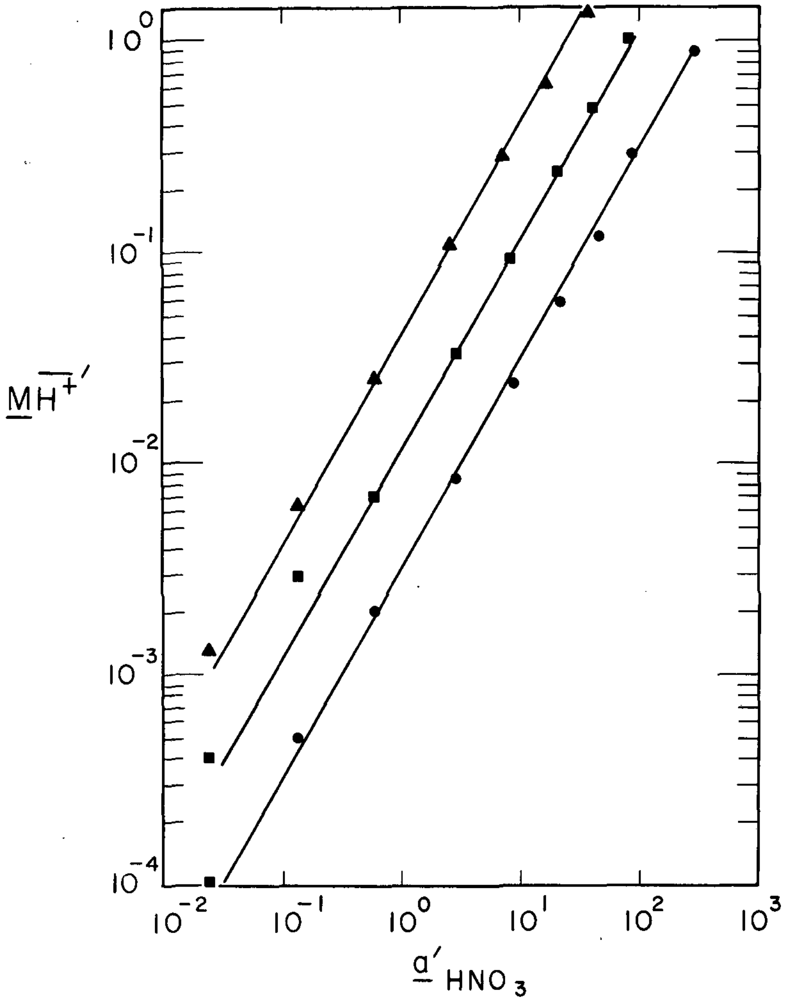


Fig. 4. Variation of acid content of organic phase (CCl$_4$ diluent) with $\underline{a}'_{HBr}$ (see page 26) for equilibrium TBP concentration of: ●, 0.0338 $\underline{M}$; ■, 0.0825 $\underline{M}$; ▲, 0.164 $\underline{M}$; ◆, 0.320 $\underline{M}$. All lines drawn with slope 1.0.



MU-28750

Fig. 5. Variation of acid content of organic phase (CCl_4 diluent) with $\underline{a}'_{HNO_3}$ (see page 26) for equilibrium TBP concentrations of: ●, 0.0302 $\underline{M}$; ■, 0.106 $\underline{M}$; ▲, 0.293 $\underline{M}$. All lines drawn with slope 1.0.

of these three acids, in dilute TBP in benzene solutions. These workers found that the dissociation as measured by electrical conductivity was negligibly small in TBP solutions of a few tenths molar or less, although $HClO_4$ in pure TBP was almost completely dissociated.

One of the conditions set forth in the derivation of Eq. (8) was that the TBP concentration be held constant. So long as $[\overline{H}^+]$ is less than 1% of $[\overline{TBP}]$, and so long as (H_2O) is within a few percent of 1.00, this condition will be reasonably well obeyed. However, the three acids under consideration all extract well enough and all attain high enough aqueous concentrations to exceed the limitations given, and corrections must be made in $[\overline{H}^+]$ which reflect the decrease in $[\overline{TBP}]$. The simplest method of correction is to choose some arbitrary equilibrium TBP concentration, generally the largest one in a given set, and calculate what $[\overline{H}^+]$ would be if all the $[\overline{TBP}]$ values were the same as the chosen one. For reasons made apparent in subsequent portions of this section (see p. 32), the relationship in the cases of $HClO_4$ and HBr has the form

$$[\overline{H}^+]' = \frac{[\overline{H}^+][\overline{TBP}]'^3}{[\overline{TBP}]^3} , \tag{9a}$$

whereas that for HNO_3 is

$$[\overline{H}^+]' = \frac{[\overline{H}^+][\overline{TBP}]'}{[\overline{TBP}]} \tag{9b}$$

The points plotted in Figs. 3-5 contain these corrections, and the adherance of the corrected points to the line whose slope is determined by those points whose correction was negligible indicates that the relationships in Eqs. (9) are the appropriate ones to be used. It is worth mention that the points associated with the largest $[\overline{H}^+]'$ values have corrections that range from only a few percent all the way up to a factor of 10.

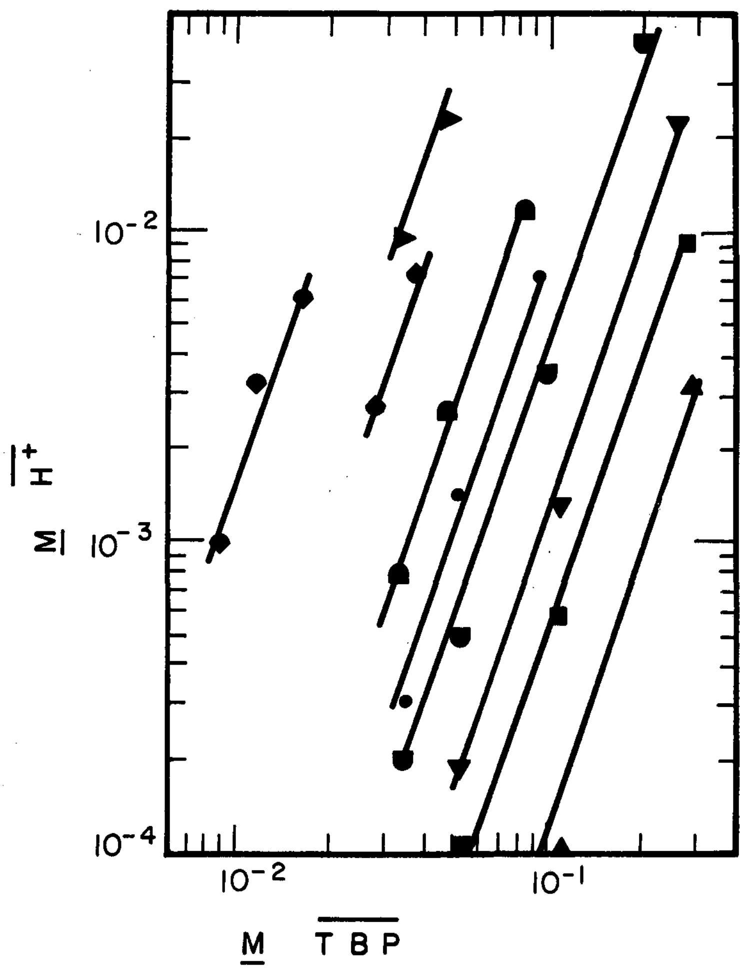
Now that Eq. (7) with y = 1 has been established as the correct representation of the extraction, it may be put to further use in determining the dependence of the extraction on TBP concentration. By holding $\underline{a}'_{HX}$ constant while $[\overline{TBP}]$ varies and going through the same procedure as used to derive Eq. (8), one obtains the expression

$$\log [\overline{H}^+]\ n\log [\overline{TBP}] + \log K'''_{HX}, \qquad (10)$$

and a plot of log $[\overline{H}^+]$ vs log $[\overline{TBP}]$ should yield a straight line of slope n.

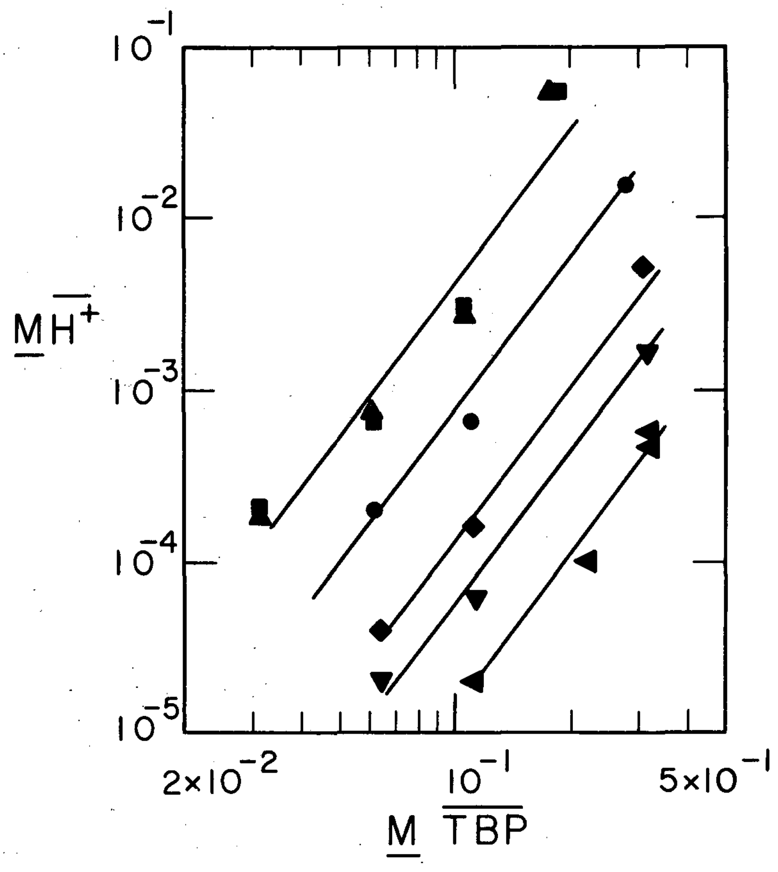
It must be reiterated that $[\overline{TBP}]$is the <u>equilibrium</u> TBP concentration, and does not include the amount of TBP bonded to H_2O or, more importantly, included in the extracting complex. The correction for $TBP \cdot H_2O$ is relatively small and is discussed more thoroughly in Section I.C.3. The correction for acid-complexed TBP is determined by noting that each molecule of acid that extracts involves n molecules of TBP; by determining n for those cases in which $[\overline{H}^+]$ is less than 1% of $[\overline{TBP}]$ the magnitude of the correction for any $[\overline{H}^+]$ can be assessed, since it is merely $n[\overline{H}^+]$. Corrections made by using these two factors yielded straight lines of slope n until at least 80% of the <u>total</u> TBP was incorporated into the bonding of the extracting species; moreover, corrections using n + 1 and n - 1 for $HClO_4$ and HBr did not yield the corresponding slopes.

Log $[\overline{H}^+]$ vs log $[\overline{TBP}]$ is plotted in Fig. 6-9 for $HClO_4$, $HReO_4$, HBr, and HNO_3. The slopes obtained are 3.0 for the first three acids and 1.0 for HNO_3. It must be noted that the data for $HReO_4$ were obtained in a different manner and by using a different inert solvent than for the other three acids (Table X). It was desired to extend the extraction to lower acid concentrations for $HClO_4$, and in order to do this the extraction of $HReO_4$ -- a homologous acid with an ionic structure and size similar to $HClO_4$ but differing in that is has a convenient radioactive tracer (Re^{186}, $t_{1/2}$ = 90hr)[62] -- was studied for TBP dissolved in octane. The advantages of octane are twofold. First, its low density causes it to be the upper phase when the phases are separated, so that it is not necessary for the pipet to pass through the much more radioactive aqueous phase in order to remove a sample of the organic phase



MU-25457

Fig. 6. Variation of acid content of organic phase (CCl_4 diluent) with equilibrium TBP concentration for aqueous $HClO_4$ concentrations of : ▲, 1.69 M; ■, 2.64 M; ▼, 3.40 M; ●, 4.07 M; ●, 4.69 M; ●, 5.05 M; ◆, 5.92 M; ▼, 6.94 M. All lines drawn with slope 3.0.



MU-28747

Fig. 7. Variation of acid content (as measured by $HReO_4$ tracer) of organic phase (iso-octane diluent) with equilibrium TBP concentration for aqueous acid concentrations of: ◀, 0.109 M $HReO_4$; ▼, 0.217 M $HReO_4$; ◆, 0.435 M $HReO_4$; ●, 0.87 M $HReO_4$; ■, 1.74 M $HReO_4$; ▲, 1.63 M $HClO_4$. All lines drawn with slope 3.0.

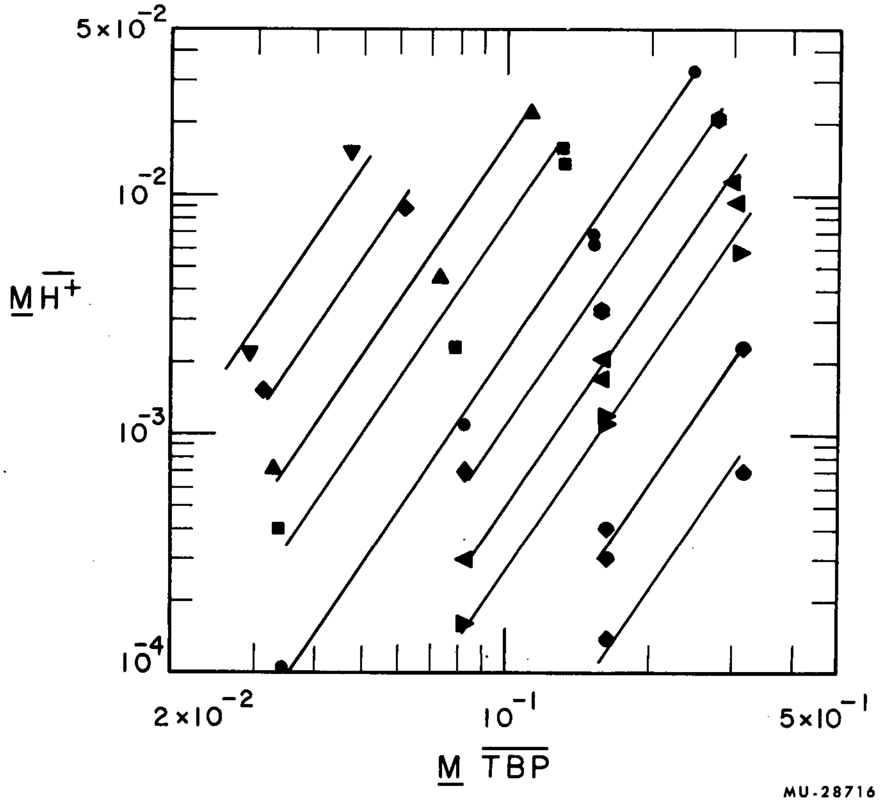
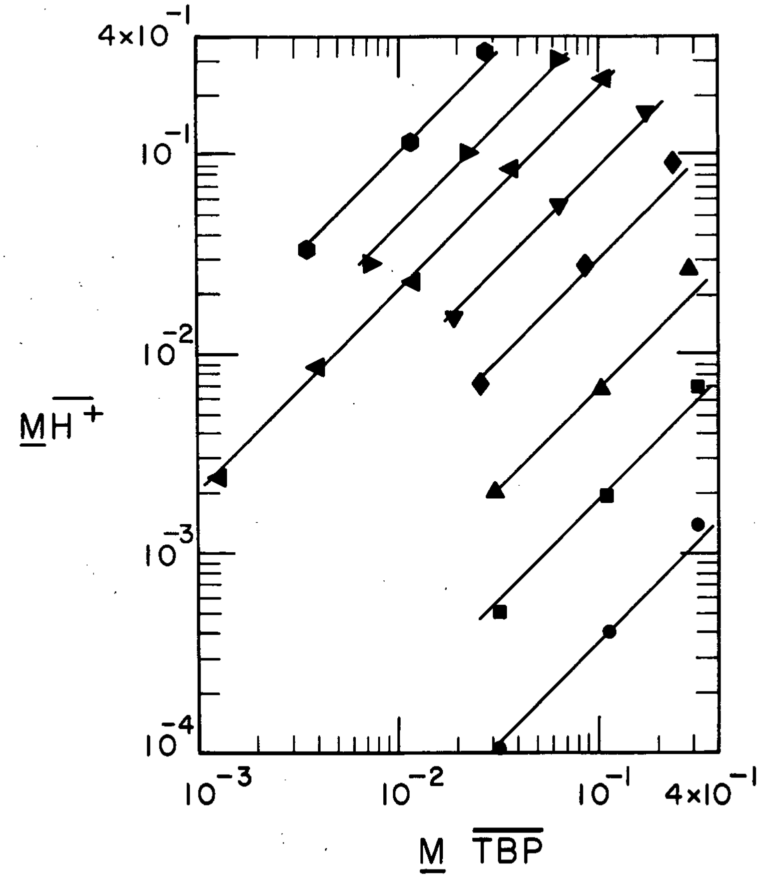


Fig. 8. Variation of acid content of organic phase (CCl_4 diluent) with equilibrium TBP concentration for aqueous HBr concentrations of: ▲, 3.21 M; ♦, 4.28 M; ►, 5.17 M; ◄, 5.57 M; ⬢ 6.07 M; ●, 6.48 M; ■, 7.12 M; ▲, 7.50 M; ◆, 8.08 M; ▼, 8.53 M. All lines drawn with slopes 3.0.



MU-28717

Fig. 9. Variation of acid content of organic phase (CCl_4 diluent) with equilibrium TBP concentration for aqueous HNO_3 concentrations of: ●, 0.202 M; ■ , 0.501 M; ▲, 1.003 M; ◆ , 2.02 M; ▼, 2.93 M; ◀ , 3.95 M; ▶ , 4.96 M; ⬢ , 6.05 M. All lines drawn with slope 1.0.

as it must when CCl_4 is used as the inert solvent. Second, and more important, the distribution ratios for strong acids increase roughly 20-fold when CCl_4 is replaced by octane. By multiplying the distribution ratio by the aqueous acid concentration, the organic acid concentration $[\overline{H}^+]$ is obtained, so that Eq. (10) may be used to evaluate n. The similarity of $HClO_4$ and $HReO_4$ can be seen in Fig. 7, where the replacement of 1.74 M $HReO_4$ by 1.63 M $HClO_4$ yielded essentially no change in the extraction behavior of $HRe^{186}O_4$ tracer.

An extensive series of experiments was also done on the extraction of tracer $HAuCl_4$ and $HAuBr_4$ out of HCl and HBr into TBP with a variety of inert solvents. In these experiments, $HAuCl_4$ and $HAuBr_4$ were in general on the order of 10^{-5} M while theHCl concentrations were 2, 6, and 10 M and the HBr concentrations were 1, 2, 4, and 6 M; and the experimentally determined quantities were the distribution ratios, D, equal to counts/min in the organic phase divided by counts/min in the aqueous phase. Analysis of the organic phase showed the H:Au:Cl ratio to be 1:1:4, indicating that $HAuCl_4$ (and analogously $HAuBr_4$) was the only acid species extracted. Under these conditions, and assuming an ion pair for the extracting species, Eq. (6b) becomes, for example,

$$K_{HAuCl_4} = \frac{\overline{(nTBP \cdot H^+ \cdot mH_2O \ldots AuCl_4^-)}}{(H^+)(AuCl_4^-)(H_2O)^m(\overline{TBP})^n}$$

$$= \frac{[\overline{nTBP \cdot H^+ \cdot mH_2O \ldots AuCl_4^-}]\gamma_{\overline{nTBP \cdot H^+ \cdot mH_2O \ldots AuCl_4^-}}}{[H^+]\gamma_{H^+}[AuCl_4^-]\gamma_{AuCl_4^-}[H_2O]^m\gamma_{H_2O}^m\ [\overline{TBP}]^n\gamma_{\overline{TBP}}^n} \ . \qquad (11)$$

In addition to the assumption made in the derivation of Eq. (7) concerning the constancy of the ratio of organic-phase activity coefficients, several simplifications in Eq. (11) can be made. Since HCl extracts very poorly, $[H^+]\gamma_{H^+}[H_2O]^m\gamma^m_{H_2O}$ is constant for a given HCl concentration. Also, since $HAuCl_4$ is in such dilute concentration, $\gamma_{AuCl_4^-}$ is very close to being constant for a given $[H^+]$. The ratio $[\overline{nTBP \cdot H^+ \cdot mH_2O \ldots . AuCl_4^-}]/[AuCl_4^-]$ is merely D, the distribution ratio. Since the concentration of acid in the organic phase is small compared with the TBP concentration, $[\overline{TBP}]$ is proportional to the total TBP concentration, $[\underline{TBP}]$ being reduced by a constant factor related to the water activity and K_{H_2O} in Eq. (2).

When these various considerations are applied to Eq. (11), the resulting expression is

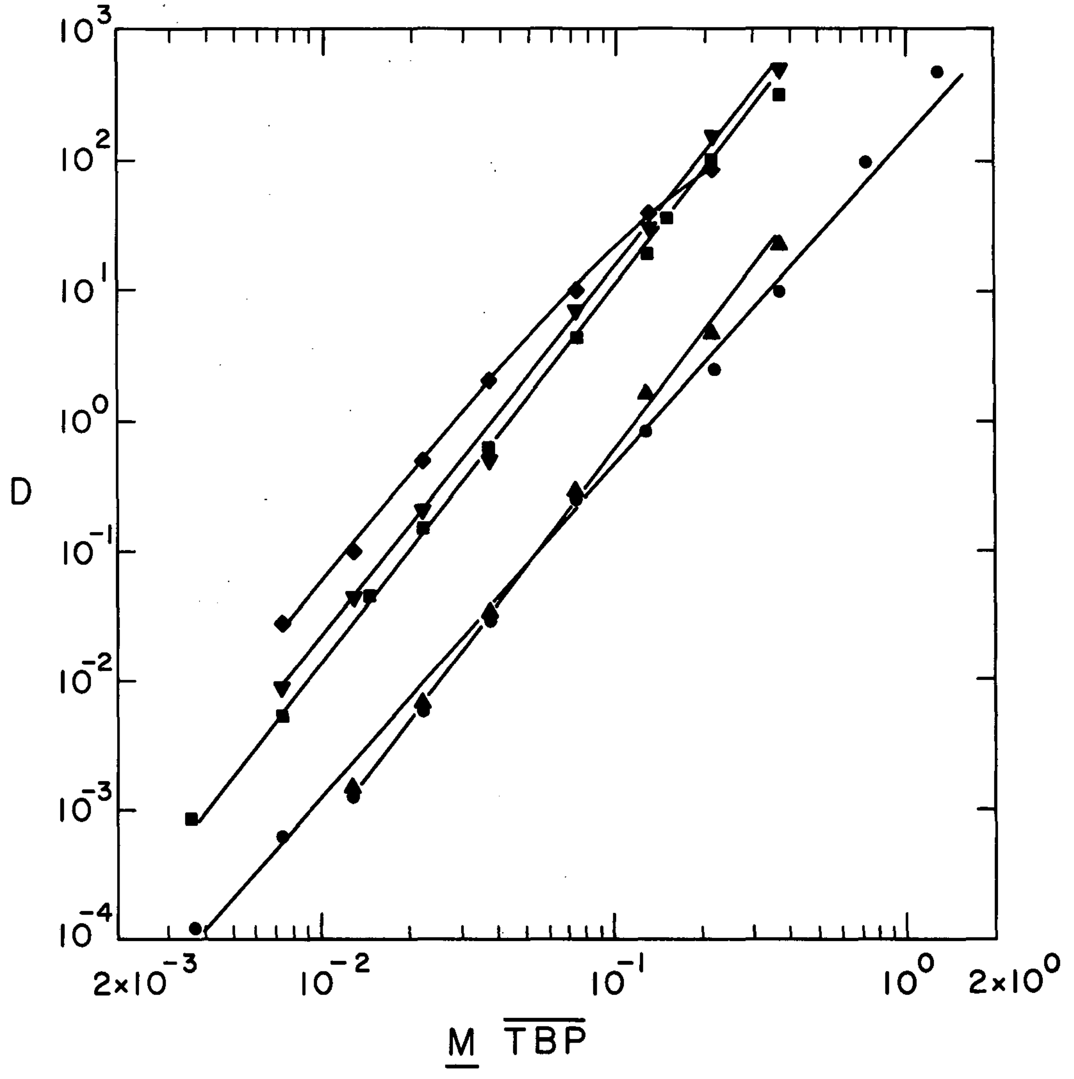
$$K'_{HAuCl_4} = \frac{D}{[\underline{TBP}]^n} , \tag{12}$$

with a similar equilibrium expression for K'_{HAuBr_4}. Taking logarithms,

$$\log D = n\log\,[\underline{TBP}] + \log K'_{HAuCl_4} , \tag{13}$$

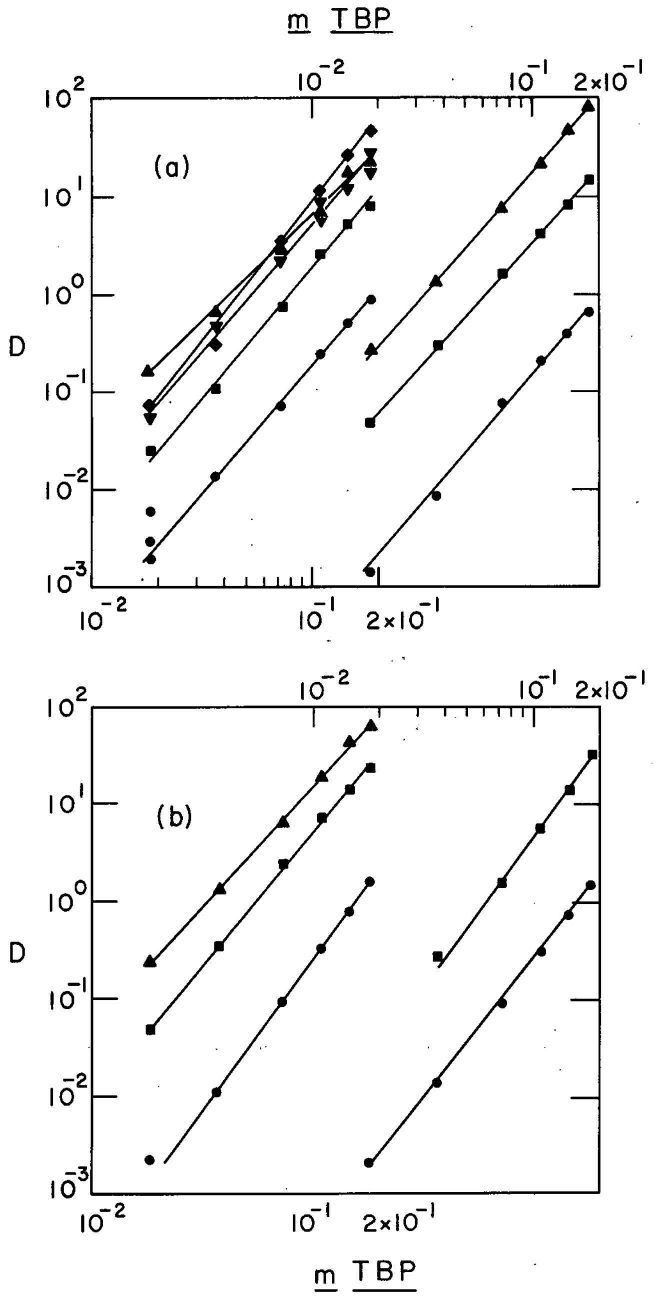
and a plot of log D vs log $[\underline{TBP}]$ should yield a straight line of slope n and thus give the dependence of the extraction on TBP concentration. Such plots are shown in Fig. 10-13 for $HAuCl_4$ extracting from 2, 6, and 10 M HCl into TBP in iso-octane, xylene, and CCl_4 (Tables XI to XIII) and $HAuBr_4$ extracting from 1, 2, 4, and 6 M HBr into TBP in xylene (Table XIV); the slopes are seen to range in value from 2.5 to 3.2.

The tendency for the slopes for the higher HCl concentrations (6 and 10 M) to fall below 3.0 has its explanation in the assumption that the extraction of HCl is negligibly small. Although this is certainly true in 2 M HCl (where $[\overline{H}^+] \approx 10^{-5}$ M for 0.15 M TBP) the extraction has started to become appreciable ($[\overline{H}^+] \approx 0.0005$ M TBP, corresponding to the complexing of 0.0015 M TBP or about 1% of the total TBP) at 6 M and is actually quite large ($[\overline{H}^+] \approx 0.01$, corresponding to a 20% reduction of $[\underline{TBP}]$) at 10 M. Since the effect of lowering $[\underline{TBP}]$



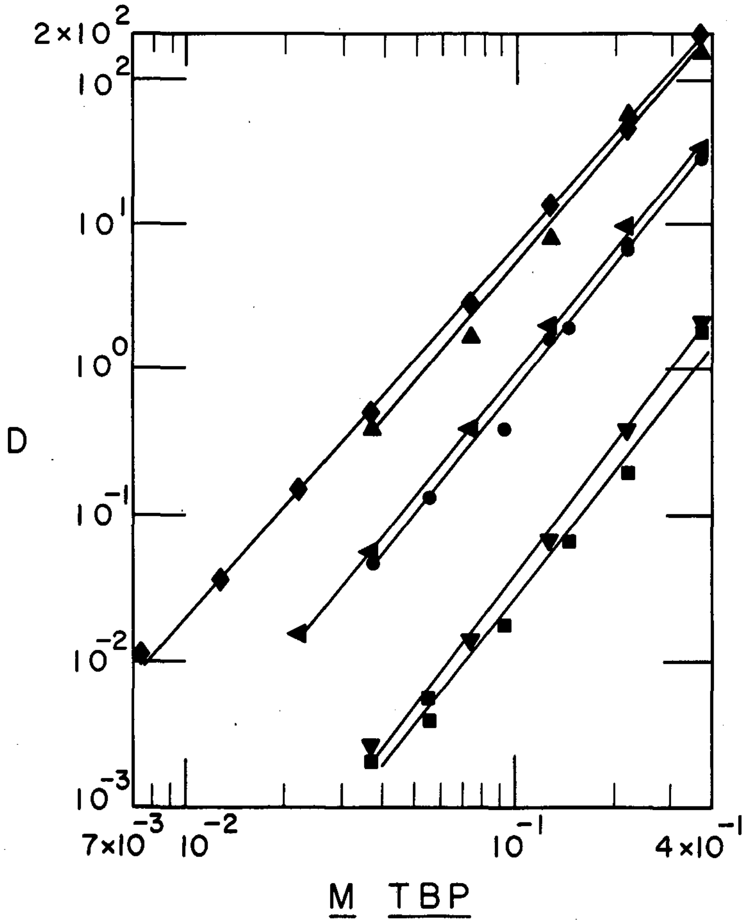
MUB-1457

Fig. 10. Variation of distribution ratio of $HAuCl_4$ with total TBP concentration (in iso-octane) for initial aqueous concentrations of: ●, 2.0 $\underline{M}$ HCl, 8×10^{-6} $\underline{M}$ $HAuCl_4$; ▲, 2.0 $\underline{M}$ HCl, 1×10^{-5} $\underline{M}$ $HAuCl_4$; ■, 6.0 $\underline{M}$ HCl, 1×10^{-6} $\underline{M}$ $HAuCl_4$; ▼, 6.0 $\underline{M}$ HCl, 1×10^{-5} $\underline{M}$ $HAuCl_4$; , 10 $\underline{M}$ HCl, 1×10^{-5} $\underline{M}$ $HAuCl_4$.



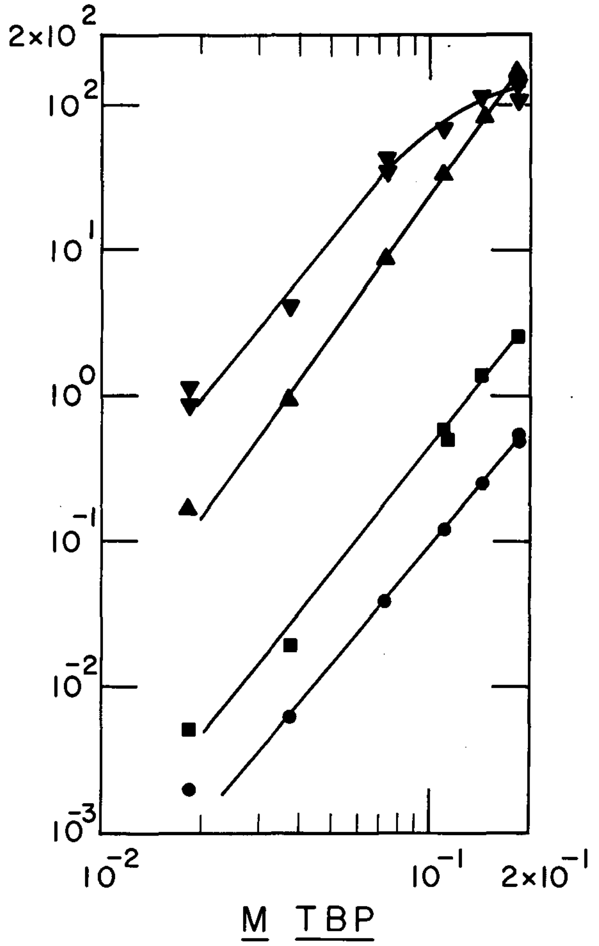
MUB-1466

Fig. 11. (a) Variation of distribution ratio of $HAuCl_4$ with total TBP concentration (in xylene) for initial aqueous concentrations of: ▼, 6.0 M HCl, 2×10^{-7} M $HAuCl_4$; ◆, 6.0 M HCl, 1×10^{-6} M $HAuCl_4$; ●, 2.0 M HCl; ■, 6.0 M HCl; ▲, 10 M HCl; lower scale, 1×10^{-5} M $HAuCl_4$; upper scale, 1×10^{-4} M $HAuCl_4$. (b) lower scale, 1×10^{-3} M $HAuCl_4$; upper scale, 1×10^{-2} M $HAuCl_4$.



MU-28718

Fig. 12. Variation of distribution ratio of $HAuCl_4$ with total TBP concentration (in CCl_4) for initial aqueous concentrations of: ■, 2.0 M HCl, 2×10^{-6} M $HAuCl_4$; ▼, 2.0 M HCl, 1×10^{-5} M $HAuCl_4$; ●, 6.0 M HCl, 1×10^{-6} $HAuCl_4$; ◀, 6.0 M HCl, 1×10^{-5} M $HAuCl_4$; ▲, 10 M HCl, 8×10^{-6} M $HAuCl_4$; ◆, 10 M HCl, 1×10^{-5} M $HAuCl_4$.



MU-28745

Fig. 13. Variation of distribution ratio of $HAuBr_4$ with total TBP concentration (in xylene) for initial aqueous concentrations of: ●, 1.1 M HBr, 1×10^{-5} M $HAuBr_4$; ■, 2.0 M HBr, 1×10^{-6} M $HAuBr_4$; ▲, 4.1 M HBr, 1×10^{-5} M $HAuBr_4$; ▼, 6.3 M HBr, 1×10^{-6} M $HAuBr_4$.

is a greater lowering of D, the effect is to make the K's in 10 M HCl fall below their expected values by a factor of 2 or more for the most concentrated TBP solutions, with the rapid reduction in HCl extraction ($\propto[\underline{TBP}]^3$) causing this effect to diminish, and the D's to become closer to the expected values, as the TBP concentration is reduced. The effect is even more apparent in the 6.3 M HBr system (Fig. 13), since HBr extracts better than HCl.

This problem could be avoided in some cases by doing the extraction from a 6.0 M LiCl-0.1 M HCl aqueous phase. The results of such an experiment are listed in Table XV and shown in Fig. 14, and it is seen that good results are achieved in iso-octane solutions of TBP (slope 3.2), whereas no improvement is noted in the CCl_4 solutions (slope 2.5).

Experiments similar to those above were carried out for $HReO_4$ tracer extracting out of 2 and 6 M HCl into TBP in iso-octane solutions (Table XVI) . The results may be seen in Fig. 15 and again a slope of 3.0 is obtained for TBP concentrations below 0.3 M.

As a further extension of the extraction system, and a conjunction with some studies being made by other workers in the group,[71] extractions of $HAuCl_4$ and $HReO_4$ out of HCl were made into tri-octylphosphine oxide (TOPO) which was dissolved in iso-octane in the case of $HReO_4$ (Table XVI) and CCl_4 in the case of $HAuCl_4$ (Table XVII). Equation (12) may be used to represent the extraction, provided $[\underline{TOPO}]$ is substituted for $[\underline{TBP}]$. The results of plotting log D vs log $[\underline{TOPO}]$ for these systems are shown in Figs. 15 and 16, and again slopes near, but usually below, 3 are found. The lowered values of the slopes can again be ascribed to the extraction of HCl, which, because of the greater basicity of TOPO, extracts from a 2 M solution to give a value of $[\overline{H}^+] = 0.005$ M for 0.1 M TOPO, corresponding to 15% of the total TOPO and because of TOPO's greater extraction of water ($[\overline{H_2O}] \approx 0.35\ [\underline{TOPO}]$)[71] to 25% of the actual equilibrium TOPO before extraction.

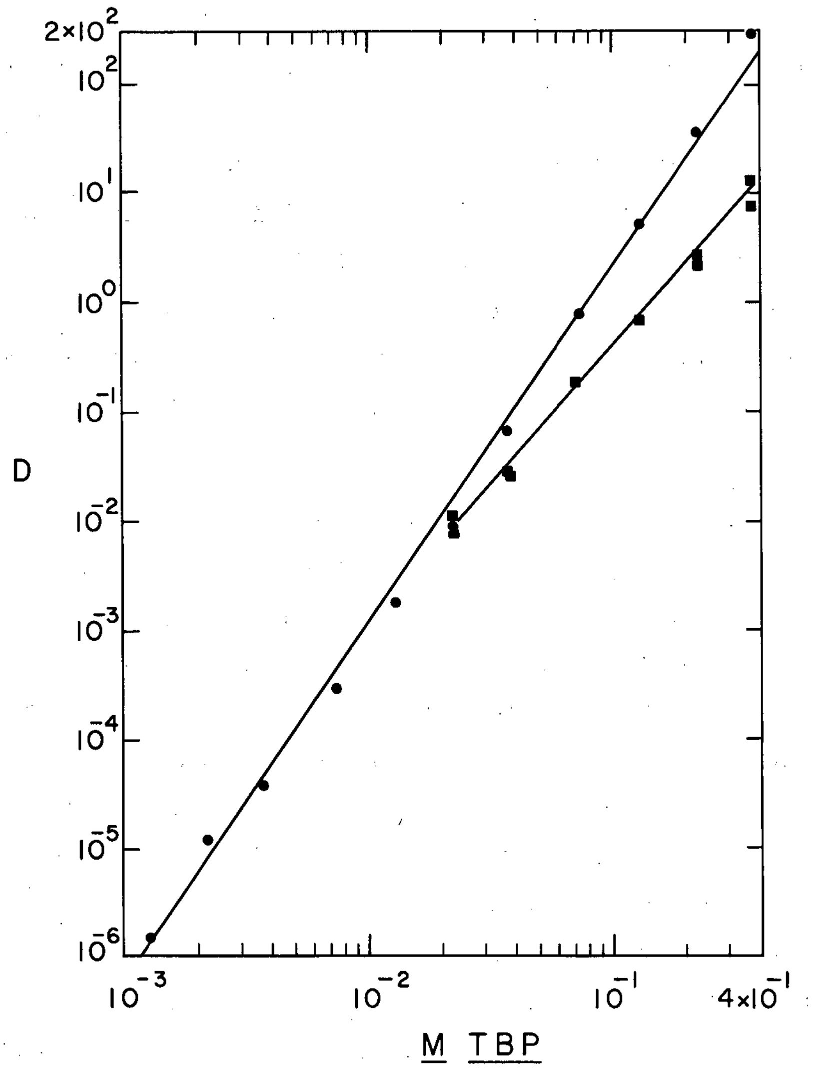
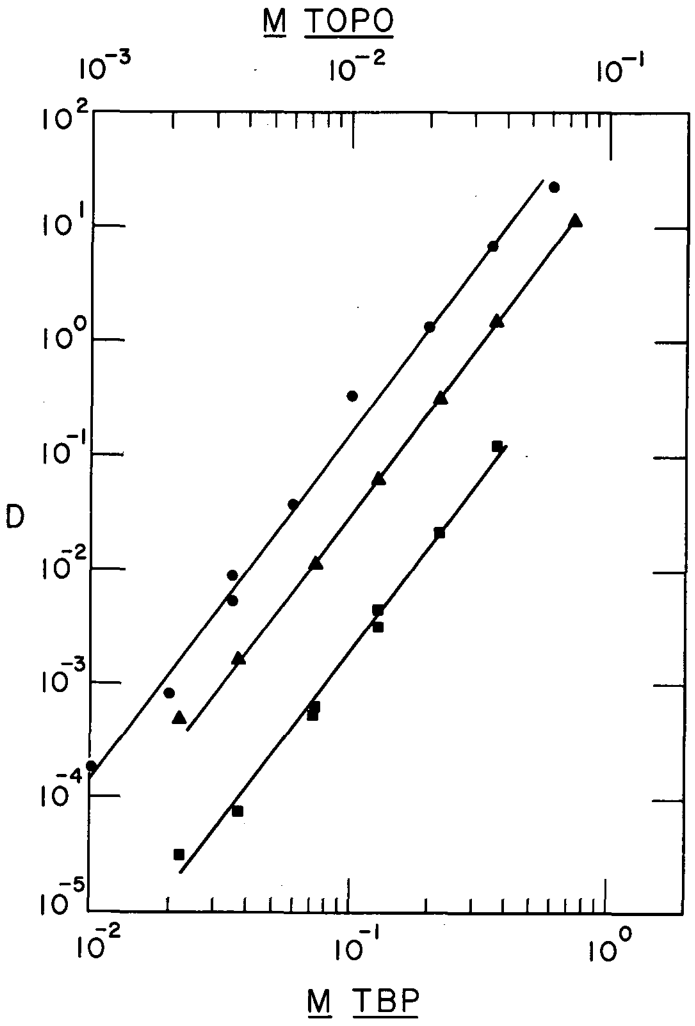
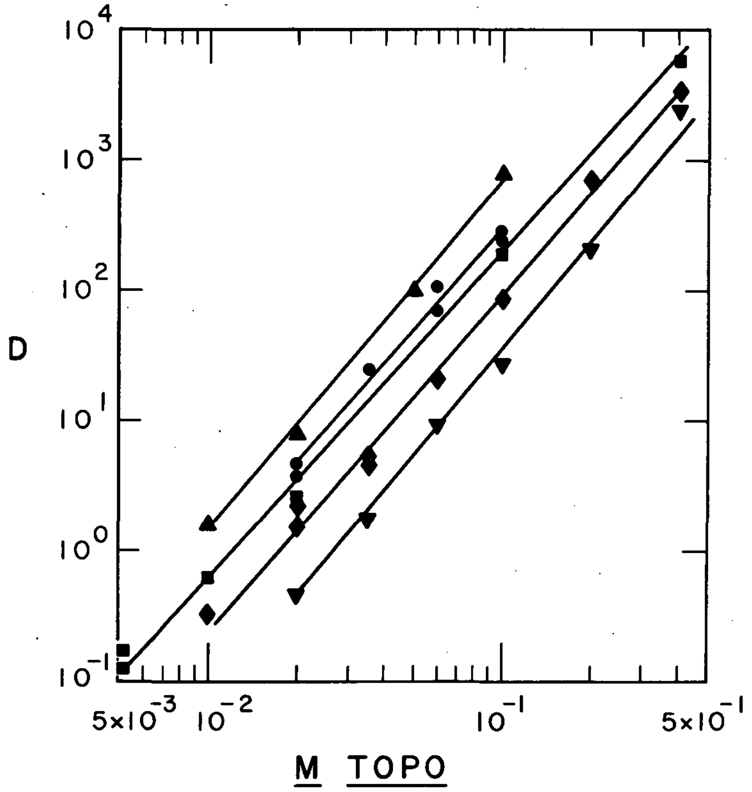


Fig. 14. Variation of distribution ratio of $HAuCl_4$ with total TBP concentration from 6.0 M LiCl-0.1 M HCl solutions, 1×10^{-5} M $HAuCl_4$ initial aqueous concentration, using inert diluents: ■, CCl_4; ●, iso-octane.



MU-28720

Fig. 15. Variation of distribution ratio of $HReO_4$ (initial aqueous concentration 1×10^{-6} M) with extractant concentration (in iso-octane) for extractants and aqueous acid concentrations of: lower scale, TBP; ■, 2.0 M HCl; ▲, 6.0 M HCl; upper scale, TOPO; ●, 0.20 M HCl.



MU-28721

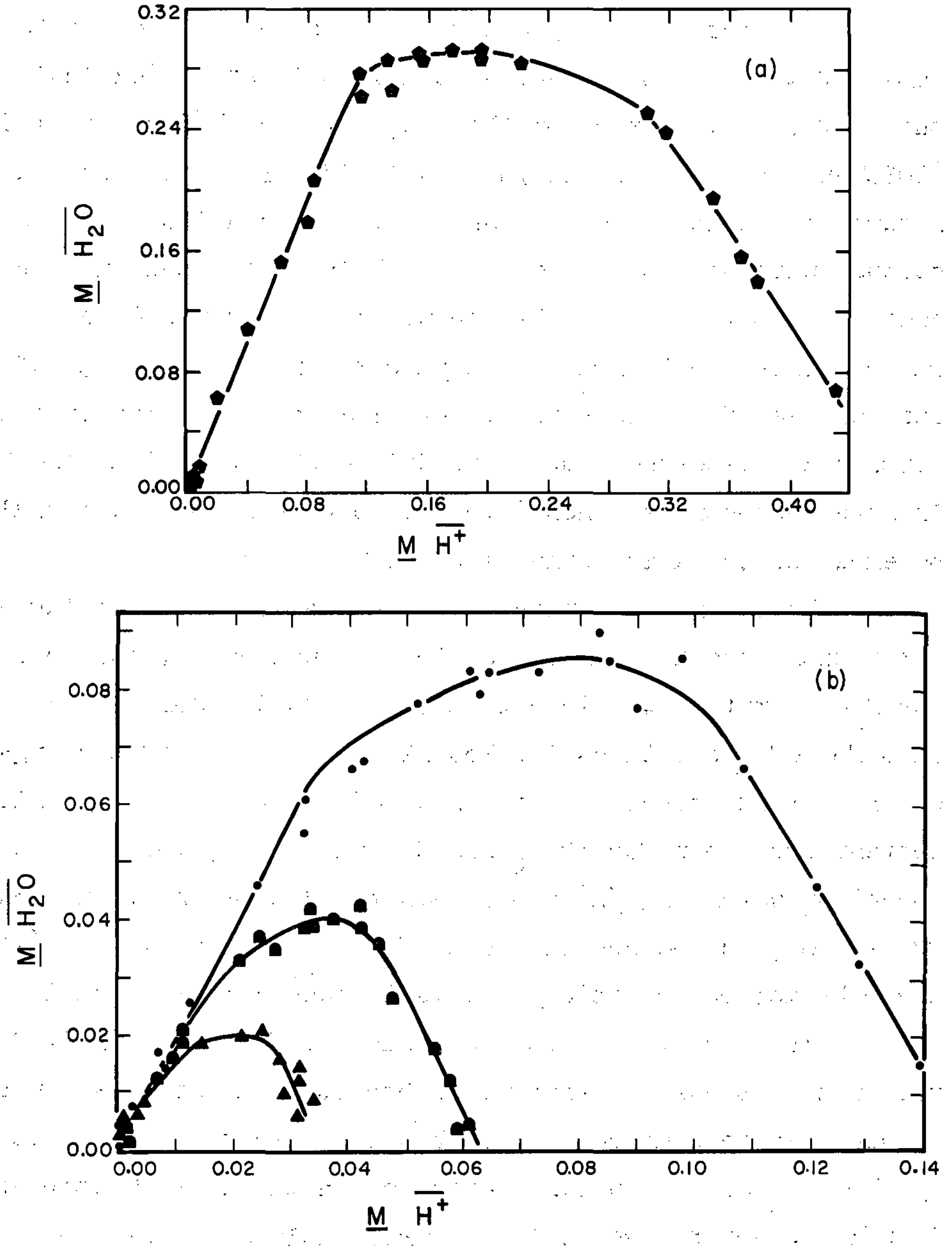
Fig. 16. Variation of distribution ratio of $HAuCl_4$ with total TOPO concentration (in CCl_4) for initial aqueous concentrations of: ▼, 0.05 M HCl, 1×10^{-5} M $HAuCl_4$; ◆, 0.20 M HCl, 1×10^{-5} M $HAuCl_4$; ■, 0.05 M HCl, 2×10^{-6} M $HAuCl_4$; ●, 0.20 M HCl, 1×10^{-6} M $HAuCl_4$; ▲, 0.20 M HCl, 2×10^{-6} M $HAuCl_4$.

3. Tributyl Phosphate-Acid-Water

The most striking observation to be made concerning the extraction of all the strong acids used in this study (excluding HNO_3) is the uniform value of 3 for the slope of log ($\bar{H}^+$) vs log [TBP] or log [TOPO] and thus for the TBP/H^+ and TOPO/H^+ ratios, independently of the nature of the inert solvent and of the acid anion. This gives a very strong indication that the species being extracted in every case is some form of trisolvated hydronium ion as discussed in Section I.A.2. The one exception, HNO_3, has been extensively investigated,[22,53,70,72-86] and has been found to extract into TBP as the undissociated molecule, forming a one-to-one complex in dilute HNO_3 solutions and higher complexes in more concentrated ones (i.e., 2 to 4 HNO_3/TBP), and would thus not be expected to exhibit the slope of 3.

In order to further test these theories concerning hydrogen ion extraction the H_2O content of the organic phase, and more particularly the H_2O/H^+ ratio, was investigated for $HClO_4$, HBr, and HNO_3 extracting into TBP-CCl_4 solutions (Tables III-IX). Plots of the organic-phase water content (corrected as discussed below) vs the organic phase acid content are shown for $HClO_4$ and HBr in Figs. 17-18. Only a negligible amount of water ($H_2O/H^+ < 0.1$) was found to extract with HNO_3 into TBP so long as the organic-phase TBP/HNO_3 ratio was > 1 (Table IX); the behavior beyond this point is duscussed in Section I.C.4.

In order to obtain the amount of H_2O actually associated with the proton it was necessary to subtract from the total amount of the H_2O present (as determined by Karl Fischer titration) the amount dissolved by the CCl_4 and the amount contained in the TBP·H_2O complex. The H_2O in CCl_4 is determined as in the previously described TBP-H_2O case (page 20) except that the decreasing activity of H_2O in the aqueous phase must be taken into account; thus the correction is $0.0099 \times N_{CCl_4} \times (H_2O)$.



MUB-1456

Fig. 17. (a) Variation of water content in the organic phase (CCl_4 diluent; M $\overline{H_2O}$ does not include water dissolved by CCl_4 or complexed as $TBP \cdot H_2O$) with acid content in the organic phase as the aqueous $HClO_4$ concentration increases for total TBP concentrations of: ⬟ , 0.366 M. (b) ●, 0.128 M; ⬟ , 0.0641 M; ▲, 0.0384 M.

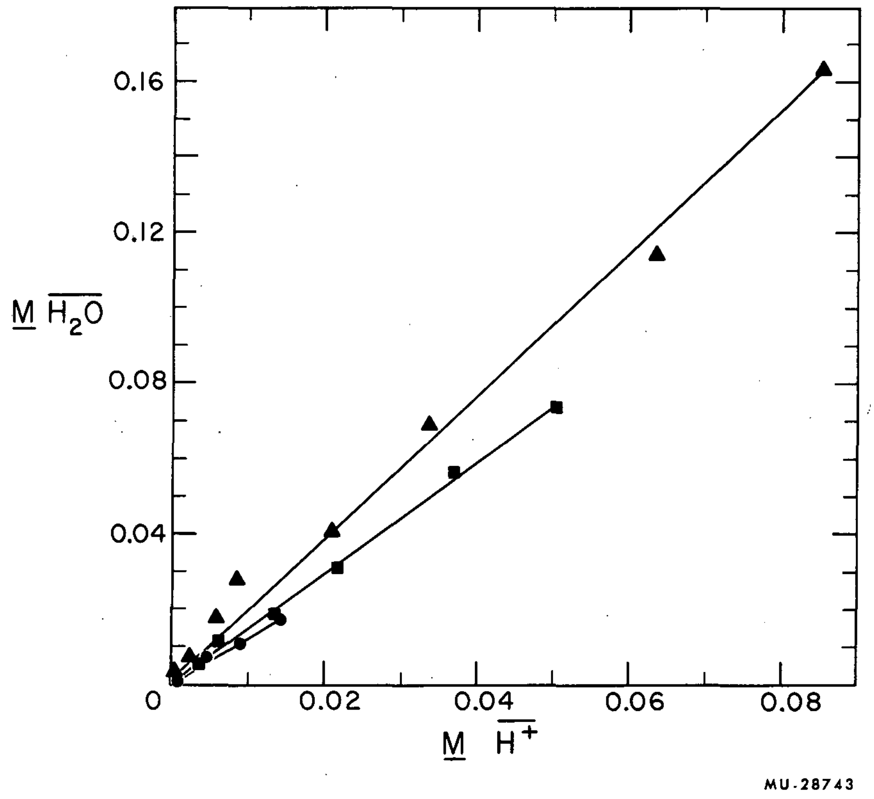


Fig. 18. Variation of water content in the organic phase (CCl_4 diluent; M $\overline{H_2O}$ does not include water dissolved by CCl_4 or complexed as TBP· H_2O) with acid content in the organic phase as the aqueous HBr concentration increases for total TBP concentrations of: ▲, 0.366 $\underline{M}$; ■, 0.183 $\underline{M}$; ●, 0.0915 $\underline{M}$.

The $TBP \cdot H_2O$ concentration can be determined in a similar manner from Eq. (2) by using $[TBP] = [\underline{TBP}] - [\overline{TBP \cdot H_2O}] - 3[\overline{H}^+]$. It was found, however, that equally good results could be obtained by using infrared anaylsis of the organic phase. The observation that led to this discovery was that as the acid concentration in the organic phase increased there was a corresponding decrease in the absorbance of the 2.72-μ peak, until at a TBP/H^+ ratio of 3 the peak completely disappeared. It has been shown in the preceding section that the extracting species has the same ratio, thus it is reasonable to conclude that when this limit is reached all or nearly all of the TBP is involved in the extraction, leaving little, if any, TBP to form $TBP \cdot H_2O$. Since this limit also marks the disappearance of the 2.72-μ peak, its absorbance was assumed to measure the amount of $TBP \cdot H_2O$ in the solution. On the other hand, the 2.90-μ peak continued to grow as more acid was extracted, suggesting that it was measuring the hydrogen-bonded water that was extracting with the acid, although no quantitative relationship between the Karl Fischer values and those given by the absorbance of the 2.90-μ peak could be determined.

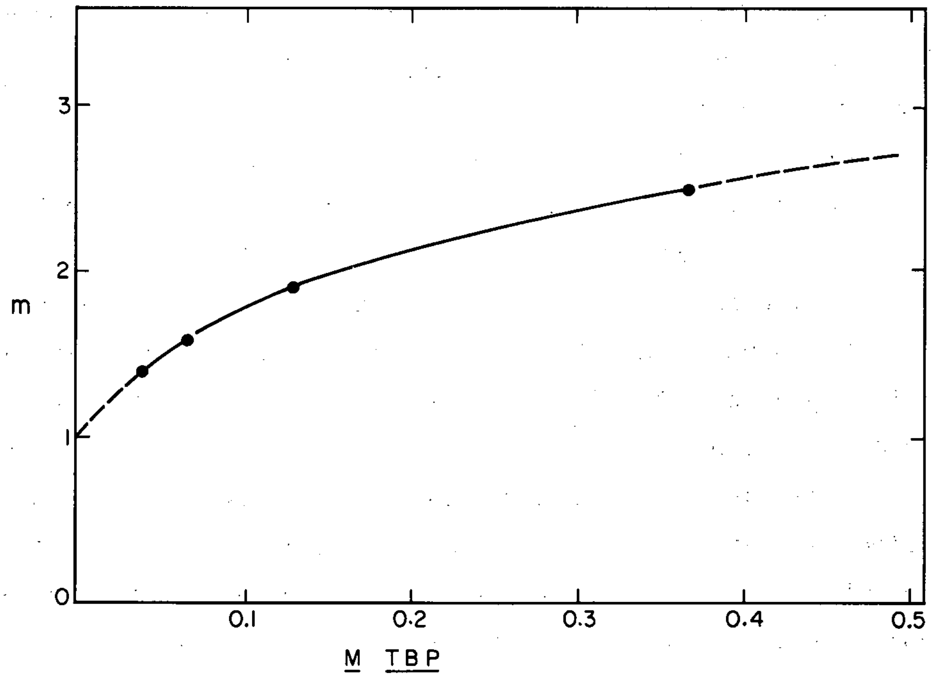
The assumption concerning the correspondence between the 2.72-μ peak and $TBP \cdot H_2O$ is supported by the behavior of the water-saturated TBP solutions, described in Section I.C.1, where the absorbance of the 2.72-μ peak measured only that portion of the water in the organic phase which could be accounted for by Eq. (2), i.e., only the species $TBP \cdot H_2O$. The calculated and spectral values for $TBP \cdot H_2O$ generally differed by less than 10%, and since the magnitude of this correction becomes smaller as the acid content increases, the accuracy was sufficient to give good values for H_2O/H^+. It must be noted that for the 10% (0.366$\underline{M}$) TBP (Fig. 17a), it was necessary to make an additional correction to the H_2O values in order to make the H_2O/H^+ line pass through the origin. The size of this correction was very close to the difference between the Karl Fischer and 2.72-μ values in Fig. 1, providing further evidence of the relationship between the 2.72-μ peak and $TBP \cdot H_2O$.

This "excess" water was considered, for purposes of correcting the total water content of the organic phase, to decrease in the same manner as $TBP \cdot H_2O$.

A plot of the initial slopes of the lines in Figs. 17a-b vs the total TBP concentration is shown in Fig. 19. Extrapolation of the curve to 0% TBP yields an H_2O/H^+ ratio of 1.0, i.e., H_3O^+. This behavior is reasonable, since as the TBP concentration is lowered the nonpolar CCl_4 would tend to discriminate against the more highly hydrated and more polar species in favor of a symmertical, TBP-shielded species, in effect enhancing the basicity of the TBP. Further evidence for such a possibility is given by the behavior of the more basic trioctylphosphine oxide (TOPO), which extracts the hydronium ion exclusively as the species $3\ TOPO:H_3O^+....ClO_4^-$ over large ranges in both the TOPO and acid concentrations.[71]

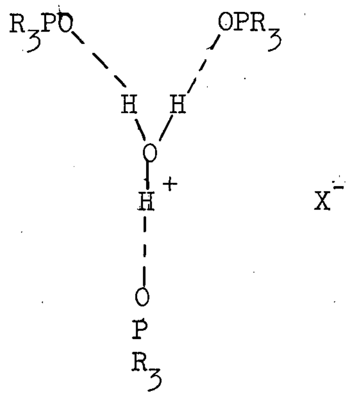
Extrapolation of the curve in Fig. 19 toward higher concentrations indicates that a value somewhat above $3H_2O/H^+$ is being approached for pure TBP, although drawing conclusions for such concentrated solutions from so few data is not justified, especially in light of the nonideal nature of such solutions. All that can be stated is that the value of 4 which was quoted previously is not unreasonable; and since it is definitely the hydronium ion which is extracting, trihydration of that ion in such a hydrophilic solution as pure TBP is certainly possible.

Several pieces of information have been presented for the extraction of a strong (completely dissociated) acid HX into TBP in CCl_4 solutions. First, there are 3 TBP molecules per hydrogen ion. Second, there are between 1 and 4 H_2O molecules per hydrogen ion, the amount depending on the TBP concentrations. And third, the species is an ion pair. On the basis of these considerations, a possible structure for the extracting species that can be formulated for very dilute TBP solutions (< 1%) is the hydronium ion hydrogen-bonded to a solvation shell of three TBP molecules,

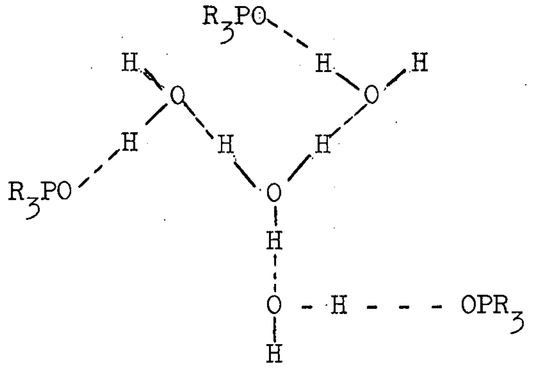


MU-26576

Fig. 19. Variation of initial $H_2O/HClO_4$ ratio in the organic phase with total TBP concentration.



where R is the buyoxy group, C_4H_9O. As the TBP concentration rises, H_2O molecules are able to enter the species and act as bridges between the hydronium ion protons and the TBP molecules, until for very concentrated TBP solutions the hydronium ion is quite possibly surrounded by a complete primary H_2O shell of three molecules, which is in turn hydrogen-bonded to three TBP molecules as a secondary solvation shell:



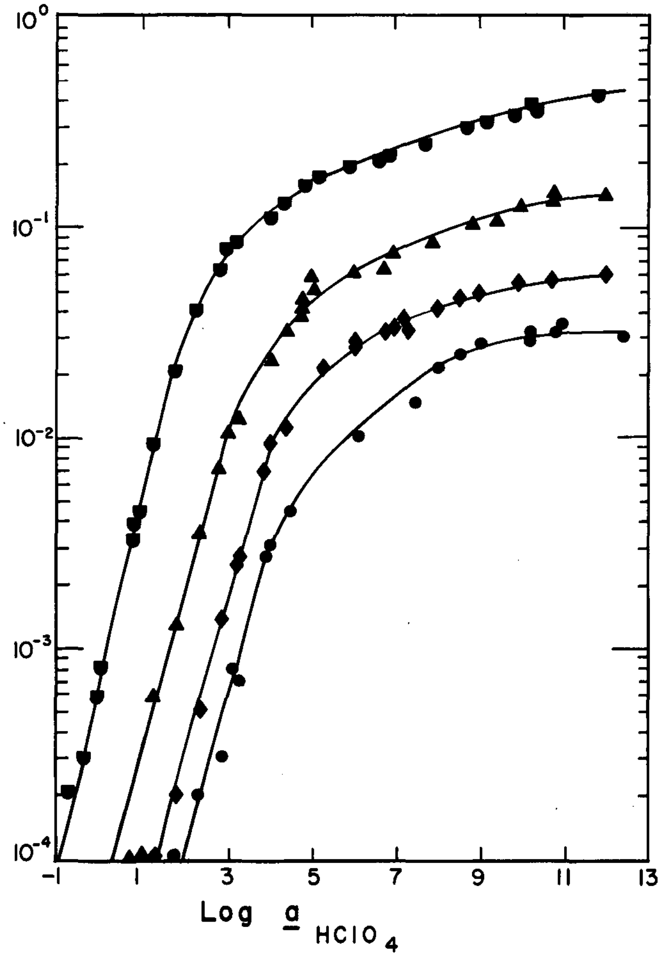
The extracting species can thus be written, in the general case, as $[3TBP \cdot H_3O^{+} \cdot (m-1)H_2O \cdots X^{-}]$, where m is between 1 and 4.

4. Concentrated Solutions

Since the extracting species have 3 TBP/H^+ for $HClO_4$ and HBr and 1 TBP/HNO_3, it might be concluded that there would be no more extracting once the stoichiometric ratio equaled the extraction-species ratio. It is found, however, that the extraction continues beyond this point for all three acids, although a marked change in the characteristics of the extraction occurs. Taking the two types of systems separately, because of the differing manner of extraction, one can make a limited analysis of this behavior.

The foregoing section has dealt with the case in which the extraction takes place as shown in Eqs. (5) and (6), where n = 3, m = 1.4 to 2.5, and the species is an ion pair. It is found, however, that $HClO_4$ extracts into TBP even after the organic-phase hydrogen ion concentration becomes greater than 1/3 of the TBP concentration, and in fact it extracts up to and a small amount past the point where $[\overline{H}^+] = [\underline{TBP}]$ (Fig. 17). In order for this to occur there must be a change in the extracting species when the stoichiometric ratio TBP/H^+ drops below 3. An indication that this is the case is seen in Fig. 20, where log $[\overline{H}^+]$ is plotted vs log $(HClO_4)$ for four different total TBP concentrations; it may be noted that the break in each curve occurs at a TBP/H^+ ratio of 3. Other experimental data that support this change are the decrease in the $\underline{H_2O}/H^+$ ratio, as seen in Fig. 17, and the decrease in slopes when log $[\overline{H}^+]$ is plotted vs log $[\underline{TBP}]$ for increasing aqueous $HClO_4$ concentrations (Fig. 21).

It must be realized that in the region where the ratio TBP/H^+ goes below 3 Eqs. (5) and (6) no longer apply, and dilute-solution calculations such as those done in the previous section cannot be made. Thus any statements about the species present must be inferred from the total (stoichiometric) concentration of each component, unless a different species is identified and defined by some spectroscopic method. With this kept in mind, it is still possible to make several qualitative statements regarding the region of high aqueous (and organic) acid concentrations.



MU-26577

Fig. 20. Variation of acid content of organic phase (CCl_4 diluent) with aqueous $HClO_4$ activity for total TBP concentrations of: ●, 0.0384 M; ◆, 0.0641 M; ▲, 0.128 M; ■, 0.366 M.

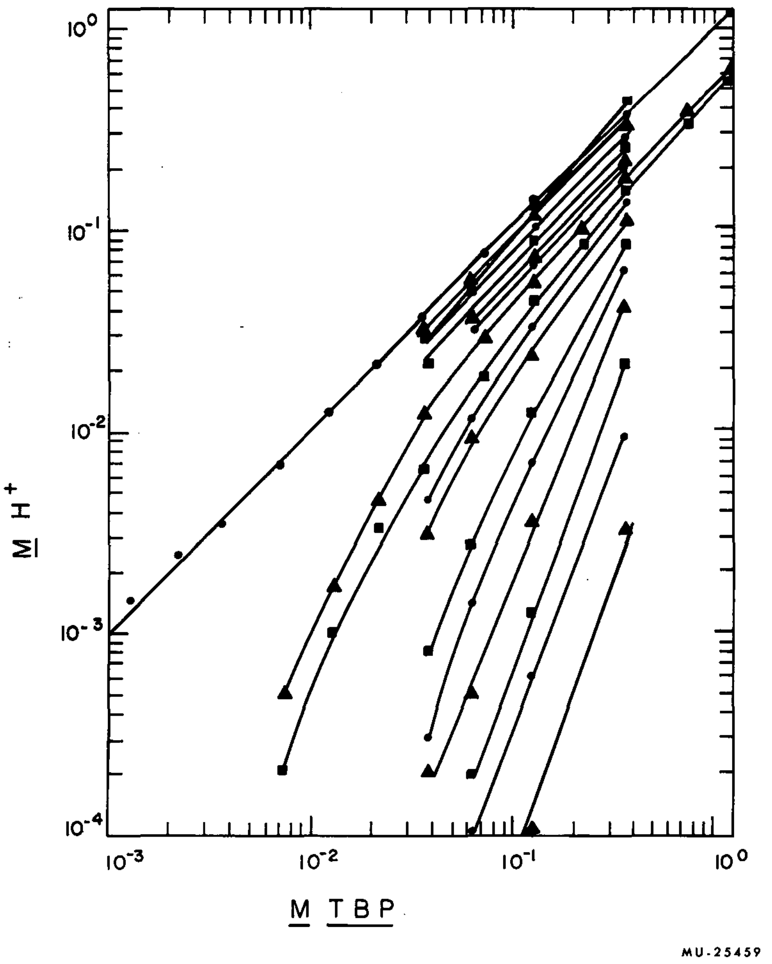


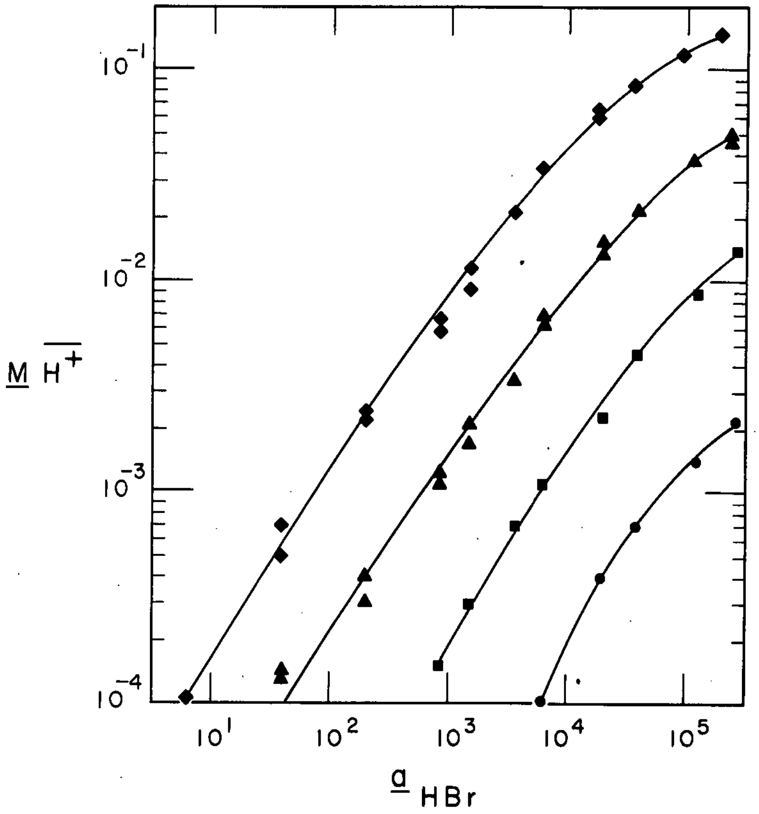
Fig. 21. Variation of acid content of organic phase (CCl_4 diluent) with total TBP concentration for increasing aqueous $HClO_4$ concentrations of (from bottom to top): 1.69, 2.64, 3.40, 4.07, 4.69, 5.22, 6.08, 6.50, 6.94, 7.47, 8.76, 8.92, 9.73, 10.5, 11.2, 11.6, and 12.5 M.

At very high external $HClO_4$ concentrations (approx. 10 M) the H_2O/H^+ ratio in the organic phase starts dropping very rapidly and approaches 0 for the highest $[\overline{H}^+]$ (Fig. 17). When the external acid is 11.6 M, the TBP/H^+ ratio is exactly 1.00 over a TBP concentration range of 10^3 (Fig. 21). Thus the stoichiometric ratio of the components yields $TBP \cdot H^+ \cdot ClO_4^-$ as the extracting species at these very high acid concentrations. An interpretation of this behavior is that the greatly reduced H_2O activity (< 0.05) allows TBP to compete more favorably as a base for the proton and, in fact, to become the primary solvating molecule. (This would be very similar to the case of a more basic trialkyl amine forming an ammonium salt.)[87] The species can then be written $TBPH^+ \ldots ClO_4^-$.

For the extraction from 12.5 M aqueous $HClO_4$ into 3.5% and 10% TBP the TBP/H^+ ratio actually falls below 1.0. This may be due to extra $HClO_4$ present in the organic phase as an ion association with $TBPH^+ \ldots ClO_4^-$ and not bonded directly to TBP. More likely, however, it is due to the attraction of the proton to the ester oxygens of the TBP, since their relative basicity has been enhanced by the reduction of the H_2O activity to the point at which they too may compete as solvating groups in the organic phase.

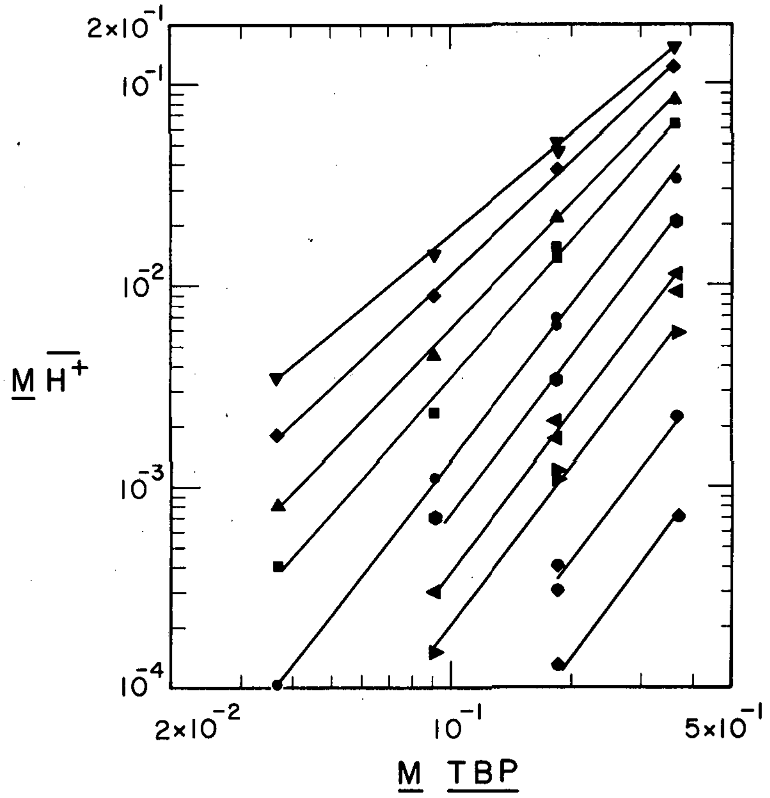
It is difficult to determine what other species are present in the transition region between 6 and 10 M aqueous $HClO_4$. From the fact that the water concentration remains relatively constant (Fig. 17) it appears that some kind of hydrated species of lower TBP content than the previously considered $3TBP \cdot H_3O^+ \cdot (m-1)H_2O \ldots ClO_4^-$ must be present; possible examples of such species include $2TBP \cdot H_3O^+ \cdot H_2O \ldots ClO_4^-$, $2TBP \cdot H_3O^+ \ldots ClO_4^-$, $TBP \cdot H_3O^+ \ldots ClO_4^-$, and $TBPH^+ \cdot H_2O \ldots ClO_4^-$.

Owing to limitations of solubility, stability, and volatility, HBr was not carried beyond 8.5 M in the aqueous phase, corresponding approximately to the $3TBP/H^+$ limit in the organic phase. For the few points where this ratio goes below 3, the behavior of HBr was similar to that described above for $HClO_4$ with regard to the H_2O/H^+ (Fig. 18) and $[\overline{H}^+]/(HX)$ (Fig. 22) curves and the plot of $[\overline{H}^+]$ vs $[\underline{TBP}]$ (Fig. 23).



MU-28748

Fig. 22. Variation of acid content of organic phase (CCl_4 diluent) with aqueous HBr activity for total TBP concentrations of: ●, 0.0366 $\underline{M}$; ■ , 0.0915 $\underline{M}$; ▲, 0.183 $\underline{M}$; ◆ , 0.366 $\underline{M}$.



MU-28722

Fig. 23. Variation of acid content of organic phase (CCl_4 diluent) with total TBP concentration for increasing aqueous HBr concentrations of (from bottom to top): 1.08, 2.14, 3.21, 4.28, 5.17, 5.57, 6.07, 6.48, 7.12, 7.50, 8.08, and 8.53 M.

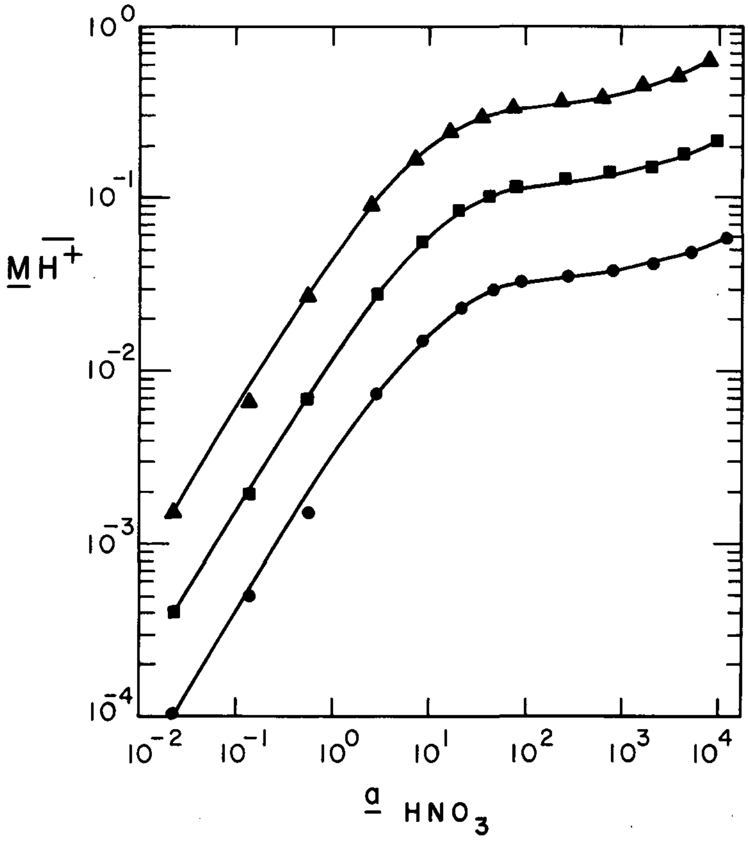
It is rather more difficult to make an anylysis of the extraction of HNO_3 beyond the one-to-one point. The nature of the extraction is certainly changing, as can be seen from the plots of log $[\overline{H}^+]$ vs. (HNO_3)(Fig. 24) and vs log [TBP] (Fig. 25). However, the characteristics of the extraction in terms of its dependence on the TBP concentration remain essentially the same, even though the HNO_3 concentration in the organic phase reaches a value twice the TBP concentration when the external (aqueous) acid is 16 M.

The most reasonable conculsion that can be made is that the HNO_3 is co-ordinating with the ester(butoxy) oxygens of the TBP, in spite of their very weak basicity. At first appraisal, such co-ordination would not be expected, since the much stronger acid $HClO_4$ showed only minimal use of these sites, even at much lower water activities than those in HNO_3. However, the presence of so much molecular HNO_3 in concentrated aqueous solutions causes appreciable extraction into CCl_4 alone (see Table IX), and thus even the weakly basic ester oxygens might be expected to be able to provide sufficient hydrogen bonding to produce the reaction

$$TBP \cdot HNO_3 + HNO_3 = TBP \cdot 2HNO_3 . \qquad (14)$$

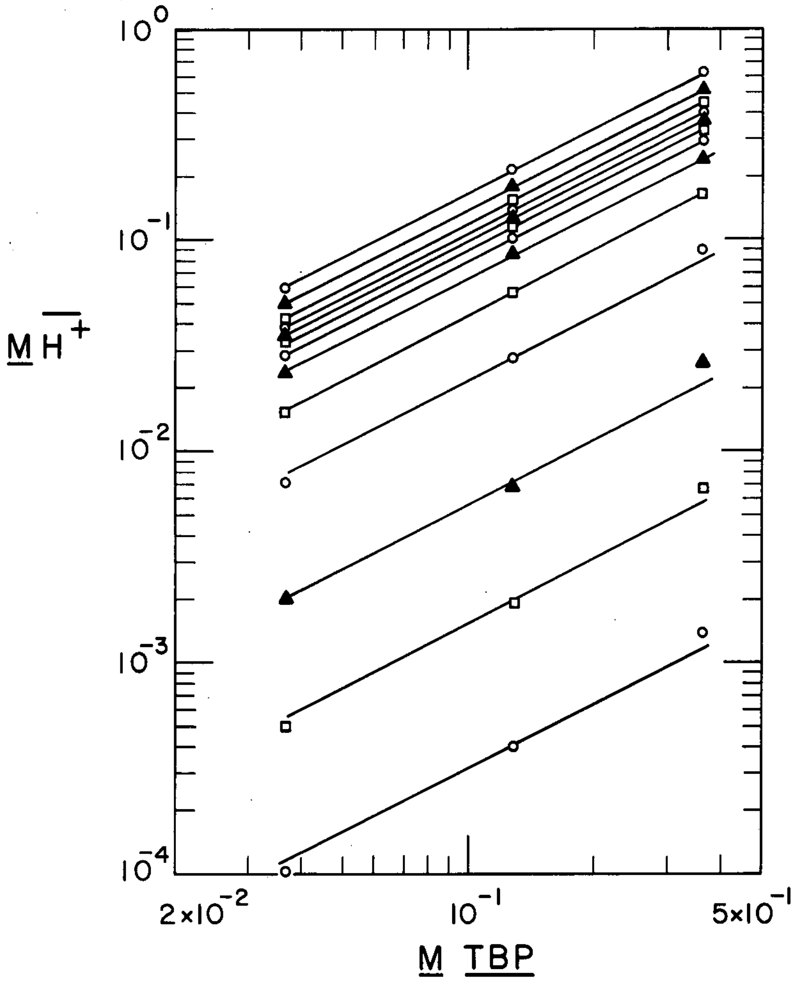
Further evidence for such bonding is the disappearance of the C-O-P triplet band at 9.5 to 10.2μ in the infrared spectrum and the concurrent appearance of a much broader band at higher wavelengths (also noted by Peppard[82]), indicating the presence of a hydrogen bond to the butoxy oxygen. No such changes are noted in $HClO_4$ below the 1:1 point.

It is also of interest to note that the extraction in this concentrated region is no longer completely anhydrous; that fairly large amounts of water (although not 1:1) are accompanying the HNO_3. This water appears in the infrared spectrum as weakly hydrogen-bonded water, with peak locations and heights similar to those in $TBP \cdot H_2O$, so that no hydronium ions are involved. A possible interpretation of the



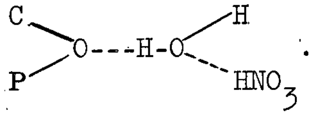
MU-28723

Fig. 24. Variation of acid content of organic phase (CCl_4 diluent; corrected for HNO_3 dissolved in CCl_4) with aqueous HNO_3 activity for total TBP concentrations of: ●, 0.0366 $\underline{M}$; ■, 0.128 $\underline{M}$; ▲, 0.366 $\underline{M}$.



MU-28724

Fig. 25. Variation of acid content of organic phase (CCl_4 diluent, corrected for HNO_3 dissolved in CCl_4) with total TBP concentration for increasing HNO_3 concentrations of (from bottom to top): 0.202, 0.501, 1.003, 2.02, 2.93, 3.95, 4.96, 6.05, 8.07, 10.08, 12.10, 14.04, and 15.80 $\underline{M}$.

presence of this water is that it is acting as a bridging molecule for the C-O-P-HNO_3 bond to form 

. It has been noted that HNO_3 extracts into benzene and tolerene as a monohydrated diamer;[83] such a species could possibly also be extracting in this case. More work is obviously needed on this problem.

In the absence of more detailed spectral evidence, however, such considerations as those described above must be treated as mere conjecture. The one definite piece of evidence--namely, the displacement of the C-O-P bond--seems to indicate that bonding is necessary for the HNO_3 in the organic phase, at least in dilute TBP solutions which would put a limit of 4 HNO_3 molecules per TBP molecule on the extraction. The fact that HNO_3/TBP ratios up to 4, but no higher have been observed, lends support to this idea.[79]

D. Summation

The extraction of acids by basic organic extractants has been seen to depend almost completely on the outcome of the competition among the anion, water, and extractant for the proton. Three separate systems can be distinguished. They are listed below in order of decreasing distribution coefficient.

1. Extractant-proton. In this system, an example of which is trilaurylamine-HCl,[88] the organic base completely captures the proton from both the water and the anion. The extraction is anhydrous, and distribution ratios are on the order of 10^4 or higher. The main function of the anion is to preserve electrical neutrality, although it does affect the distribution ratio by its effect on the water structure; the larger the acid anion, the better the extraction.

2. Extractant-proton-anion. In this system, an example of which is tributyl phosphate—HNO_3,[20-22] the anion forms the primary solvation for the proton in the organic phase and the acid distributes itself between the two phases on the basis of its ability to hydrogen-bond to either the water or the organic base. Distribution ratios are on the order of 10; their magnitude is dependent on the balance between the hydrogen-bond energy contributed by the acid and the energy lost through water-structure disruption; thus the larger the molecular acid, the better the extraction.

3. Extractant-proton-water. In this system, an example of which is tributyl phosphate—$HClO_4$—H_2O,[19] the water provides the proton solvation. The extraction then becomes a competition between the organic base and the water for the hydronium ion, and distribution ratios are on the order of 10^{-2}. The anion plays the same role as in the first system, that of a charge neturalizer, and again the larger the anion, the better the extraction.

No mention has yet been made of polybasic acids such as H_2SO_4 or H_3PO_4. When these acids ionize, the anion has both acidic and basic properties, making it similar to a water molecule. The resulting aqueous hydration of the anion, without the structure-breaking properties of the monobasic acid anions, causes these acids to extract quite poorly into most solvents.

It must be realized that there are no sharp lines of demarkation between the three types of systems described above. For instance, HNO_3 extracting into tribenzyl amine combines both 1 and 2 to give very high extraction,[87] while H_2SO_4 into trilaurylamine combines 1 and 3 and gives somewhat reduced extraction.[89] Similarly, trioctyl phosphine oxide—$HClO_4$ belongs to 3 at aqueous $HClO_4$ concentrations below 0.1 M, while it is of the first type above 2 M, the change in water activity over this relatively small range being enough to shift the proton solvation from water to the organic base.[71] Nevertheless, provided the relative base strengths of the anion, water, and organic solvent can be evaluated, it is possible to predict with a fair degree of accuracy how well an acid will extract and what form the extracting complex will take.

II. ION EXCHANGE

A. Introduction

Ion exchange, like solvent extraction, has been known to exist for over 100 years.[90] However, its development had to wait until reproducible resins with certain specific exchange properties, i.e., synthetic resins, were made available. Once such resins were synthesized[91] investigation was begun on the determination of their exchange characteristics, and again the impetus was provided by the need of the atomic scientists for quick and easy separation methods.[92,93] Reviews of the early work are available[94-98] and will not be discussed to any great extent here. More recent work is covered almost yearly in "Annual Reviews of Physical Chemistry"[99] and, with emphasis on analytical applications, biennially in Analytical Chemistry, Review Issue.[100] Several books on ion exchange are available,[101-105] the most recent being an exceptionally fine and complete treatment by Helfferich.[106]

Ion exchange was first treated as a surface phenomenon, since in the original exchanges (clays, soils, etc.) the surface area was the controlling factor.[107] It later became obvious, especially when the synthetic resins were perfected, that the exchange depended not on particle size but on the number of exchange sites available to the ions.[108] Thus all the explanations that have appeared within the last 15 years have begun by assuming that the exchange is a chemical equilibrium between two electrolyte solutions--the internal or resin phase, containing the resin ions (i.e., those ions which are part of the resin matrix), their counter ions, water (both free and as ion hydration), and perhaps some nonexchange electrolyte from the external or aqueous phase, which phase contains all the mobile (nonresin) ions in solution. The reaction under investigation is then

$$A + \overline{B} = \overline{A} + B, \qquad (15)$$

where A and B are any two species able to undergo exchange from one phase to the other and the superscript bar denotes the resin phase.

The equilibrium constant for this reaction is

$$K = \frac{(\bar{A})(B)}{(A)(\bar{B})} = \frac{[\bar{A}][B]}{[A][\bar{B}]} \cdot \frac{\gamma_{\bar{A}}\gamma_B}{\gamma_A\gamma_{\bar{B}}} , \qquad (16)$$

where parentheses denote activity and brackets concentration.

In general practice, standard states for both phases are chosen to be those of the ideal 1 m solution with the properties of the infinitely dilute solution; in other words, both phases are considered as aqueous electrolyte solutions. Under these conditions, the system can be considered to be a Donnan-type equilibrium,[109] with K = 1, and a concentration constant, Q, can be written as

$$Q = \frac{[\bar{A}][B]}{[A][\bar{B}]} = \frac{\gamma_A\gamma_{\bar{B}}}{\gamma_{\bar{A}}\gamma_B} \quad . \qquad (17)$$

Resin selectivities among various ions can thus be related to the ratio of their activity coefficients in the two phases.

From known values of γ_A/γ_B and experimentally determined Q's, the ratio of the resin-phase activity coefficients can be obtained, and this has been done for a variety of ions.[110-122] However, this treatment does nothing toward explaining why the ratios differ and what causes the resin to prefer one ion over another. In order to obtain this information, it is necessary to go to physical models of ion-exchange systems and consider what effect the different physical and chemical properties of the two phases have on the free energies of the various ions in the system.

Ion-exchange resins consist of a polymerized cross-linked hydrocarbon matrix, such as styrene-divinylbenzene or a polyacrylate, to which have been affixed ionic groups. Examples of such groups are sulfonate or carboxylate ions for cation exchange and substituted ammonium ions for anion exchange. Each ionic group has associated with it a counter ion of opposite charge in order to preserve electrical neutrality. It is these counter ions which undergo exchange, under certain conditions, with ions in aqueous solution.

When such a resin is put into contact with a dilute aqueous solution, the resin absorbs water, the exact amount depending on the degree of cross-linkage and the types of ions contained in the resin. The resin may then be considered as a concentrated electrolyte solution, somewhere on the order of 6 to 7 molal for usual resins of moderate (8 to 12%) cross-linkage. However, there are three significant differences, aside from the relatively high fixed concentration, between this resin phase and the external aqueous phase:

1. One of the ions in the resin phase is fixed and relatively immobile, its mobility being limited by the extent to which the hydrocarbon matrix can shrink or swell with concentration changes.

2. Electrostatic interactions are stronger in the resin phase, since the effective dielectric constant lies somewhere between that for the hydrocarbon matrix and that of pure water.

3. The water in the resin phase has less co-operative structure; i.e., the water molecules are, on the average, hydrogen-bonded to fewer other water molecules than in a dilute aqueous solution.

These three factors are considered in greater detail to subsequent paragraphs, and selectivities based on these considerations are evaluated in light of the known experimental data.

Factor 1, the fixed resin ion, leads to the already considered Donnan-membrane treatment. However, the ability of the resin to shrink or swell leads to the consideration of another term in Eq. (3)--a term which takes into account the osmotic free energy developed by the resistance of the resin toward expansion or contraction. It has been proposed[123] that this free energy takes the form

$$RT \ln Q = \pi (\bar{V}_B - \bar{V}_A) + RT \ln (\gamma_A \gamma_{\bar{B}} / \gamma_{\bar{A}} \gamma_B), \qquad (18)$$

where π is the osomatic swelling pressure and $\bar{V}_B$ and $\bar{V}_A$ are the partial molal volumes of the exchanging species in the resin phase. However, although the qualitative agreement of this idea with experiment was correct, the $\pi(\bar{V}_B-\bar{V}_A)$ term proved too small to account for the magnitude of Q,[114,124] and other considerations must play a part in resin specificaties.

Factor 2, more intense electrostatic interactions in the resin phase, owes its origin to several causes, as follows.

(a) The resin-solution phase has a high concentration of ions, and even moderately concentrated salt solutions may have dielectric constant values below 50 because a significant fraction of the water molecules is oriented around the ions. That is, the proportion of "free" water is reduced.[125,126]

(b) A large proportion of the wet resin volume (about 1/2 or more, for moderately cross-linked resins) is made of hydrocarbon matrix with a low dielectric constant, similar to that of benzene ($\epsilon = 2.3$).

(c) There is a reduction in the cooperative effect of the water dipoles in producing a large moment because of disorganization of the water structure.

Since electrostatic interactions are enhanced in the resin phase, ion pairing has been advanced as a possible explanation for resin specificity,[127-129] especially in light of the fact that cation-resin affinity for an ion generally increases with increasing charge and decreasing hydrated radius.[130] Again it appears that for cation resins this explanation, although qualitatively correct, is unable to completely account for observed selectivities.[131]

In anion exchange, furthermore, ion pairing is, at most, a minor factor, for several reasons. Firstly, strong ion-ion interactions between relatively large monovalent anions and large resin ions similar to the triphenylmethylammonium ion would not be expected to occur, owing to the low density and relative inaccessibility of the charges. Secondly, ion pairing would greatly favor highly charged ions, whereas the experimental evidence shows, upon careful investigation, that the converse is true.[132] Thirdly, many pairs of ions that differ only in their size show greater resin preference for the larger of the two,[120,133-136] in opposition to the expectation from ion pairing considerations.

Resin selectivity has also been ascribed to the polarizability of the counter ion by the field of the resin ion or vice versa.[137-140] Although this idea may have some application to cation exchange, and although it could by no means be considered to be the only factor, there are so many exceptions to the orders predicted from anion polarizabilities as measured by ionic refraction[132,136,139] that some other explanation is necessary for anion exchange.

Factor 3, the partial disruption of the normal structure of water, is due to the intrusion of the resin matrix into the water structure and to the high concentration of ions in the resin solution. In water at room temperature each molecule is hydrogen-bonded, on the average, to about three other water molecules in a pseudotetrahedral short-range structure.[9] Inside the resin phase, however, this short-range order is disturbed and broken up by the high concentrations of resin ions and counter ions. These ions occupy solution volume, and tend--to a greater or lesser extent depending upon their charge and size--to orient the water dipoles around themselves. Furthermore, the hydrocarbon matrix of the resin intrudes into the solution and confines the water and mobile ions to relatively narrow capillary pores and sheets with one, and possibly two, dimensions of the order of magnitude of 10Å.

Thus a water molecule in the resin phase is hydrogen-bonded, on the average, to fewer other water molecules than in the dilute external solution.

Factor 3, leading to differences between the ion-water and the water-water interactions in both the resin and the external aqueous phase, must be considered as a possible reason for resin selectivity. The hydration of ions in the resin phase will certainly be reduced below that in the dilute external solution. This is due, as in any concentrated electrolyte solution, to the smaller ratio of water molecules to ions, and to the fact that there is not sufficient room in the resin pores to allow as complete secondary solvation of the ion as in the dilute solution phase. That is, at distances from the ion greater than a few angstroms, there exist in the resin phase relatively nonpolarizable ions and hydrocarbon matrix, while in a dilute aqueous solution essentially only polarizable and orientable water molecules occur in the vicinity of the ion. However, ions that are so strongly hydrated in the external solution as to possess a primary shell of coordinated water molecules certainly tend to retain this coordinated shell in the resin phase, at least for resins of not too high a cross-linking. For example, it has been shown that the hexaquochromium (III) ion keeps its primary hydration shell in a cation-exchange resin.[141] It may be surmised, however, that the solvation of this first water shell itself will be greatly disturbed in the resin phase.

A small, highly charged ion will prefer the aqueous phase, as its transfer into the resin requires a loss of hydration energy. However, the larger the ion and the smaller its charge, the smaller its degree of hydration in the aqueous phase and the less hydration energy it can and does lose on passing into the resin phase. Thus, in an exchange process, the larger, less hydrated ion is pushed into the resin phase so that the smaller ion can achieve maximum hydration in the dilute external phase. The value of the equilibrium quotient for the exchange is larger as the disparity in the hydration of the ions is greater.

The idea that the larger the ion is, the less well it is hydrated and the more strongly it is forced into the resin phase is not correct if the ion has structural features or groups that are strongly hydrophilic. For instance, for anions of similar size and structure, the degree of hydrolysis of the anion, or the strength of the parent acid, is an indication of the strength of the interaction of the ion with water. The more strongly an anion picks up a proton (the weaker the parent acid), the more strongly the anion (hydrogen-) bonds to a water molecule, and the more strongly it prefers the dilute external solution phase to the concentrated resin phase.

The difference between the water-water interactions in the two phases must also be considered. The dilute external solution has essentially the hydrogen-bonded structure of pure water. The addition of ions disrupts this structure. Small, highly charged ions reorganize the nearest water molecules into their own hydration shell, and orient and polarize water molecules for some distance. On the other hand, large, low-charged ions break up a large volume of the water structure but do not have a sufficiently high charge density to tightly bind the nearest water molecules. The hydrogen-bonded water structure can be thought of as an elastic framework which tends to oppose the entrance of the intruding large ion. The limiting case is furnished by an uncharged molecule such as CCl_4 which is actually kept out of solution by the water structure. (Large anions such as $FeCl_4^-$, $AuCl_4^-$, etc., are similar to the CCl_4 molecule but with a single negative charge distributed over the chlorine atoms, and so should also be affected by this opposition of the water structure, though to a smaller extent.) In the resin phase, the water structure is already so badly disrupted that it offers much less opposition to the entrance of a large ion. The larger the ion, the more easily it is transferred out of the dilute aqueous solution into the less ordered water structure of the resin phase, yielding the same selectivity order as already indicated above by consideration of the ion-water interactions alone.

An obvious limitation on the foregoing is the size of the ion-exchange resin pores. When an ion is too large to fit into the pores without considerable expenditure of energy to expand the resin matrix, it is discriminated against by the resin. Since resins do not have a single pore size, but a distribution of sizes, and the average value decreases with increasing cross-linkage, the pore-size limitation is least important for the lower-cross-linked resins. For normal-sized ions and for resins of normal cross-linking (8 to 12% divinylbenzene content), and with the pore-size limitation kept in mind, it may be stated that in an ion-exchange reaction, the less highly hydrated (larger) ion is preferentially ejected by the water structure into the resin phase, and the more highly hydrated (smaller) ion preferentially solvates in the dilute aqueous phase, thus maximizing the water-water and water-ion interactions in the system.

Two other interactions are of interest in any attempt to describe ion-exchange behavior. These are the anion-cation attractive forces in the aqueous phase, and the resin ion-counter ion attractions in the resin phase. In dilute solutions the former are very small, owing to the high dielectric constant of water and the relatively great distance between ions. The latter, however, may be quite significant in the cation resin[128,129] (although not for the anion resin, as has already been discussed), because of the high concentration of the ions, the breakdown of the water structure, and the relative accessibility of the charge. The effects of ion-resin interactions are considered as each system investigated in this study is described in the "Results and Discussion" (Section II, C) as are also the effects of aqueous ion-ion interactions in concentrated solutions.

B. Experimental Method

1. Anion Exchange

a. Reagents

The formic, acetic, and trichloroacetic acids were Baker and Adamson reagent grade. The butyric acid was Baker and Adamson technical grade, 98-100%, and the caproic acid was Matheson, Coleman, and Bell, mp -5 to -3° C. The valeric and trimethylacetic acids were Eastman White Label. Seventy-three percent sodium methyldichloroacetate from United Mineral and Chemical Corp. was acidified with 3 M HCl at 0° C, and the methyldichloroacetic acid was extracted into ether and distilled under reduced pressure.

One-molar solutions of the sodium salts of each of the acids were prepared by placing the appropriate weighed amount of each acid in freshly boiled distilled water and adding NaOH pellets (Baker and Adamson reagent grade, 97% minimum) with stirring until a pH of 7.5 was reached, then diluting with boiled distilled water to the final volume. For all these solutions, the final pH was between 7.3 and 7.5. The 1 M solutions of all the salts of acids with pK≈5 were titrated with standard HCl, using a pH meter; the concentrations of the salts of the stronger acids were determined from the weight of the acid. All lower concentrations were made by dilution of the 1 M solutions with freshly distilled water. The chloride content of the salts was determined to be 1% or less in all cases except for the methyldichloroacetate (3%), and corrections, where significant, were applied. The Dowex AG-1 × 10, 100–200 mesh, analytical grade anion-exchange resin was obtained from Bio-Rad Laboratories. The resin was washed alternately with 3M HCl and water several times and rinsed with water until the rinse water was chloride-free. The washed resin was allowed to air-dry for three days, dried over anhydrous $Mg(ClO_4)_2$ in a vacuum desiccator for eight days, and stored in an airtight bottle.

The resin capacity was determined to be 2.692 meq/g by complete elution of the chloride ion from the resin with 3 M $HClO_4$ and titration of the displaced chloride. The volume of water absorbed by the resin when placed in contact with a salt solution was found to be 0.5 ml/g.

b. Procedure

Exactly 1.000 g resin and 10.00 ml of salt solution were placed in a 30 ml polyethylene bottle with a polyethylene screw top, and shaken for 10 to 14 hours. Two 4.00-ml samples were removed through frittered glass filters and titrated by the Volhard method to determine the chloride displaced from the resin by the salt. By use of this information plus the initial salt concentration (corrected for the water absorbed by the resin) and the resin capacity, and assuming no resin invasion (no nonexchange electrolyte), the quantities listed in Table XVIII were calculated. (Actually, of course, there is some nonexchange electrolyte present in the resin when in contact with the 1.0 M solutions, or even with the 0.02 M solutions. But this leads to less than 5 to 10% error in the values of Q and D listed in Table XX for the 1.0 M solutions, and a progressively smaller error for the more dilute ones.)

All work was done at room temperature, 23 ± 2° C.

2. Cation Exchange

a. Reagents

The cation-exchange resins were Dowex AG 50W-X12, a styrene-type sulfonic acid exchanger, and Bio-Rex 70, an acrylic-type carboxylic acid exchanger, both obtained from Bio-Rad Laboratories, Richmond, California. The liquid cation exchanger was dinonylnaphthylenesulfonic acid (DNNS), obtained from King Organic Chemicals, Norwalk, Connecticut. The salt and acid solutions were prepared by volumetric dilution of accurately analyzed saturated solutions of reagent-grade material [except CsCl, which was 95% CsCl+ 5% (RbCl+ KCl)] with distilled H_2O. The radioactive tracers, their properties, and the processing (if any) are shown in Table XIX.

b. Procedure

Batch measurements were made as described for anion exchange, except that the amounts of resin and solution were adjusted for optimum tracer distribution and the aliquots were γ-counted instead of titrated. For the alkali tracers 0.1000 g resin was shaken with 10.00 ml solution and the tripositive tracers were either 0.1000 g resin and 10.00 ml solution or 0.0500 g resin and 5.00 ml solution. The resins used in the batch experiments had been previously washed with HCl and distilled water and dried as described for the anion-exchange resins. Measurements made on the liquid ion exchanger (DNNS) were conducted in the same manner as in the tracer experiments described in Section I.B. 2.a.

In order to investigate the behavior of alkali tracers on Dowex-50W, several adjustable-head ion-exchange columns were prepared; they are described in Table XX. Each column was loaded by insertion of a glass-wool plug 2 cm above the tip and washing a slurry of resin in 6 M $HClO_4$ through the column until it was filled to within 1 cm of the top, then placing a glass wool plug on the top of this resin column. The filled column was washed first with approx 20 column volumes of 6 M $HClO_4$ and then with approx 20 column volumes of the salt or acid solution under investigation in order to convert it to the desired ionic form. In order to minimize swelling and shrinking differences in the resin column as the solution concentration was changed, a relatively high (X12) cross-linked resin was used, and preshrinking with 6 M $HClO_4$ eliminated any significant further shrinkage at higher solution concentrations.

For the investigation of the Bio-Rex 70, a single column identical in size to Column 2 (Table XX) was prepared in a similar manner, except that the column was loaded with a slurry of resin in 8 M LiCl and only the Li salts were used as eluting agents, because of the weak acid nature of the resin. This resin was more susceptible to shrinking and swelling than the Dowex-50, owing to the lack of cross-linking in the acrylic polymer, which resulted in the resins being under a fair degree of pressure when dilute solutions were being used. By using a slower drop rate, more time was allowed for equilibrium in these cases; the lack of anomalous behavior at low concentrations indicates that the excess pressure had no appreciable effect on the exchange.

The volume of solution necessary to elute a tracer ion from the column was determined by placing 10 μliters of the tracer ion solution on the glass wool plug, allowing it to sink into the plug, and immediately beginning the elution of the tracer at a flow rate of approx 1 drop/min. The elution volume was observed to be independent of the drop rate under these conditions, indicating that equilibrium conditions were being closely approximated for all determinations. In order to determine the volume required for elution a present number of drops was measured into a small test tube by a photoelectric drop counter, which then actuated the mechanism of a fraction collector that positioned a new test tube under the column. The tubes were counted by using a well-type Na(Tl)I crystal scintillator and a single-channel pulse-height analyzer, the tube with the greatest activity corresponding to the peak in the elution curve. Volumes were converted from drops to milliliters from a separate determination of the number of drops per ml for the eluting solution.

A similar method was used for the tritiated water elution, except that the drops were collected in 10 ml of scintillator solution for β-counting. The scintillator solution was made up as follows: 1200 ml toluene, 1200 ml dioxane, 720 ml absolute ethanol, 156 g naphthalene, 15.6 g 2,5 diphenyloxazole (PPO), and 0.3 g 1,5-bis-2-

(5-phenyloxazolyl)-benzene (POPOP). These samples were counted by using two phototubes in coincidence in order to reduce the stray radiation background.

Most of the deteminations were made by using two or three tracers at once in order to keep the conditions for the different tracers as alike as possible, especially in those cases in which the elution volumes for two tracers were very similar. Two or more determinations were made for almost every tracer in each solution; the elution volumes were reproducible to within 5% for almost every case. No difference in exchange behavior was observed when Na^{24} produced by neutron irradiation of $NaHCO_3$ was used in place of carrier-free Na^{22}, or when a solution of tracer Na^{22} in 10 M HCl was saturated with NaCl and 10 μliters of this saturated solution was used to load the column. This lack of change indicated that the elution volumes obtained were independent of the amount of tracer cation as long as this amount was negligible in comparison with the capacity of the resin.

By using three different-sized columns it was possible to investigate the concentration range from 0.4 M to saturation for the alkalies in all salt and acid solutions except HAc and the lower concentrations of LiAc in Dowex-50W, which were done batch-wise. Three different methods were used to determine the relative amounts of resin in these columns; the results of these methods agreed to within 5%. The first was to calculate the total volume of resin from the dimensions of each column, the second was to determine the volume of H_2O needed to elute I^- tracer from each column, and the third was to compare elution volumes for identical tracers and solutions on different columns.

The volume of water external to the resin beads was determined by using I^- tracer as described above. The total volume of water in the column was determined by weighing the wet column plus resin, then removing the resin from the column and drying and weighing both the resin and the column; the difference between the wet column + resin and the dry column + dry resin represented the weight (and volume, assuming $d_{H_2O} = 1.00$) of the H_2O. The difference between this volume and that found by the I^- is the amount of H_2O inside the resin phase, i.e., the internal water volume.

In order to confirm the total water volume figure, and to determine whether the entire volume of the resin was being sampled by the eluting solution, 20µℓ of tritiated water was eluted as previously described (see table below).

Elution of H_xT_yO from ion-exchange columns.
(See explanation of units in Appendix.)

Column	Eluant	M	m	vol	Vol_{H_2O}
1	H_2O	——	——	1.39	1.39
1	LiCl	6.02	6.92	1.26	1.10
1	LiCl	13.2	20.3	1.22	0.79
4	H_2O	——	——	3.49	3.49

The value obtained by using H_2O as the eluting agent was within 2% of that obtained by the weighing method. When 6 M LiCl was the eluting agent, however, the elution volume was just 7.5% less than for pure water, while in 13 M LiCl it was only 10% less. These volumes are much larger than those obtained for the tracers (as will be seen in Table XXVII), implying that H_2O is preferentially absorbed by the resin. Since the total volume of the resin column was kept constant by the glass wool plugs, and since the hydrocarbon-matrix volume was constant, the implication is that some portions of the internal resin volume that are available to the water are not available to the ions. This could possibly be due to the shrinkage of the resin and the subsequent closing off of some of the resin pores and capillaries to the ions; more likely, the higher ionic concentration of the resin is causing it to have a greater preference for the solvating H_2O than for the alkaki cations, yielding an ion-exclusion effect.[142]

The volumes that will be shown in Figs. 30-43 are the result of subtracting from the total volume needed to elute the tracer the free column volume i.e., the volume of solution in the column that is being sampled by the tracer--and then converting to the corresponding volume of H_2O in the salt solution, so that salt molalities can be plotted in the abcissa. All volumes are recalculated to apply to Column 2.

By linearly extrapolating the Na tracer elution volumes in the various salts to 0.1 M and comparing them with the batch determinations described below, a conversion factor between elution volume and distribution ratio was obtained.[143] For Column 2, this factor was 0.38 ± .03 as compared with the theoretical value of 0.375 based on the resin weight.

Distribution ratios for the Batch-method resin cation-exchange determinations (Tables XXX and XXXI) were determined from the equation

$$D = \frac{10\,(\text{counts/min per ml original solution-counts/min per ml aqueous phase})}{(\text{counts/min per ml aqueous phase})}, \qquad (19)$$

while those for the DNNS were determined from

$$D = \frac{(\text{counts/min per ml organic phase})}{(\text{counts/min per ml aqueous phase})}\,, \qquad (20)$$

all counts being first corrected for background.

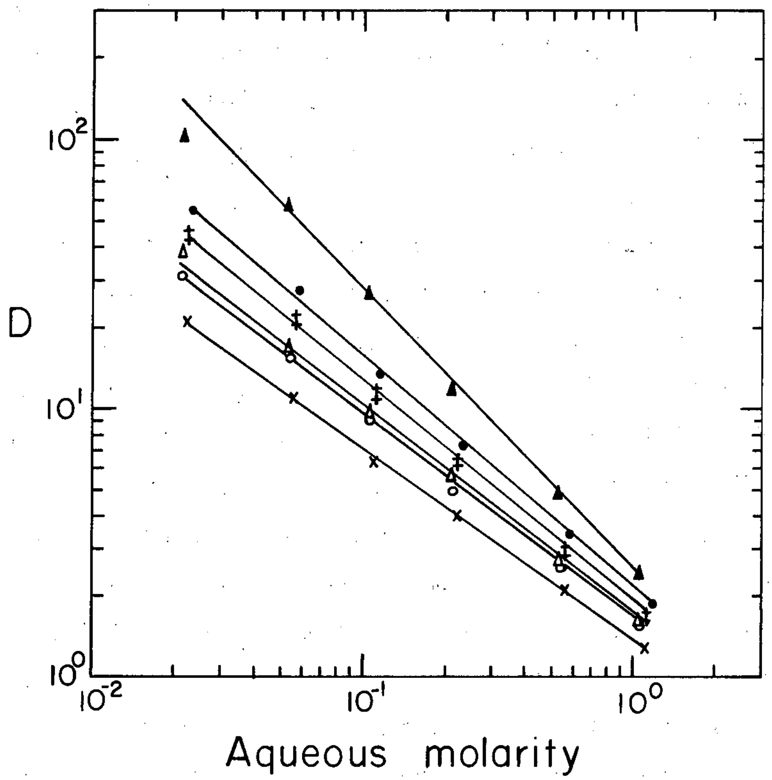
All experimental work was done at room temperature, 23 ± 2°C.

C. Results and Discussion

1. Anions

In order to test the ideas presented in the introduction, a homologous series of anions that differ in only one parameter--e.g., size or degree of hydration--is needed. To such series are available, both based on the fatty acid anions. The first, in which the anions differ only is size, is the aliphatic carboxylate ions $CnH_{2n+1}CO_2^-$; the second in which the anions differ mainly in degree of hydration, is the trisubstituted acetate ions, $(CH_3)_nCl_{(3-n)}CCO_2^-$. Their properties and use are described below.

The predicted effect on ion size has been tested by determining the order or resin selectivity for the fatty acid anions acetate, butyrate, trimethylacetate, valerate, and caproate against the common ion, chloride. This was done at total aqueous phase concentrations of 1.0, 0.5, 0.2, 0.1, 0.05, and 0.02 $\underline{M}$, and the results are shown in Table XVIII and Fig. 26. The symbol Q, the concentration constant, is defined as $Q = [\bar{A}][Cl]/[A][\overline{Cl}]$, where the superscript bar means resin-phase concentration in millimoles per gram of resin, and no bar means aqueous-phase concentration in millimoles per milliliter of solution. Similarly the distribution ratio D is defined as $D = [\bar{A}]/[A]$. The charge on these fatty acid anions is concentrated in the carboxylate group, and so this group is the principal source of hydration for the ions. Furthermore, these anions are all derived from weak acids of the same strength, and so the hydration of the carboxylate group in each is comparable, leaving primarily the increasing size of the hydrocarbon tail as a selectivity factor. In going from acetate to caproate, the increasing size of the hydrocarbon tail must increasingly disturb the hydrogen-bonded water structure of the dilute external solution, so that the larger the tail, the more strongly the anion should be pushed into the less structured resin phase. This leads to



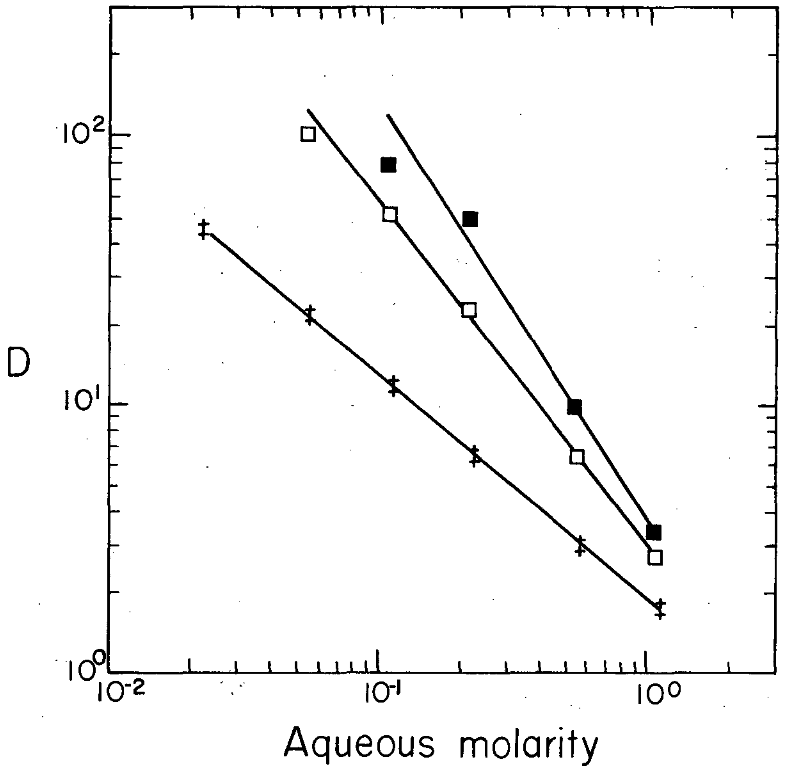
MU-25024

Fig. 26. Variation of distribution ratio of sodium salts of fatty acids on Dowex-1 with total aqueous molarity for: X, acetate; O, formate; △, butyrate; ‡, trimethylacetate; ●, valerate; ▲, caproate.

to the predicted order of resin selectivity acetate $<$ butyrate $<$ valerate $<$ caproate, which is that observed experimentally. Trimethylacetate has a more compact structure than its straight-chain isomer, valerate, and so has a somewhat smaller value of D and Q. These selectivity orders cannot be explained by a simple electrostatic ion-pairing model.

Besides the effect of ion size, the effect of specific ion hydration was also tested. The sequence of anions trimethylacetate, methyldichloroacetate, and trichloracetate was used. In replacing a methyl group with a chloro group, the size of the anion is held substantially constant, but the inductive effect of the chlorine atom transforms the anion into a progressively weaker base. That is, the corresponding acids become progressively stronger, as can be seen in Table XXI, where are listed the ionization constants for the similar acids acetic, chloroacetic, and trichloroacetic. Since the carboxylate of the increasingly chlorine-substituted anion is less basic toward capturing a proton from water it also interacts less strongly with water molecules. That is, the anion of the stronger acid is more weakly solvated by water. Thus, it would be expected that trimethylacetate would prefer the dilute external solution more than the weaker base, methyldichloroacetate; and the latter ion, in turn, would prefer the aqueous phase more than the still weaker base, trichloroacetate. This is precisely the experimentally observed order, as given in Table XVIII and Fig. 27.

The effects of ion size (water-structure-breaking factor) and of specific ion hydration may act in opposite directions. Usually the latter dominates in determining the order of anion selectivity. Formate and acetate ions (Table XVIII and Fig. 26) furnish an example. From the agrument given above for the larger fatty acid anions, it might be expected that the larger acetate ion would be preferred by the resin over formate. But in the earlier example, all the anions were of the same base strength, whereas formate is a weaker base than



MU-25025

Fig. 27. Variation of distribution ratio of sodium salts of chloro fatty acids on Dowex-1 with total aqueous molarity for: ‡, trimethylacetate; □, methyl-dichloroacetate; ■, trichloroacetate.

acetate (Table XXI), so that its carboxylate group interacts more weakly with water than that of the acetate ion. The stronger ion hydration of acetate than of formate holds the former preferentially in the external aqueous phase, giving the observed resin order formate > acetate < butyrate.

It will be noted that Q shows a slow increase in value as the aqueous molarity decreases (excluding 0.02 M values, which have large experimental errors) for all except trichloroacetate, where exactly the reverse occurs. This trend has been correlated with the change in the resin composition, X_{Cl}, and is in agreement with published data by other workers.[138] However, recent work has shown that this apparent trend is due to the fact that only one of the anions (Cl) in the solution is determined experimentally and the other quantities are calculated from this value.[121, 148] If the other anion (A) is determined and calculations made on the basis of its concentrations, the Q values are found to decrease with decreasing aqueous molarity. Thus it appears that variations in Q are due more to compounding of experimental errors than to actual changes in the resin selectivity. In the case of trichloroacetate the range of Q values seems excessively large to the ascribed solely to experimental errors, however, and it is possible that some other factor such as changes in activity coefficient ratios in the resin phase with resin composition may be playing some part in the observed variation. Further work on these systems is definitely necessary before any conclusions can be drawn.

The ideas previously presented concerning the effects of ion size and ion hydration, which have been confirmed by the experimental results of the fatty acid anions, can be extended to other systems. One particular system of interest is the selectivity sequence $F^- < Cl^- < Br^- < I^- < ClO_4^- < AuCl_4^-$,[120,133-136] which is anomalous to both the ion-pairing and polarization explanations. It may be observed that these ions get progressively larger and become weaker bases, both factors leading to the actually observed order. For the smaller F^- and Cl^- ions, the effect of better solvation in the dilute aqueous phase is probably the predominant factor (the greater hydration of F^- relative to Cl^- is indicated by the relative strengths of the parent hydrohalic acids and by the smaller limiting equivalent conductivity of F^-). For Cl^-, Br^- and I^-, both factors probably contribute significantly, and for the larger, less highly hydrated ions I^-, ClO_4^-, and $AuCl_4^-$, the disruption of the water structure is probably the more important factor.

It is difficult to explain this sequence solely on the basis of electrostatic ion pairing of the resin quaternary amine group with the anion. The ions Cl^-, Br^-, and I^- have similar limiting equivalent conductivities, (Table XXI), indicating approximately the same effective (hydrated) radii, and the limiting equivalent conductivity for ClO_4^- is considerably less, indicating a still larger effective radius in solution. If only electrostatic ion pairing were important in determining anion selectivities, Cl^-, Br^- and I^- should then be bound to the resin about equally, and all much more strongly than ClO_4^-, in contradiction to the experimental facts. Also, any explanation based solely on anion polarizability fails in the ClO_4^-–I^- case, as I^- has a larger ionic refraction than ClO_4^-.

In summary, then, it is seen that for anions of weak acids, the specific effect of ion hydration is the predominant one, and the more basic the ion the more it prefers the dilute external phase. For large anions, or those of strong acids, ion hydration is less important, and the effect of disrupting the hydrogen-bonded water structure of the dilute external solution becomes more important--the more so as the ion becomes larger. That is, in the exchange, the large ion is ejected out of the solution into the less structured resin phase (pore size permitting), as such behavior maximizes the ion-water and water-water interactions in the total system. It is suggested that these differences in ion-water interactions (ion hydration) and water-water interactions (water-structure) between the resin and aqueous phase are the principal origins of anion selectivity with the usual synthetic organic resins, rather than any specific resin ion—counter ion or resin matrix—counter ion interactions, as is postulated in any electrostatic ion-pairing model or in one based solely on anion polarizability.

2. Alkalies

The distribution ratios for hydrogen and the alkali ions between sulfonic-acid-type resins and dilute aqueous solutions progress in the order Li < H < Na < K < Rb < Cs.[130] Many authors have attempted to provide an explanation for this behavior; an excellent and thorough review is given by Helfferich.[106] These treatments are usually based on one of two considerations--either resin swelling and the resultant osmotic pressure[123] or some specific electrostatic attraction between the resin ion and its counter ion.[127-128] Both of these are in turn based on the size of the hydrated ion--the former in terms of the amount of swelling caused by the variously sized ions, the latter in terms of the distance between the positive and negative charges as determined by the hydrated size--and both give the experimentally observed order.

There is a third major consideration, one that has not been so thoroughly investigated as the others, which also yields the experimentally observed order. This explanation ascribes the selectivity of the resin to the differences in the water-water and ion-water interactions that occur in each phase. These interactions were discussed in detail in the Introduction for the general case of ion partition between water and a resin and it was shown that both effects--ion hydration and disruption of the water structure--cause the aqueous phase to favor the smaller, more highly hydrated ion over the larger, less hydrated ion, so that the latter is forced into the resin. Application of these ideas to the alkalies gives rise to the observed order for the distribution ratios as a consequence of the efforts of the system to maximize the water-water and ion-water interactions.

Since it has been shown that there are at least three "independent" explanations of the resin-selectivity order of the alkalies, none of them can be said to be unique. Instead, it seems reasonable to assume that the true picture is a composite of all the theories, and that each is valuable for different aspects of the problem of resin selectivity. The approach used in this presentation primarly emphasizes the role of the electrostatic interactions in both phases in terms of the water-water, ion-water, and ion-ion attractive forces. Such a treatment must, of necessity, be qualitative in nature, and only results relative to some standard system can be obtained; nevertheless, it should prove useful for understanding and predicting resin selectivities.

In any aqueous electrolyte solution the three interactions described above are always present. These same interactions are present in the resin phase, although to different extents (a fourth interaction, that between the resin matrix and the ions, is not considered important for the alkalies; however it may be for larger ions such as the triphenylmethylammonium ions.)[131] In dilute aqueous solutions the ion-ion interactions are small owing to the large interionic separation and high dielectric constant of water, and may be neglected. The resin phase, however, is a moderately concentrated solution (about 6 molal) for the usual resins (8 to 12% divinylbenzene content), and ion-ion interactions may be of some importance even when the external solution is dilute. This leads to the experimental observation that the activity coefficients of ions in the resin are below unity even when the external aqueous solution is extrapolated to infinite dilution.[121]

As the aqueous-phase concentration rises, the ion-ion interactions in that phase cease to be negligible and must be explicitly considered, as well as the effects of the greater ionic concentration on the water-water and ion-water interactions. If the exchange process is considered as a competition for the cation among the water, the anion, and the resin sulfonate group (RSO_3^-), the effect of the increasing ionic concentration is to decrease the amount of water available for solutions of ions as reflected by the lowering of the water activity. This drop in the water activity enhances the ability of the anion and RSO_3^- to act as solvators and causes the ion-ion interactions in both phases to take on increasing importance.

One more characteristic of ion exchange in concentrated solutions is resin invasion by nonexchange electrolyte from the aqueous phase. This invasion electrolyte can attain appreciable amounts for very concentrated aqueous solutions (> 10M), with the nonexchange electrolyte concentration equaling and even surpassing the resin ion—counter ion concentration.[149] The nonexchange electrolyte has some slight selectivity properties, but in general it is similar in constitution to the aqueous phase; the result of the resin invasion is to increase D over that which would be observed if there were no invasion.

Each of the interactions in the system will have an effect on the exchange behavior of the cations. As already seen, water solvation (hydration) tends to hold them in the aqueous phase; anion solvation (complex formation) does the same. On the other hand, solvation by the resin sulfonate group (resin-ion association) enhances the distribution ratio; the same is true for resin invasion. By evaluating the relative importance of these four effects in a given system, it should be possible to make qualitative predictions concerning the distribution ratios of cations in concentrated solutions.

The equation for the exchange of a tracer cation (A) of charge n with a monovalent cation (B) on the resin may be written

$$A + n\overline{B} = \overline{A} + nB, \tag{21}$$

where charges and ion hydration have been omitted for simplicity and the superscript bar denotes the resin phase. The corresponding equilibrium constant is

$$K = \frac{(\bar{A})\ (B)^n}{(A)\ (\bar{B})^n} = \frac{[\bar{A}][B]^n}{[A][\bar{B}]^n} \cdot \frac{\gamma_{\bar{A}}\gamma_B^n}{\gamma_A\gamma_{\bar{B}}^n}\ , \qquad (22)$$

where parentheses denote activity and brackets denote concentration.

For dilute aqueous solutions it is possible to make two assumptions concerning Eq. (22). The first is that there is negligible resin invasion, so that $[\bar{B}]^n$ is a constant. This implies that the activity coefficients in the resin phase are also constant, since $\gamma_{\bar{B}}^n$ is constant for a given $[\bar{B}^n]$ and $\gamma_{\bar{A}}$ has a characteristic value related to $[\bar{B}]^n$ that is essentially constant so long as $\bar{A}$ is in tracer concencentration (Harned's Rule).[150] The second assumption is that the ratio of the activity coefficients (γ_B^n/γ_A) in the aqueous phase remains constant over the concentration range of [B].

Using the definition $[\bar{A}]/[A] \equiv D$ and substituting the above assumptions into Eq. (22) results in the expression

$$K' = D[B]^n, \qquad (23)$$

and taking logarithms of both sides of Eq. (23) yields, after rearrangement,

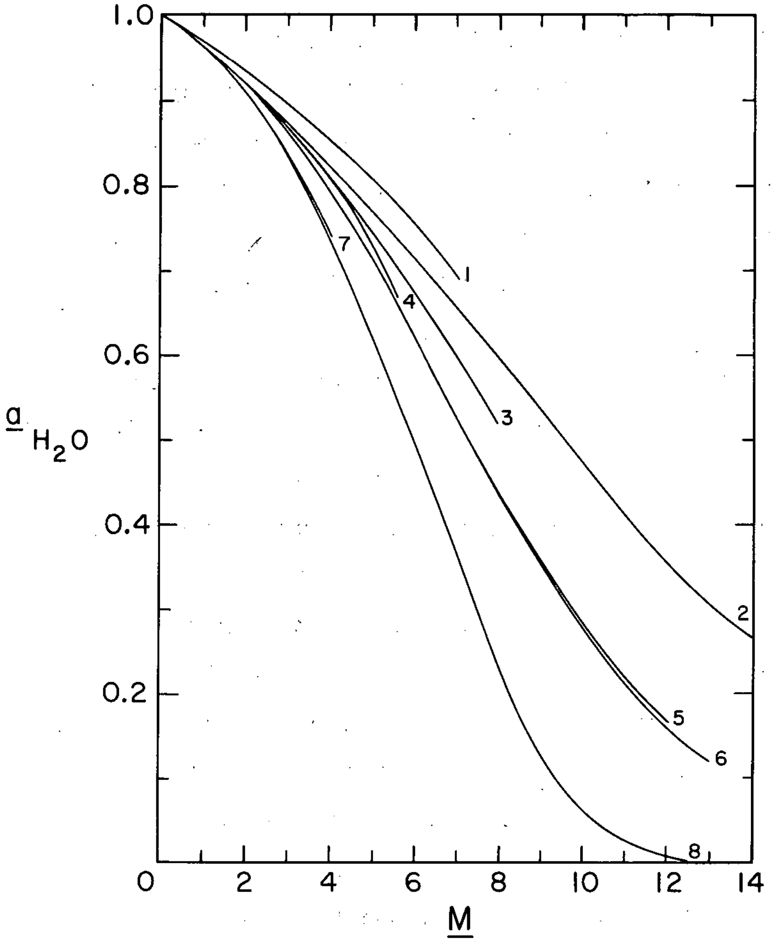
$$-\log D = n \log [B] + \log K'. \qquad (24)$$

Thus it would be expected that a plot of log D vs log [B] would yield a straight line of slope -n, where n is the charge of the tracer cation.

As can be seen in Figs. 30-42, each of the tracers in each of the solutions studied (except HAc, see page 105) either has or is approaching a slope of -1.0, as required by Eq. (24). However, it may be noted that all these lines sooner or later deviate from slope -1.0 as the concentration increases; this deviation marks the breakdown of one or both of the assumptions made in the derivation of Eq. (24). From Fig. 29 it will be seen that the activity coefficients of the various salts and acids deviate widely from one another as the concentration rises; it seems reasonable that these variations would have a profound effect on the activity coefficient ratio in the aqueous phase. Furthermore, resin invasion, which changes $[\bar{B}]^n$, becomes important above 1 M concentration in the aqueous phase, thus it appears that in fact neither of the assumptions would be expected to be valid when the aqueous concentration exceeds a value of a few tenths molal. From considerations of the nature of the various electrostatic interactions that take place, an attempt is made below to explain, in a qualitative manner, the exchange behavior exhibited by the alkali tracers in these more concentrated solutions.

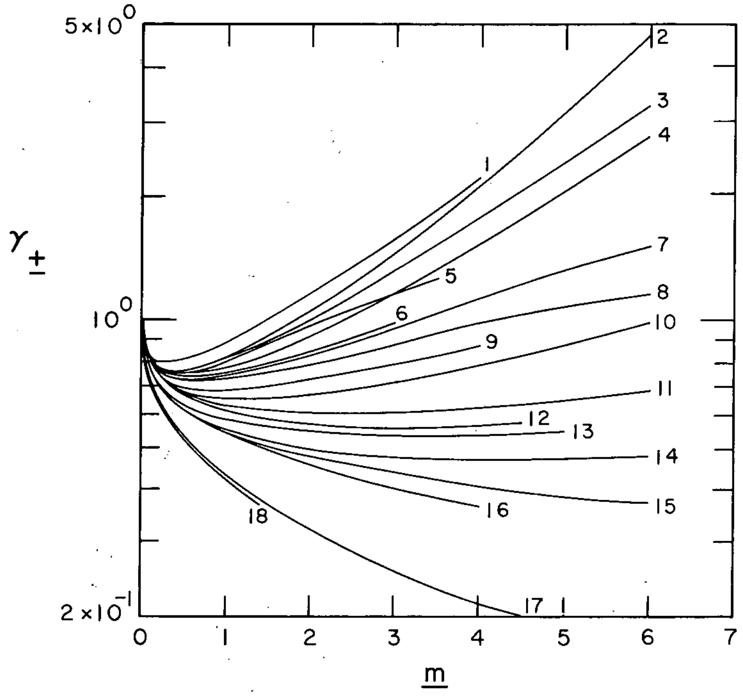
In the following discussion of the distribution of Na, Rb, and Cs tracers between the various solutions and the resins, the water activities and activity coefficients shown in Figs. 28 and 29 are used as a guide to the extent of water-water, ion-water, and ion-ion interactions in the aqueous and resin phases. The systems are considered more or less in order increasing complexity. The major portion of the discussion concerns the sulfonate resin (Dowex-50W), and is followed by a short comparison of the results on the carboxylate resin in order to emphasize the role of resin-ion interactions.

The first solution to be considered is $LiClO_4$ (Fig. 30 and Table XXII). The ClO_4^- ion is a very poor solvator for cations, which means that the competition between the water and the resin sulfonate group for solvating the cations plays the major role in determining the distribution ratios (elution volumes) of the tracers. As the concentration increases, the water activity drops quite rapidly, which enhances the ability of RSO_3^- to act as a solvator. Since the smaller the cation the more avidly it seeks solvation, the effect of the drop in water activity is to force the smallest ion, Li, into the resin phase more strongly. This reflected in the corresponding decrease of the $^{V}H_2O$ of Cs below that for "ideal" exchange, where Cs, being relatively



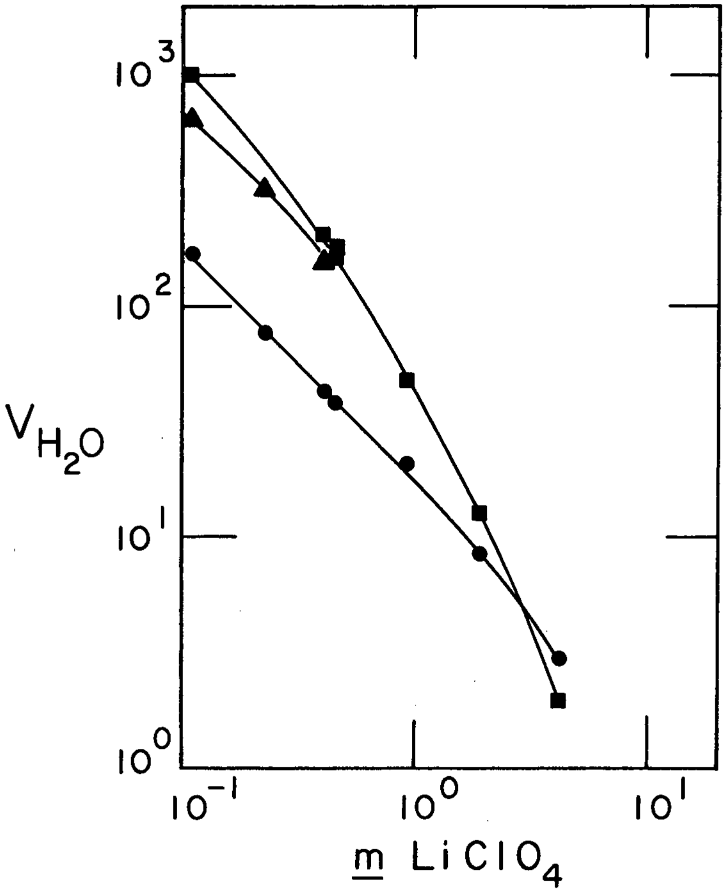
MU-28725

Fig. 28. Variation of water activity with aqueous molarity[144] of: 1, CsCl; 2, HNO_3[151]; 3, $LiNO_3$; 4, LiAc; 5, HCl; 6, LiCl; 7, $LiClO_4$; 8, $HClO_4$.



MU-28749

Fig. 29. Variation of activity coefficients with aqueous molality[144] of: 1, $LiClO_4$; 2, $HClO_4$; 3, HCl; 4, LiCl; 5, CsAc; 6, NaAc; 7, $LiNO_3$; 8, HNO_3[151]; 9, LiAc; 10, NaCl; 11, $NaClO_4$; 12, Li toluenesulfonate; 13, RbCl; 14, CsCl; 15, $NaNO_3$; 16, Na toluenesulfonate; 17, $RbNO_3$; 18, $CsNO_3$.



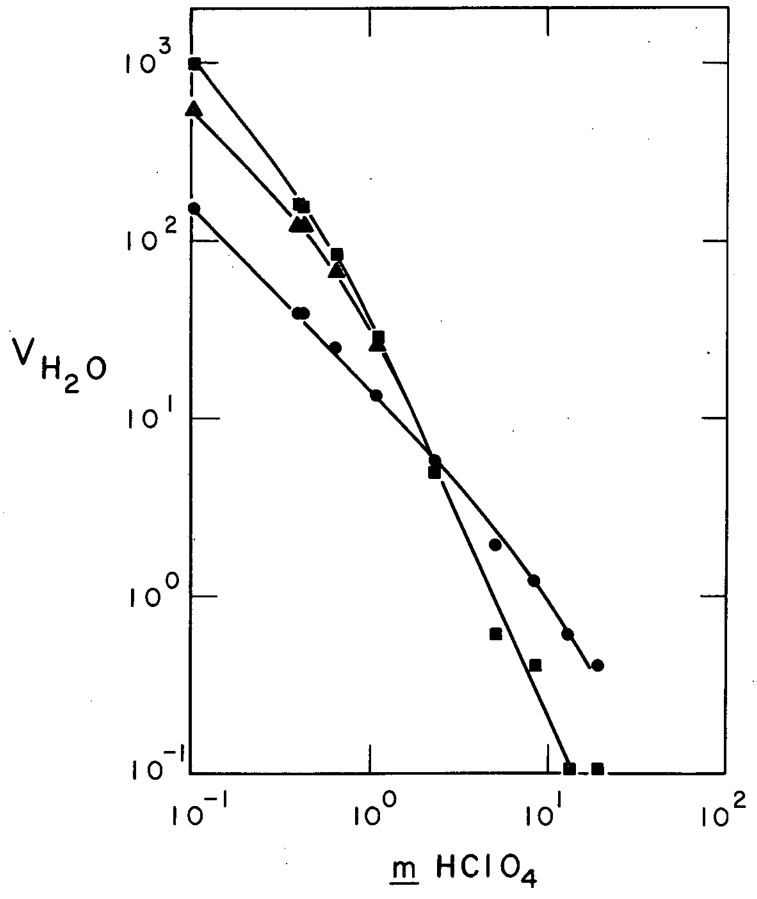
MU-28726

Fig. 30. Variation of elution volume of H_2O on Dowex-50W with $LiClO_4$ molality for alkali tracers: ●, Na; ▲, Rb; ■, Cs.

unsolvated owing to its large size and low charge density, is being forced out of the resin phase by the enhanced Li uptake. Since the solvation of Na is almost as great as that of Li, only a small decrease is noted in the Na curve. The disparity in extent and need of solvation between Na and Cs, coupled with the decreasing hydration of Li and Na, is sufficient to cause the dilute-solution selectivity order to completely invert in the more concentrated solutions so that Na is actually held more tightly on the resin than is Cs. Rb and Cs should also cross, and an extrapolation of the Rb curve indicates that this will happen. Solubility limitations (the Rb^{86} tracer was formed at rather low specific activity from the naturally occurring $Rb^{85,87}$) prevented obtaining of data at $LiClO_4$ concentrations above 0.4 M; in solutions in which the Rb salt was soluble, Rb assumed its proper place in the inverted order found for concentrated solutions (see e.g., HNO_3, below).

The behavior of the tracers in $HClO_4$ (Fig. 31 and Table XXIII) is very similar to that in $LiClO_4$, except that the crossing of Na and Cs occurs somewhat sooner and the concentration limit is considerably higher. Recently published work[153] agrees with that reported here for the region of the Na-Cs crossing, but shows a leveling off of both the Na and Cs curves at higher concentrations, as opposed to the sharp dropoff seen in Fig. 31; the discrepancy may be due to a difference in the method of subtracting free column volumes.

It is of interest to note that an appreciable $^{V}H_2O$ is found for Na tracer even in 19 m (10 M) $HClO_4$; and in fact the Na curve, which deviates from linearity at a higher concentration than in $LiClO_4$, is that which would be expected from a comparison of the activity coefficient ratios of $NaClO_4$ to $LiClO_4$ and to $HClO_4$. This implies that the resin sulfonic acid has about the same degree of dissociation as the Li or Na salt form, even in contact with 10 M $HClO_4$, so that the lack of exchange exhibited by, e.g., carboxylate resins in the acid form is not seen in the solfonate resins, implying that the resin is in the strong-acid category. Recent studies have confirmed, through the use



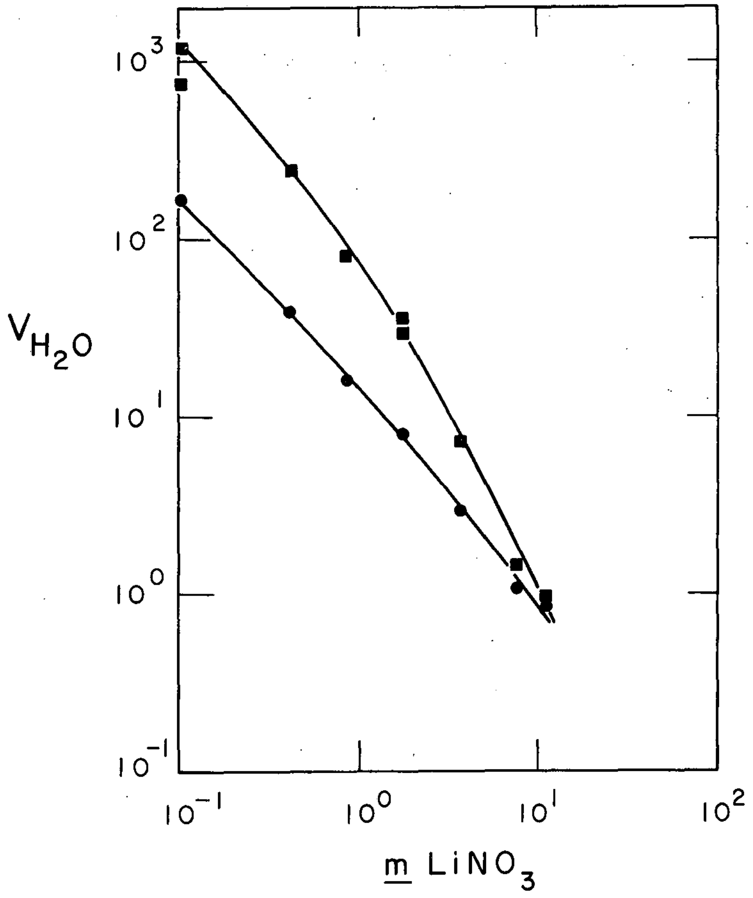
MU-28727

Fig. 31. Variation of elution volume of H_2O on Dowex-50W with $HClO_4$ molality for alkali tracers: ●, Na; ▲, Rb; ■ , Cs.

of nuclear magnetic resonance techniques, that the polystyrene sulfonic acids, both resins[154,155] and water-soluble linear polymers,[156] have acid strengths comparable to the strong mineral acids.

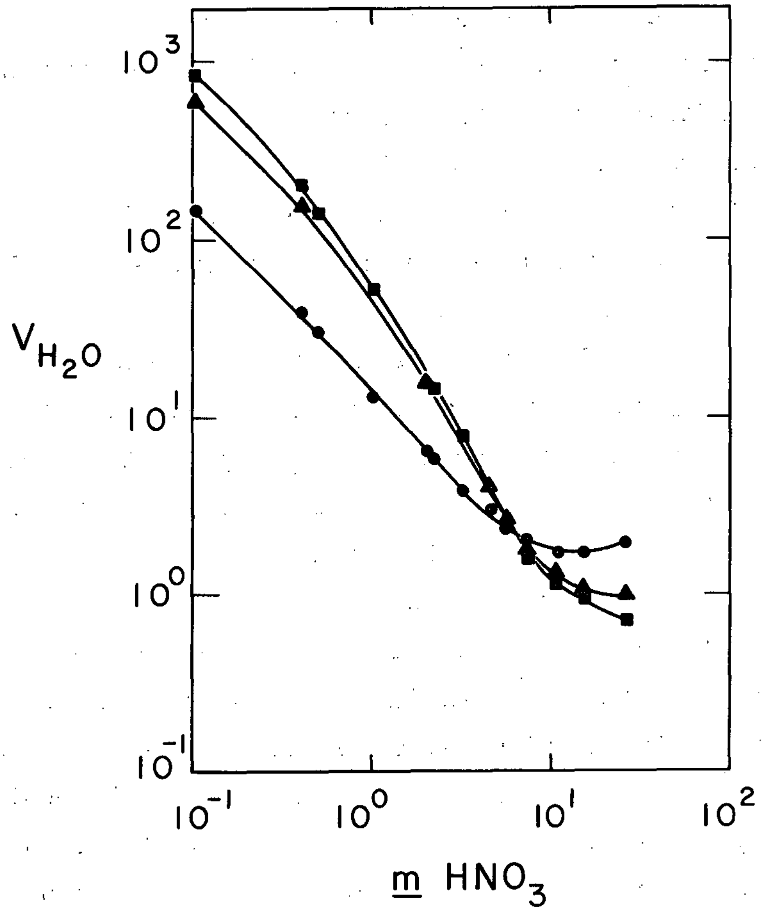
The next system in order of complexity is $LiNO_3$ (Fig. 32 and Table XXIV). In changing from ClO_4^- to NO_3^- an anion has been selected that shows stronger solvating ability for the monovalent cations. The main effect of this new solvator is to hold cations in the aqueous phase through some sort of ion association such as ion-pair formation or "localized hydrolysis",[144,157] and the smaller the cation, the more strongly it is held. The extent of exchange is now a competition between two major effects--one, the dropping water activity and enhanced RSO_3^- solvation, which are favoring the uptake of Li over the tracers (as in the $LiClO_4$ case); the other, the attraction for the Li^+ by the NO_3^- in the aqueous phase, which tends to allow the uptake of Cs and to a lesser extent Na. It can be seen from Fig. 32 that the former effect (ion dehydration) is still uppermost, in the curves are approaching each other and are deviating downward from the straight line; the fact that they have not crossed at 11 m (8.5 M) $LiNO_3$ while the $LiClO_4$ curves crossed at 3 m gives some idea of the extent to which the NO_3^- has acted as a complexing agent for the Li^+ in the aqueous phase, although part of the difference is certainly due to the greater activity of the H_2O in $LiNO_3$.

In HNO_3 (Fig. 33 and Table XXV) the same considerations as for the $LiNO_3$ hold true, except that the much greater solvating power of the NO_3^- ion for H^+ (to form associated or molecular HNO_3) causes the anion-cation attraction effects to predominate at the higher concentrations, lowering the effective concentration of H^+ and producing an upturn in all three curves. Since the water activity is still falling, and since a major portion of the NO_3^- ions is bound to the H^+ ions, the solvating ability of the RSO_3^- is still very much in evidence, as can be seen by the clearly reversed order of elution Cs < Rb < Na.



MU-28728

Fig. 32. Variation of elution volume of H_2O on Dowex-50W with LiNO$_3$ molality for alkali tracers: ●, Na; ▲, Rb; ■, Cs.



MU-28729

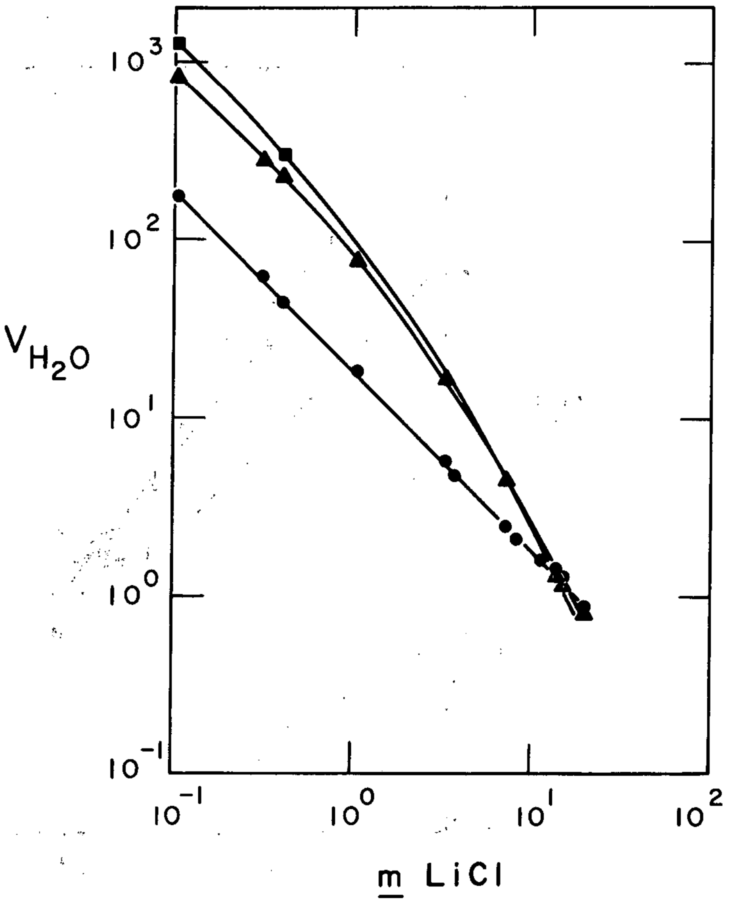
Fig. 33. Variation of elution volume of H_2O on Dowex-50W with HNO_3 molality for alkali tracers: ●, Na; ▲, Rb; ■, Cs.

LiCl (Fig. 34 and Table XXVI) and HCl (Fig. 35 and Table XXVII) are essentially similar to the corresponding nitrates. Because of the higher solubility of LiCl (13.5 M or 20 m) as compared with $LiNO_3$ the order reversal is seen for all three tracers (although the Cs data are rather sparse), in agreement with other work.[158,159] In the HCl the reversal is obvious; that the Rb and Cs curves show no sign of deviation upward indicates that HCl is more highly dissociated at high concentrations than HNO_3. On this basis the upturn of Na in HCl is anomalously large, although it is in agreement with previous work.[160] This may be due to resin invasion, which is greatest for HCl;[149] no other explanation is readily apparent.

Although HBr was not studied in these series of experiments, it has recently been reported on in the literature.[153] It was found that the Na-Cs reversal occurred at 5.5 M (approx 7 m) HBr and that the upturn was much smaller; both effects are those which would be expected for an acid of strength intermediate between HCl and $HClO_4$.[27]

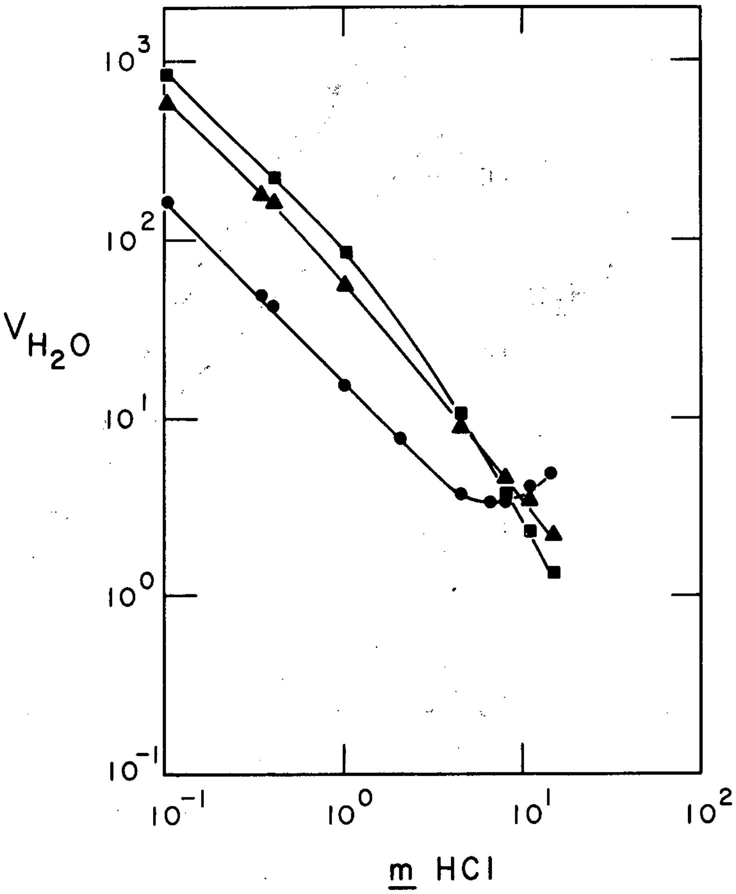
In order to provide a comparison with the foregoing solutions of strongly hydrated salts and acids, the tracers were eluted with CsCl (Fig. 36 and Table XXVIII). In these solutions the water activity remains relatively high and no crossing is observed, although the two curves do approach each other slightly at the highest concentrations. The upward deviation indicates either that the Cs^+ and Cl^- are undergoing some sort of association or, more likely, that the resin invasion by the aqueous solutions is enhancing the distribution ratios for both tracers; both effects are possible.

As a final example of the effects of strong anion competition for the cation, the LiAc curves for Na and Cs (Fig. 37 and Tables XXIX and XXX) are instructive. In this solution, the Ac^- acts as a strong complexing agent for the Li^+, mostly through localized hydrolysis. The result of this complexing is to reduce the effective concentration of the eluting solution, so that the distribution ratios for Na and Cs



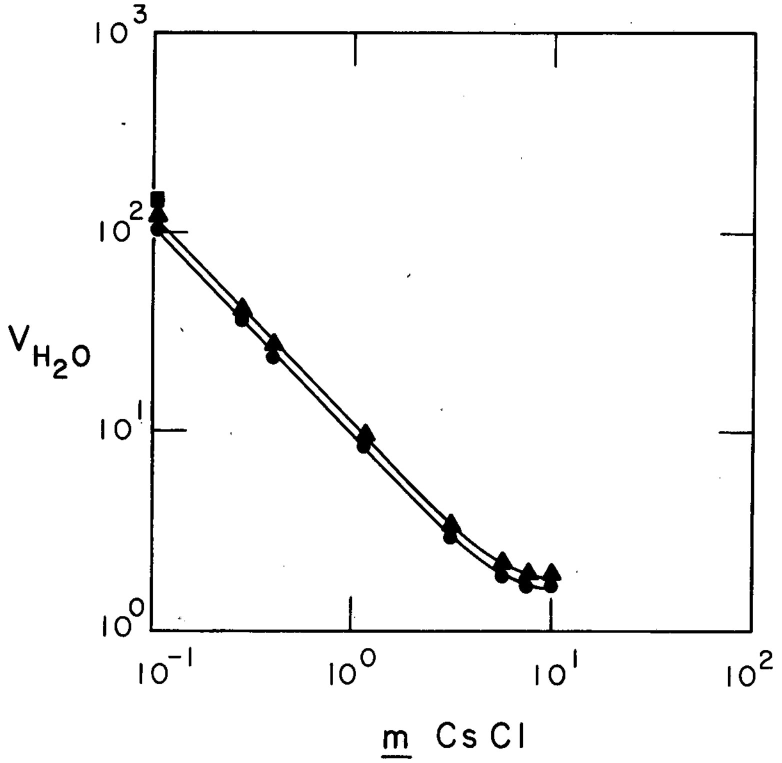
MU-28730

Fig. 34. Variation of elution volume of H_2O on Dowex-50W with LiCl molality for alkali tracers: ●, Na; ▲, Rb; ■, Cs.



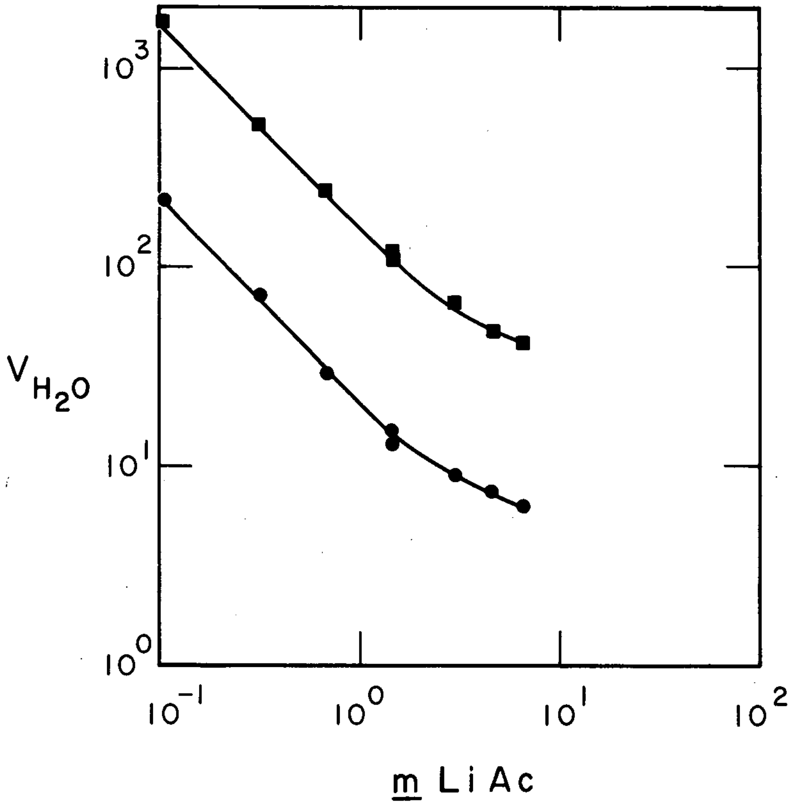
MU-28731

Fig. 35. Variation of elution volume of H_2O on Dowex-50W with HCl molality for alkali tracers: ●, Na; ▲, Rb; ■, Cs.



MU-28746

Fig. 36. Variation of elution volume of H_2O on Dowex-50W with CsCl molality for alkali tracers: ●, Na; ▲, Rb; ■, Cs.



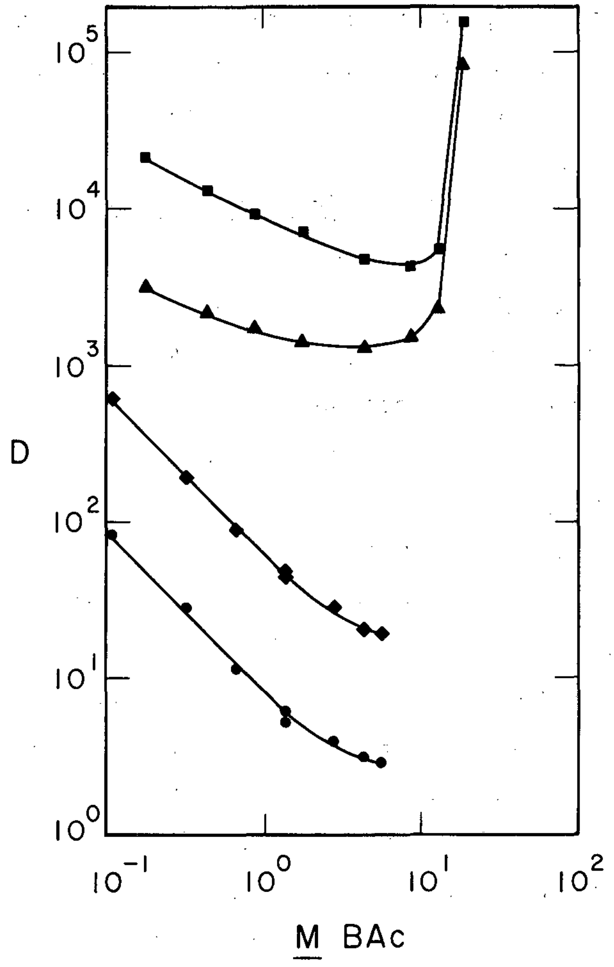
MU-28732

Fig. 37. Variation of elution volume of H_2O on Dowex-50W with LiAc molality for alkali tracers: ●, Na; ▲, Rb; ■, Cs.

are above those for the previously considered Li salts, although it is of interest to note that the initial slope is the same (i.e., -1.0). In the more concentrated region the two curves diverge, owing to the greater complexing of Na^+ than of Cs^+ by Ac^-, and both curves deviate upward from the straight line, owing to the increasingly greater competition by the Ac^- for the Li^+ and to the resin invasion by the aqueous solution.

In the case of HAc (Fig. 38 and Table XXX) the anion has almost completely replaced water as the primary solvator for the proton, the acid being only about 1% ionized. This results in very high distribution ratios (note that the axes in Fig. 38 are log D vs log molarity for both LiAc and HAc) and very flat curves for both Na and Cs. The main features, as in HCl and HNO_3, are the upturn and the tendency toward crossing. It is of interest to note that the value of D_{Cs} at the lowest HAc concentration (2.1×10^{4}) corresponds to a concentration of about 1.4×10^{-3} $\underline{M}$ for any of the previously studied acids, if a slope of -1.0 is assumed below 0.1 $\underline{M}$ for the Cs curves. Since the calculated hydrogen-ion concentration in HAc is 1.42×10^{-3} $\underline{M}$ it appears that at low concentrations the presence of the un-ionized HAc has very little, if any, effect on the exchange process.

All the acids studied on Dowex-50W exhibited a much greater tendency toward causing the Na and Cs curves to cross than the corresponding Li salts. Since the crossing has been attributed primarily to the dehydration of the ions, and their subsequent bonding to the resin, the implication is that the hydrogen ion is a better dehydrating agent than is the lithium ion in concentrated solutions, although the hydration numbers in dilute solution are almost identical.[36,144] This is in agreement with the ideas presented in the section on solvent extraction where the proton is considered to take the form of a trihydrated hydronium ion, which would tend to hold its primary hydration shell very strongly, much more so than the alkali ions.



MU-28752

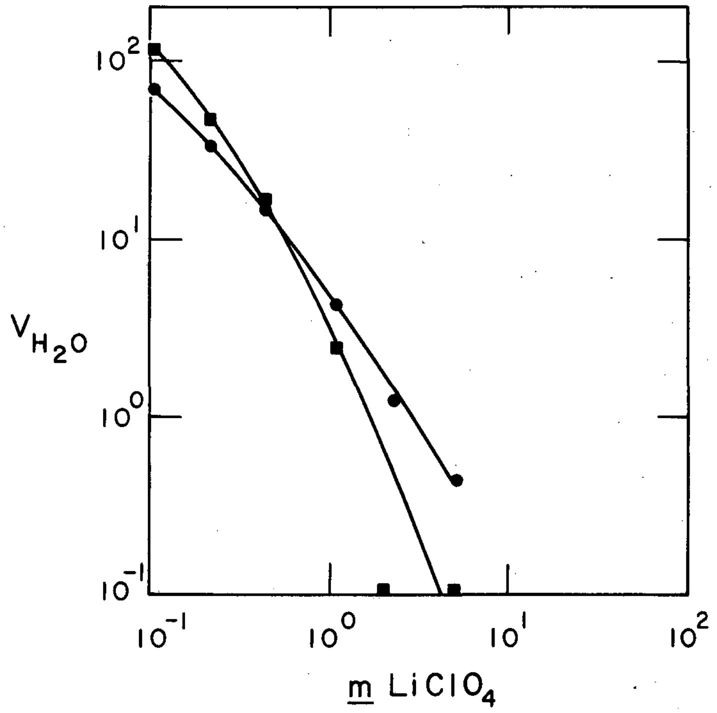
Fig. 38. Variation of distribution ratio on Dowex-50W with aqueous molarity for solutions and alkali tracers: LiAc; ●, Na; ◆, Cs; HAc; ▲, Na ■, Cs.

In order to stress the resin-ion interactions, the four Li salt solutions were used as eluting agents for the Na and Cs tracers on Bio-Rex 70, a polyacrylic carboxylate-type resin. Since the carboxylic acid anions show strong attractions for cations, the differences in the tracer behavior on each resin with the same salt solutions are presumably due to this greater interaction.

It can be seen from the curves for $LiClO_4$ (Fig. 39 and Table XXXII), $LiNO_3$ (Fig. 40 and Table XXXIII), and LiCl (Fig. 41 and Table XXXIV) that almost the same behavior occurs as was noted for the Dowex-50W sulfonate resin, except that the curves are closer together in dilute solutions, the crossing points fall at much lower concentrations, and the downward deviations are more severe. All three of these effects can be ascribed to the greater preference of the carboxylate resin for Li^+ then RSO_3^- for Li^+ -- a preference so great that in concentrated solutions the Cs was being eluted almost immediately, with the V_{H_2O} being on the order of the experimental error, 0.1 ml.

As a check on the assumption that the stronger resin attraction for the cations was the cause of the differences between the resins, LiAc was used as an eluting agent (Fig. 42 and Table XXXV). Since the aqueous and resin ions are essentially identical, it would be expected that the activity coefficient ratios in both phases should be very similar, so that aside from resin invasion Eq. (24) should be applicable. That such is the case can be seen from Fig. 42, where the two curves are exactly parallel and the slight upward deviation found for both ions is, in all probability, due entirely to resin invasion.

As a final example of resin-ion interaction, it is instructive to consider a resin of much greater coordinating ability than those used in this series of experiments, namely Dowex-A1, a chelating resin.[161] This resin has imidodiacetate groups attached to a styrene-divinylbenzene matrix and has a chelating ability similar to that of EDTA. These resin groups are able to partially replace water as a coordination



MU-28733

Fig. 39. Variation of elution volume of H_2O on Bio-Rex 70 with $LiClO_4$ molality for alkali tracers: ●, Na; ■, Cs.

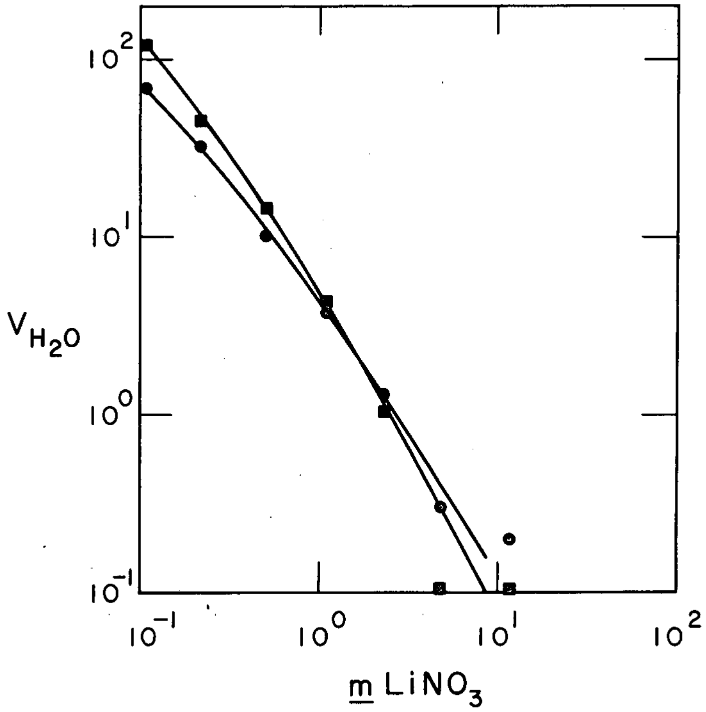
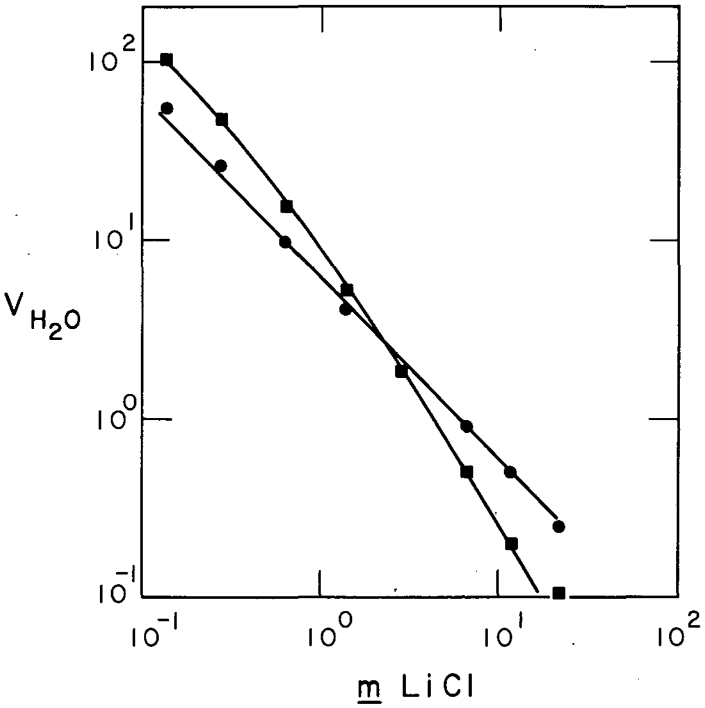
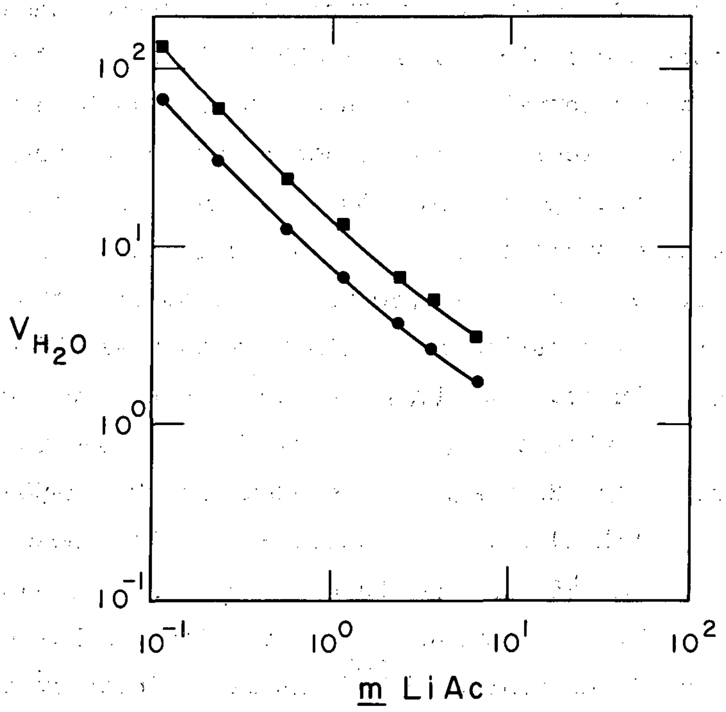


Fig. 40. Variation of elution volume of H_2O on Bio-Rex 70 with $LiNO_3$ molality for alkali tracers: ●, Na; ■ , Cs.



MU-28735

Fig. 41. Variation of elution volume of H_2O on Bio-Rex 70 with LiCl molality for alkali tracers: ●, Na; ■, Cs.



MU-28736

Fig. 42. Variation of elution volume of H_2O on Bio-Rex 70 with LiAc molality for alkali tracers: ●, Na; ■ , Cs.

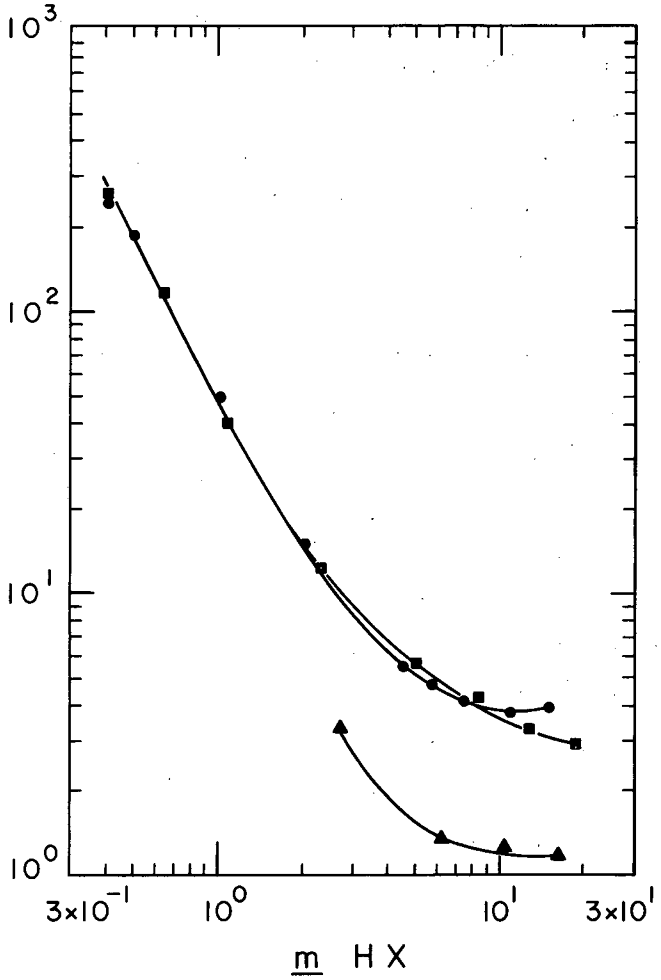
for the cations, so the order of the distribution ratios is K < Na < Li < H,[162] i.e., in reverse order to those observed in dilute solution for both sulfonate and carboxylate resins.

In summation, it has been shown that by consideration of the water-water, ion-water, and ion-ion interactions in each phase, as reflected in the decreasing water activity and consequent RSO_3^- solvation of the ions, the distribution of alkali tracers between cation-exchange resins and concentrated aqueous solutions can be given a qualitative explanation. Since these considerations are generally applicable to all cation-exchange systems, they should be of help in the prediction of resin selectivities for all ions on the basis of such interactions.

It had been noted previously by other authors[160,163] that Be has a very low distribution ratio between Dowex-50 and concentrated HCl solutions. In order to determine whether this was general behavior for Be, since a doubly charged ion would be expected to go onto the resin rather strongly, Be tracer was eluted from Dowex-50W with $HClO_4$ and HNO_3 (Table XXXVI) and these data, along with those for HCl,[160] are plotted in Fig. 43. It can be seen that the HCl data are anomalous, owing no doubt to chloro-complex formation, as has been previously postulated[163] and confirmed.[164] It is of interest to note that there is slight upturn of the $HClO_4$ curve, suggesting that Be represents the transition between the alkalies with their steeply falling curves and the sharp upturns noted in the following section for the tripositive ions.

3. Tripositive Ions

It had been noted several years ago that the distribution ratios of several lanthanide ions showed a very sharp increase above 4 M HCl.[165,166] Recently the same behavior has been noted for both lanthanide and actinide ions in $HClO_4$. In order to determine whether this increase was peculiar to rare-earth-type ions, and, if not, to ascertain



MU-28737

Fig. 43. Variation of elution volume of H_2O on Dowex-50W for Be tracer with aqueous molalities of: ▲, HCl^{160}; ●, HNO_3; ■ , $HClO_4$.

the reasons for this upturn, several tripositive ions were distributed between a cation exchanger and varying concentrations of $HClO_4$. Since ClO_4^- is a noncomplexing anion, the exchange would be expected to be controlled by the competition between water and the sulfonate group as solvators for the cation.

As a means of investigating these controlling factors, one of the ions chosen was $Cr(H_2O)_6^{+++}$, which is known to have a long half-life (≈ 32 hours)[167] for the exchange of its water molecules in acid solution, and is also known to retain these water molecules when it undergoes exchange from dilute solution with hydrogen ion on the resin.[141] Origninally, the only other ion to be investigated was $Fe(H_2O)_6^{+++}$, since the size of Fe^{+++} is identical to within a few hundredths of an angstrom to that of Cr^{+++},[168] but the waters of hydration are extremely labile and undergo essentially instantaneous exchange. By comparison of the two, it was hoped to observe only those effects caused by the difference in the lability of the first-shell water of hydration and consequently gain some insight into the bonding of ions to the resin. However, the iron tracer was found to yield slopes of less than 3 in dilute solution, therefore $Sc(H_2O)_6^{+++}$ was also investigated as an ion with labile hydration, although Sc^{+++} is of somewhat larger size than Fe^{+++} (0.83 Å compared with 0.67 Å).[168]

Since the iron tracer was certainly in the tripositive state at the start of the exchange, there is no apparent reason why it should fail to ratain this charge throughout the experiment. One possible explanation is partial hydrolysis to some sort of hydroxy compound, although this seems highly unlikely in acid solution of 0.1 to 1 M $HClO_4$. Another explanation is a partial reduction of the ferric ion by resin impurities, although these should not have been present in the DNNS (see below), where the same behavior is observed. A third possible effect is exchange site loading by the tracer, since the amount of tracer Fe in the solutions corresponded to several percent of the total exchange sites at very high distribution ratios; very little study has been done on effects of resin composition on distribution ratios for cation resins. Since none of these effects should take place at higher $HClO_4$ concentrations, and since Fe tracer shows normal tripositive ion behavior in terms of its distribution ratio at the minimum of the log D vs log $[HClO_4]$ curve, the iron was assumed to be tripositive in this region; the behavior of Sc tracer confirms this assumption.

In order to eliminate any possible effects due to steric restriction caused by the resin pore size (see Introduction, p. 71), the experiments were conducted using both Dowex 50-X12, a rather highly cross-linked resin, and 0.1 M solutions of dinonyl napththalene sulfonic acid (DNNS) in a mixture of heptane and iso-octane, a so-called "liquid ion exchanger." The essentially identical behavior of the tracers in the two different systems (Figs. 44 and 45 and Tables XXXVII and XXXVIII) indicates that any appreciable pore-size effects were absent; such differences as did exist are discussed subsequently.

The exchange behavior of the tripositive ions between the resin and dilute aqueous acids should conform to Eq. (23) with n equal to 3. As previously mentioned, Fe tracer did not show this behavior, yielding a slope of about 2.5 when plotted in accordance with Eq. (24). Both Cr and Sc tracers obeyed this equation, however, and it may be noted that, in accordance with the general picture presented for dilute-solution exchange in the preceding section, the distribution ratios for Sc are larger than those for Cr, since Sc is the larger, and therefore less hydrated, ion. Similar behavior has been noted for the lanthanide ions in dilute $HClO_4$, the (crystollographically) largest ion having the highest distribution ratio.[169,170]

Consider now the exchange in more concentrated $HClO_4$ solutions. Taking first Dowex 50-W resin (Fig. 44), one sees that the D's for Fe and Cr remain essentially identical (provided the previously mentioned Fe deviation is neglected) up to about 2 M $HClO_4$, with the Sc above,

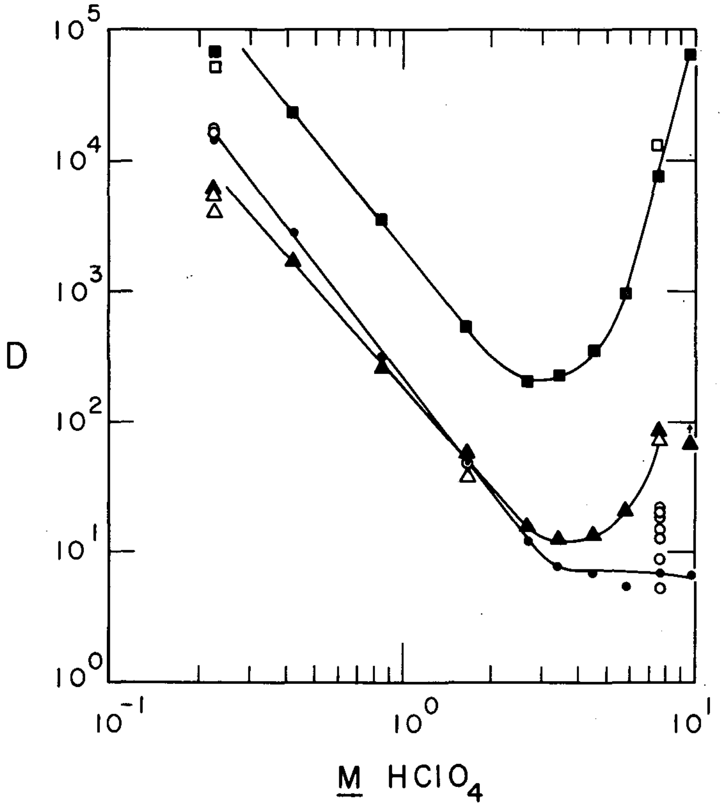
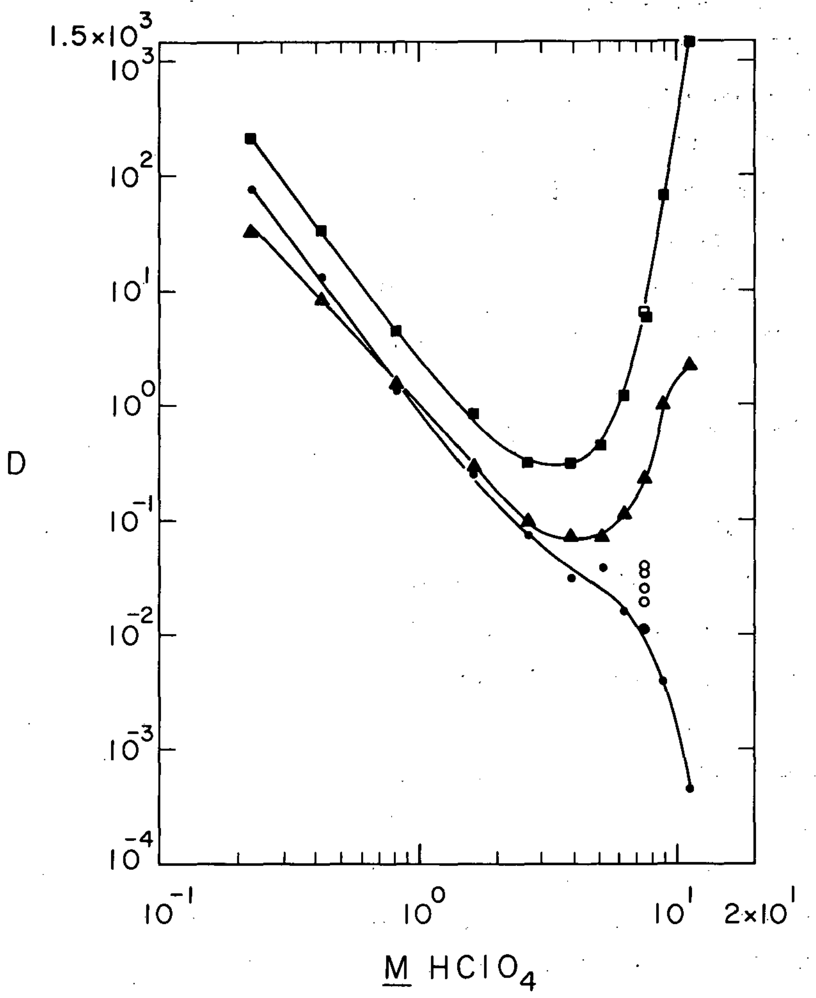


Fig. 44. Variation of distribution ratio on Dowex-50W with $HClO_4$ molarity for tripositive tracers: ▲, Fe; ●, Cr; ■, Sc. Open symbols are time studies (see page 119).



MU-28744

Fig. 45. Variation of distribution ratio in DNNS with $HClO_4$ molarity for tripositive tracers: ▲, Fe; ●, Cr; ■, Sc. Open symbols are time studies (see page 119).

and parallel to, the Cr. At this point the Fe begins to deviate upward from the straight line, going through a minimum at 3.5 M after which it turns up very sharply (the point at 9.8 M $HClO_4$ is shown with an arrow because severe, possibly Fe-catalyzed, resin decomposition was noted in this sample, which would tend to lower the distribution ratio). The Sc behaves in a similar manner, its curve being exactly parallel to that of the Fe above 4 M $HClO_4$. The Cr, on the other hand, keeps on dropping until a more or less constant value of D is maintained over the region of 4 to 10 M $HClO_4$. Data of other workers for Am and Eu tracers have recently been reported;[153] their behavior is identical to that of Sc.

Almost identical behavior to that found for the resin is shown when the exchanger is DNNS (Fig. 45), with the exception that the Cr, instead of remaining constant, falls off very rapidly as the $HClO_4$ concentration increases; and the slope of the Fe rise is not so steep. Since the experimental conditions were such that the only difference in the Fe and Cr is the lability of the hydration shell, this factor must be responsible for the anomalous behavior of $Cr(H_2O)_6^{+++}$.

Tripositive ions, since they have in general a primary hydration shell of six water molecules plus a fairly extensive secondary hydration shell, would be expected to show marked changes in behavior with changes in the water activity. In concentrated $HClO_4$ solutions, in the presence of the strongly hydrated hydronium ion and the concordant low water activities, it might be expected that the tripositive ions (except possibly Al) would become partially dehydrated, especially if there were some other solvator, such as a sulfonate ion, which could act to replace the coordination sites left vacant by the dehydration. The $Cr(H_2O)_6^{+++}$ ion, on the other hand, would keep its hydration shell for an appreciable period of time, even in very concentrated acid solutions, because of the slow kinetics of the water exchange. Under these conditions, it seems reasonable that the labile ions, seeking solvation, would enter the resin phase and use sulfonate ions to complete their primary solvation shells, forming very strong bonds with the resin ions.

$Cr(H_2O)_6^{+++}$, however, being a rather large ion with a complete primary hydration shell, which exchanges only slowly for RSO_3^-, would remain in the aqueous phase, owing to the tendency of the hydronium ions, also seeking solvation, to enter the resin phase very extensively, and thus exclude the more weakly bonding $Cr(H_2O)_6^{+++}$.

The case is more clear-cut when DNNS is the exchanger, since such complications as resin invasion (nonexchange electrolyte), secondary ion hydration, and nonbonded water would be expected to be minimized because of its more organic-solvent-like nature. It is a weaker acid than RSO_3H, so that the proton is very much favored over the large, hexahydrated Cr ion, and even the Fe ion is beginning to be affected.

The foregoing ideas can easily be checked by carrying out a study of the change in distribution ratio with time. Since the $Cr(H_2O)_6^{+++}$ does slowly undergo exchange of its waters of hydration, it would be expected that in solutions of low water activity another solvator, specifically a sulfonate group, could replace the water. Thus it might be predicted that the distribution ratio of Cr tracer would gradually increase with time, as more and more ion pairs were formed with the resin, until values approaching those for Fe were obtained. Since the exchange is a slow process, and since only those few exchanges which occurred between the H_2O molecules coordinated to the Cr ion and the sulfonate group would give an increase in D, this process would most probably take on the order of months to approach completion; however, the trend should be evident over a shorter period of time, e.g., a few weeks. Sc and Fe, on the other hand, would be expected to maintain the same D over these periods of time, since they are undergoing continuous exchange between H_2O and sulfonate groups in a state of dynamic equilibrium.

Distribution ratios for several different molarities taken over a period of several weeks are shown by open symbols in Figs. 44 and 45 and listed in Tables XXXIX and XL, and it can be seen that essentially no differences occur in any of the points with the exception of those for Cr tracer in 7.5 M $HClO_4$, where a roughly exponential increase with time occurs for the first week in the distribution ratios with both Dowex-50 and DNNS, giving confirmation to the ideas expressed above; results for longer times are probably incorrect (on the low side) because of degradation of both Dowex-50W and DNNS by the $HClO_4$.

It thus appears that some rather definite conclusions can be made about the bonding of tripositive ions to ion-exchange resins. In dilute solutions, the ions retain the primary hydration shell and are bonded in the resin by electrostatic attraction through the waters of hydration. As the water activity falls, and in the absence of complexing ions in the aqueous phase, those ions which are able to do so lose part of their waters of hydration and replace them with resin-sulfonate groups, forming strong resin-ion complexes and thus yielding very high distribution ratios. Those ions which do not rapidly exchange their primary hydration shells are excluded from the resin and only slowly, as they undergo ligand exchange, are they able to increase their distribution ratios.

Similar, although not so definite, conclusions can be drawn for the monovalent ions. In this case also the decreasing water activity causes the ions to seek solvation from other sources, and bonding with the resin sulfonate ions is certainly a major factor in influencing resin selectivities. More quantitative treatment of the various interactions must await more complete thermodynamic data on mixed electrolytes and concentrated solutions; the best that can be said at this time is that from considerations of the intermolecular water structure and of the competition for the cation by water, aqueous anions, and resin anions it is possible to give a qualitative explanation of observed resin selectivities.

III. CONCLUSIONS

It has been shown that solvent extraction and ion exchange can be treated in terms of maximizing electrostatic interaction within a given system. All the experimental data given herein deal with processes involving the transfer of either ions or dipolar molecules from an aqueous phase to one which is less aqueous in terms of its physical and chemical properties, within a system where the two phases are readily distinguishable. It has been found that the extent to which such processes take place depends on the outcome of the competition among several factors, the most important being water-water, ion-water, and ion-ion interactions in the aqueous and resin phases, and dipole-water, dipole-ion, and dipole-dipole interactions in the organic solvent phase. By evaluating the relative importance of the various interactions, it is possible to predict qualitatively how a particular aqueous species will behave toward extraction or exchange. As more data on other systems are made available, the interactions can be more accurately evaluated, and in the final analysis a comprehensive theory of ion exchange and solvent extraction will emerge. It is hoped that the ideas presented herein will aid in the formulation of such theory.

ACKNOWLEDGEMENTS

There are a great many people whose part in the completion of this thesis requires recognition. First and foremost of these is the originator and director of this research, Dr. Richard M. Diamond, for whose guidance and inspiration I am eternally grateful. To Mab Tocher, for material aid and moral support in the solution of many of these research problems, I extend my deepest appreciation. Out of the great number of people in the various support groups at LRL who gave me assistance on the technical level, I would particularly like to thank Dick Yoes, Dick Boltin, and Bob McCracken of Health Chemistry, Harold Rothaker and Dan Westfall of Stores, Bert Watkins of Shops, and Gloria Carrillo, Mary Lou Hasey, Joanne Hall and Alberta Proteau of the Chemistry Office for the many services rendered during my stay at the Radiation Laboratory. I am indebted to John Conway and George Shalimoff for the use of and advice on the Beckman IR-5 and to Diana Lee, Ursula Abed, and Eileen Burnett for numerous difficult and accurately done analyses. Among the faculty, I would like to express my appreciation to Dr. Kenneth Street, thesis director and chairman of the thesis committee, and the rest of the thesis committe for their comments and criticisms of this work, to my "prelim" committe for their interest and consideration, and to Dr. George C. Pimentel for his aid in the analysis of the infrared absorbtion data. To my scientific contemporaries — the graduate students, postdoctoral fellows, summer and foreign visitors, and staff of the Radiation Laboratory — and I cannot possibly list each of you; I can merely thank you one and all for making my stay at the Laboratory such an enjoyable one. Finally, I wish to thank my wife Kathleen for her typing of countless manuscripts, for the care of my worldly needs, and for patience and understanding such as only a wife could provide during my years of graduate study.

This work was performed under the auspices of the U.S. Atomic Energy Commission.

Definitions of Symbols Used in Column Headings of Tables

All concentrations are in moles/liter unless otherwise specified.

$[A]$	Concentration of fatty-acid anion in aqueous phase.
$[\bar{A}]$	Concentration of fatty-acid anion in resin phase (mmoles/gram).
a or $\underline{a}$	Aqueous-phase acid activity.
a' or $\underline{a}'$	Corrected aqueous-phase acid activity.
a_{H_2O}	Aqueous-phase water activity.
Anion	Acid anion under consideration, generally with Na as cation.
aq	Counting rate of aqueous phase or aliquot thereof (counts/min or scales/min).
Au	Initial concentration of $HAuCl_4$ or $HAuBr_4$ in aqueous phase.
BX	Salt or acid under consideration.
C_{aq}	Counts/min, aqueous phase.
C_o	Initial counts/min, aqueous phase.
C_{res}	Counts/min, resin phase.
Cap	Packager's listed capacity of ion-exchange resin.
CCl_4	Water-saturated CCl_4 or water concentration therein.
Chemical form	Chemical Mode or chemical combination of purchased isotopes or reactor targets.
$[Cl]$	Concentration of chloride ion in aqueous phase.
$[\overline{Cl}]$	Concentration of chloride ion in resin phase (mmoles/gram).
Column	Identification number of ion-exchange column.
D	Distribution ratio as $\frac{\text{mequivalents per g resin}}{\text{mequivalents per ml solution}}$, $\frac{\text{counts/min per g resin}}{\text{counts/min per ml solution}}$, or $\frac{\text{counts/min per 2 ml organic phase}}{\text{counts/min per 2 ml aqueous phase}}$.
D(M)	Distribution ratio defined in terms of molarity.
D(m)	Distribution ratio defined in terms of molality.
Dia	Diameter of ion-exchange column (millimeters).
eluant	Salt or acid being used as eluting solution for ion-exchange column.

$\overline{H}^+$	Organic-phase acid concentration.
$\overline{H}^{+'}$	Organic-phase acid concentration, corrected.
HBr	Aqueous-phase HBr concentration.
HCl	Aqueous-phase HCl concentration.
$HClO_4$	Aqueous-phase $HClO_4$ concentration.
HNO_3	Aqueous-phase HNO_3 concentration.
$HReO_4$	Initial concentration of $HReO_4$ in aqueous phase.
$\overline{H_2O}$	Concentration of water associated with acid species in organic phase.
H_2O_{ir}	Organic phase water content as determined from 2.72-µpeak in infrared.
H_2O_{KF}	Concentration of water in organic phase as determined by Karl Fischer titration, may or may not be corrected for water dissolved in CCl_4.
H_2O_{net}	Concentration of water associated with TBP in organic phase.
λ^o	Limiting equivalent conductance.
length	Length of ion-exchange column (centimeters).
liquid	Liquid water.
M or *M*	Molarity or final molarity.
M_o	Initial molarity.
m or *m*	Molality or final molality.
N	Normalization factor for ion-exchange columns.
org	Counting rate of organic phase or aliquot thereof (counts/min or scales/min).
processing	Purification and solution procedures used for radioisotopes.
Q	Equilibrium quotient.
resin	Brand name of resin used in ion-exchange column.
source	Origin of isotope or reactor used to produce same.
$T_{\frac{1}{2}}$	Half-life of radioisotope.
ΔT	Duration of shaking for ion-exchange studies.
TBP	Water-saturated 0.128 *M* TBP.

$\overline{TBP}$	Equilibrium concentration of free TBP in organic phase.
$\overline{TBP}'$	Corrected equilibrium concentration of free TBP in organic phase.
$\underline{TBP}$	Total concentration of TBP in organic phase.
TBP_{H^+}	Concentration of TBP associated with acid species in organic phase.
TBH_{H_2O}	Concentration of TBP associated only with H_2O in organic phase.
$\underline{TOPO}$	Total concentration of TOPO in organic phase.
tracer	Radioactive tracer under consideration.
vapor	Water vapor.
vol	Volume of solution used to elute tracer (ml).
volume	Volume of ion-exchange resin in column (cm^3).
vol_{cor}	Volume of solution used to elute tracer, corrected for free column volume (ml).
$\overline{vol}_{cor}$	Normalized vol_{cor} (ml).
vol_{H_2O}	Volume of water in vol_{cor} (ml).
$\overline{vol}_{H_2O}$	Normalized vol_{H_2O} (ml).
vol_{I^-}	Volume of water needed to elute I^- tracer from column (ml).
Vol_{T_2O}	Volume of water needed to elute H_xT_yO from column (ml).
X_{Cl}	Mole fraction of resin in chloride form.
weight	Weight of ion-exchange resin (g).
wt_{H_2O}	Weight of water associated with ion-exchange resin (g).
2.72	Concentration of water as determined by absorbance of 2.72-μ peak, corrected for absorbance by water dissolved in CCl_4.
2.90	Concentration of water as determined by absorbance of 2.90-μ peak.

Table I. Extraction of H_2O by solutions of TBP in CCl_4.

TBP	$\overline{\text{TBP}}$	H_2O_{KF}	CCl_4	H_2O_{net}	2.72	2.90
0.0013	0.0008	0.0104	0.0099	0.0005	0.0002	0.0003
0.0022	0.0010	0.0111	0.0099	0.0012	0.0004	0.0004
0.0037	0.0032	0.0104	0.0099	0.0005	0.0003	0.0003
0.0073	0.0064	0.0108	0.0099	0.0009	0.0010	0.0009
0.0128	0.0112	0.0115	0.0099	0.0016	0.0011	0.0020
0.0220	0.0192	0.0126	0.0098	0.0028	0.0029	0.0027
0.0366	0.0323	0.0141	0.0098	0.0043	0.0038	0.0041
0.073	0.064	0.0191	0.0097	0.0094	0.0078	0.0098
0.128	0.112	0.0265	0.0096	0.0169	0.0160	0.0180
0.220	0.196	0.384	0.0093	0.0291	0.0244	0.0320
0.366	0.318	0.0687	0.0089	0.0598	0.0482	0.0690
0.73	0.65	0.1600	0.0079	0.1521	0.0833	0.1607
1.28	1.12	0.3818	0.0064	0.3754	0.1587	0.480
2.20	1.90	1.0044	0.0039	1.0005	0.298	1.20

Table II. Infrared absorption frequencies of H_2O, HDO, and D_2O under various conditions.

	H_2O			HDO				D_2O		
	vapor[a]	CCl_4	TBP	liquid[b]	vapor	TBP	liquid	vapor	TBP	liquid
ν_3	2.66	2.69	2.72	2.94	2.70[b]	2.87[d]	2.94	3.58	3.70	4.00
ν_1	2.74	2.76	2.90	3.05	3.68	3.89[e]	4.00	3.75	3.95	4.18
$2\nu_2$	3.17	f	3.12		3.56	3.54	g	h	4.26	g
ν_2	6.27	h	6.17	6.08	7.14	7.13	6.85	8.48	8.39	8.20

[a] data from Ref. 66.

[b] data from Ref. 67.

[c] ν_3 = asymmetric stretch, ν_1 = symmetric stretch, $2\nu_2$ = first harmonic of bending motion, ν_2 = bending motion.

[d] overlapped by ν_1 (H_2O).

[e] overlapped by ν_1 (D_2O).

[f] not seen.

[g] no listed value

[h] masked by CCl_4 absorption.

Table III. Extraction of $HClO_4$ by various solutions of TBP in CCl_4.

$\underline{TBP}$	M_o	M	m	a	a_{H_2O}	a'	$\bar{H}^+$	$\bar{H}^{+'}$	TBP_{H_2O}	TBP_{H^+}	$\overline{TBP}$	$\overline{TBP}'$
0.00128	11.6	11.6	22.6	6.2×10^{10}	0.007	---------	0.0014	------	0	0.0013	0	------
0.00219	11.6	11.6	22.6	6.2×10^{10}	0.007	---------	0.0024	------	0	0.0022	0	------
0.00366	11.6	11.6	22.6	6.2×10^{10}	0.007	---------	0.0035	------	0	0.0037	0	------
0.00732	6.94	6.94	9.8	8.1×10^4	0.334	2.6×10^4	0.0002	0.0011	0.0003	0.0006	0.0064	0.0114
	7.47	7.47	10.8	2.5×10^5	0.270	6.7×10^4	0.0005	0.0045	0.0002	0.0015	0.0055	0.0114
	11.6	11.6	22.6	6.2×10^{10}	0.007	---------	0.0069	------	0	0.0073	0	------
0.0128	6.94	6.94	9.8	8.1×10^4	0.334	2.5×10^4	0.0010	0.0018	0.0005	0.0030	0.0093	0.0114
	7.47	7.47	10.8	2.5×10^5	0.270	6.5×10^4	0.0017	0.0062	0.0003	0.0051	0.0074	0.0014
	11.6	11.6	22.6	6.2×10^{10}	0.007	---------	0.0128	------	0	0.128	0	------
0.0219	6.94	6.94	9.8	8.1×10^4	0.334	2.3×10^4	0.0033	0.0033	0.0006	0.0099	0.114	0.114
	7.47	7.47	10.8	2.5×10^5	0.270	6.0×10^4	0.0046	0.0143	0.0003	0.0138	0.0078	0.0114
	11.6	11.6	22.6	6.2×10^{10}	0.007	---------	0.0216	------	0	0.0219	0	------
0.0366	6.94	6.93	9.8	8.0×10^4	0.334	1.9×10^4	0.0064	0.0556	0.0008	0.0192	0.0166	0.0342
	7.47	7.46	10.8	2.4×10^5	0.270	---------	0.0126	------	0	0.0366	0	------
	11.6	11.6	22.6	6.2×10^{10}	0.007	---------	0.0366	-----	0	0.0366	0	------
0.0732	6.94	6.92	9.8	8.0×10^4	0.334	1.5×10^4	0.0186	0.1618	0.0008	0.0558	0.0166	0.342
	7.47	7.44	10.8	2.0×10^5	0.270	---------	0.0288	------	0	0.0732	0	------
	11.6	11.6	22.6	6.2×10^{10}	0.007	---------	0.0751	------	0	0.0732	0	------
0.128	6.94	6.90	9.7	6.5×10^4	0.340	---------	0.0436	------	0	0.128	0	------
	7.47	7.41	10.7	1.0×10^5	0.276	---------	0.0556	------	0	0.128	0	------
	11.6	11.5	22.5	5.0×10^{10}	0.007	---------	0.1330	------	0	0.128	0	------
0.219	6.94	6.86	9.6	6.0×10^4	0.348	---------	0.0839	------	0	0.219	0	------
	7.47	7.37	10.7	1.5×10^5	0.276	---------	0.1020	------	0	0.219	0	------
	11.6	11.4	22.2	5.0×10^9	0.008	---------	0.2224	------	0	0.219	0	------
0.732	6.94	0.61	9.2	4.0×10^4	0.378	---------	0.3340	------	0	0.732	0	------
	7.47	7.09	10.1	1.2×10^5	0.315	---------	0.3800	------	0	0.732	0	-----
	11.6	10.8	19.8	4.3×10^9	0.020	---------	0.7587	------	0	0.732	0	------
1.28	6.94	6.34	8.7	2.0×10^4	0.415	---------	0.6015	------	0	1.28	0	------
	7.47	6.80	9.5	6.0×10^4	0.356	---------	0.6711	------	0	1.28	0	------
	11.6	10.4	18.5	9.9×10^8	0.032	---------	1.2441	------	0	1.28	0	------

Table IV. Extraction of $HClO_4$ by 0.00384 M TBP in CCl_4.

M_o	M	m	a	a_{H_2O}	a'	$\overline{H}^+$	$\overline{H}^{+'}$	H_2O_{KF}	H_2O_{IR}	$\overline{H_2O}$	TBP_{H_2O}	TBP_{H^+}	$\overline{TBP}$	$\overline{TBP}'$
3.40	3.40	3.95	6.7×10^1	0.809	5.1×10^1	0.0001	0.0001	0.008	0.005	0.003	0.0041	0.0003	0.0340	0.0342
4.07	4.07	4.90	2.2×10^2	0.722	1.5×10^2	0.0002	0.0002	0.008	0.004	0.004	0.0037	0.0006	0.0341	0.0342
4.69	4.69	5.85	7.0×10^2	0.645	3.9×10^2	0.0003	0.0003	0.007	0.003	0.004	0.0033	0.0009	0.0342	0.0342
5.05	5.05	6.4	1.4×10^3	0.600	7.2×10^2	0.0008	0.0009	0.006	0.003	0.003	0.0030	0.0024	0.0330	0.0344
5.22	5.22	6.7	2.1×10^3	0.577	1.0×10^3	0.0007	0.0007	0.008	0.003	0.005	0.0029	0.0021	0.0334	0.0342
5.92	5.92	7.9	8.1×10^3	0.478	3.1×10^3	0.0027	0.0048	0.008	0.002	0.006	0.0020	0.0081	0.0283	0.0342
6.08	6.08	8.2	1.2×10^4	0.453	4.3×10^3	0.0031	0.0068	0.008	0.002	0.006	0.0018	0.0093	0.0273	0.0342
6.50	6.50	9.0	3.0×10^4	0.292	6.1×10^3	0.0045	0.0132	0.009	0.001	0.008	0.0010	0.0135	0.0239	0.0342
8.15	8.14	12.3	1.4×10^6	0.190	1.4×10^5	0.0099	0.644	0.016	0	0.016	0.0002	0.0297	0.0085	0.0342
9.33	9.32	15.2	2.8×10^7	0.089	---------	0.0146	-----	0.019	0	0.019	0	0.0384	0	----
9.73	9.71	16.4	1.1×10^8	0.063	---------	0.0213	-----	0.020	0	0.020	0	0.0384	0	-----
10.1	10.1	17.5	3.4×10^8	0.044	---------	0.0244	-----	0.021	0	0.021	0	0.0384	0	-----
10.4	10.4	18.5	9.9×10^8	0.032	---------	0.0278	-----	0.016	0	0.016	0	0.0384	0	-----
11.2	11.2	21.2	1.6×10^{10}	0.012	---------	0.0314	-----	0.012	0	0.012	0	0.0384	0	-----
11.2	11.2	21.2	1.6×10^{10}	0.012	---------	0.0288	-----	0.010	0	0.010	0	0.0384	0	-----
11.6	11.6	22.6	6.2×10^{10}	0.007	---------	0.0315	-----	0.014	0	0.014	0	0.0384	0	-----
11.7	11.7	23.0	7.6×10^{10}	0.006	---------	0.0336	-----	0.009	0	0.009	0	0.0384	0	-----
12.5	12.5	26.5	2.6×10^{12}	0.001	---------	0.0312	-----	0.006	0	0.006	0	0.0384	0	-----

Table V. Extraction of $HClO_4$ by 0.0641 M TBP in CCl_4.

M_o	M	m	a	a_{H_2O}	a'	$\overline{H}^+$	$\overline{H}^{+\prime}$	H_2O_{KF}	H_2O_{IR}	$\overline{H_2O}$	TBP_{H_2O}	TBP_{H^+}	$\overline{TBP}$	$\overline{TBP}'$
2.64	2.64	2.97	1.8×10^1	0.861	1.4×10^1	0.0001	0.0001	0.012	0.011	0.001	0.0073	0.0003	0.0565	0.0637
3.40	3.40	3.95	6.7×10^1	0.809	4.8×10^1	0.0002	0.0003	0.011	0.010	0.001	0.0069	0.0006	0.0556	0.0637
4.07	4.07	4.90	2.2×10^2	0.722	1.3×10^2	0.0005	0.0007	0.012	0.010	0.002	0.0061	0.0015	0.0565	0.0637
4.69	4.69	5.85	7.0×10^2	0.645	3.5×10^2	0.0014	0.0022	0.012	0.008	0.004	0.0053	0.0042	0.0546	0.0637
5.05	5.05	6.4	1.4×10^3	0.600	6.3×10^2	0.0026	0.0049	0.010	0.008	0.002	0.0047	0.0078	0.0516	0.0637
5.22	5.22	6.7	2.1×10^3	0.577	8.8×10^2	0.0027	0.0052	0.014	0.007	0.007	0.0045	0.0081	0.0515	0.0637
5.92	5.91	7.9	8.0×10^3	0.478	2.5×10^3	0.0071	0.0290	0.017	0.005	0.012	0.0029	0.0213	0.0399	0.0637
6.08	6.07	8.2	1.1×10^4	0.453	3.1×10^3	0.0095	0.0665	0.020	0.004	0.016	0.0023	0.0285	0.0333	0.0637
6.39	6.37	8.8	2.4×10^4	0.406	5.7×10^3	0.0111	0.1178	0.021	0.002	0.019	0.0018	0.0333	0.0290	0.0637
6.50	6.49	9.0	2.8×10^4	0.392	6.3×10^3	0.0112	0.1208	0.022	0.001	0.021	0.0017	0.0336	0.0288	0.0637
7.47	7.45	10.8	2.0×10^5	0.270	---------	0.0215	-----	0.033	0	0.033	0	0.0641	0	-----
8.15	8.12	12.3	1.0×10^6	0.190	---------	0.0278	-----	0.037	0	0.037	0	0.0641	0	-----
8.15	8.12	12.3	1.0×10^6	0.190	---------	0.0270	-----	0.035	0	0.035	0	0.0641	0	-----
8.76	8.73	13.8	6.0×10^6	0.130	---------	0.0323	-----	0.039	0	0.039	0	0.0641	0	-----
8.92	8.89	14.2	1.0×10^7	0.117	---------	0.0338	-----	0.039	0	0.039	0	0.0641	0	-----
9.33	9.29	15.1	1.5×10^7	0.097	---------	0.0373	-----	0.040	0	0.040	0	0.0641	0	-----
9.33	9.30	15.2	2.0×10^7	0.089	---------	0.0330	-----	0.042	0	0.042	0	0.0641	0	-----
9.73	9.69	16.3	1.0×10^8	0.064	---------	0.0420	-----	0.039	0	0.039	0	0.0641	0	-----
9.73	9.69	16.3	1.0×10^8	0.064	---------	0.0422	-----	0.043	0	0.043	0	0.0641	0	-----
10.1	10.1	17.5	3.4×10^8	0.044	---------	0.0449	-----	0.036	0	0.036	0	0.0641	0	-----
10.5	10.5	18.7	1.0×10^9	0.030	---------	0.0479	-----	0.027	0	0.027	0	0.0641	0	-----
11.2	11.1	21.0	8.0×10^9	0.013	---------	0.0548	-----	0.018	0	0.018	0	0.0641	0	-----
11.6	11.5	22.4	5.0×10^{10}	0.008	---------	0.0578	-----	0.012	0	0.012	0	0.0641	0	-----
12.5	12.4	26.3	1.0×10^{12}	0.001	---------	0.0588	-----	0.004	0	0.004	0	0.0641	0	-----
12.5	12.4	26.3	1.0×10^{12}	0.001	---------	0.0612	-----	0.005	0	0.005	0	0.0641	0	-----

Table VI. Extraction of $HClO_4$ by 0.128 <u>M</u> TBP in CCl_4.

M_o	M	m	a	a_{H_2O}	a'	$\overline{H}^+$	$\overline{H}^{+}{}'$	H_2O_{KF}	H_2O_{IR}	$\overline{H_2O}$	TBP_{H_2O}	TBP_{H^+}	$\overline{TBP}$	$\overline{TBP}'$
1.69	1.69	1.85	5.6×10^0	0.923	4.8×10^0	0.0001	0.0001	0.022	0.020	0.002	0.016	0.0003	0.112	0.113
2.09	2.09	2.30	7.4×10^0	0.900	6.0×10^0	0.0001	0.0001	0.023	0.019	0.004	0.015	0.0003	0.113	0.113
2.64	2.64	2.97	1.8×10^1	0.861	1.4×10^1	0.0006	0.0006	0.023	0.020	0.003	0.014	0.0018	0.112	0.113
3.40	3.40	3.95	6.7×10^1	0.809	4.5×10^1	0.0013	0.0014	0.022	0.018	0.004	0.013	0.0039	0.111	0.113
4.07	4.07	4.90	2.2×10^2	0.722	1.2×10^2	0.0036	0.0044	0.025	0.018	0.007	0.011	0.0108	0.106	0.113
4.69	4.68	5.84	6.9×10^2	0.645	3.0×10^2	0.0071	0.0109	0.031	0.014	0.017	0.009	0.0213	0.098	0.113
5.05	5.04	6.4	1.2×10^3	0.600	4.9×10^2	0.0113	0.0256	0.034	0.013	0.021	0.008	0.0339	0.086	0.113
5.22	5.21	6.7	2.0×10^3	0.577	6.9×10^2	0.0124	0.0303	0.038	0.012	0.026	0.007	0.0372	0.084	0.113
6.08	6.06	8.2	1.2×10^4	0.453	2.7×10^3	0.0241	0.2340	0.056	0.008	0.048	0.004	0.0732	0.053	0.113
6.39	6.36	8.8	2.2×10^4	0.406	4.0×10^3	0.0321	------	0.061	0.006	0.055	0.002	0.0903	0.030	0.113
6.50	6.47	9.0	2.6×10^4	0.392	4.6×10^3	0.0324	------	0.066	0.005	0.061	0.002	0.0972	0.029	0.113
6.94	6.90	9.7	6.5×10^4	0.340	---------	0.0404	------	0.071	0.004	0.067	0.000	0.1212	0.007	0.113
6.94	6.90	9.7	6.5×10^4	0.340	---------	0.0425	------	0.072	0.004	0.068	0	0.128	0	-----
7.47	7.42	10.7	1.2×10^5	0.276	---------	0.0523	------	0.080	0.002	0.078	0	0.128	0	-----
8.15	8.09	12.2	1.0×10^6	0.195	---------	0.0624	------	0.081	0.002	0.079	0	0.128	0	-----
8.15	8.09	12.2	1.0×10^6	0.195	---------	0.0608	------	0.084	0.001	0.083	0	0.128	0	-----
8.76	8.70	13.7	6.0×10^6	0.133	---------	0.0640	------	0.084	0.001	0.083	0	0.128	0	-----
8.92	8.85	14.1	8.0×10^6	0.120	---------	0.0730	------	0.084	0.001	0.083	0	0.128	0	-----
9.73	9.65	16.2	8.0×10^7	0.066	---------	0.0849	------	0.085	0	0.085	0	0.128	0	-----
9.73	9.65	16.2	8.0×10^7	0.066	---------	0.0829	------	0.090	0	0.090	0	0.128	0	-----
10.4	10.3	18.3	6.0×10^8	0.034	---------	0.0983	------	0.084	0	0.084	0	0.128	0	-----
10.8	10.7	19.6	3.0×10^9	0.022	---------	0.1085	------	0.067	0	0.067	0	0.128	0	-----
11.2	11.1	21.0	8.0×10^9	0.013	---------	0.1208	------	0.046	0	0.046	0	0.128	0	-----
11.6	11.5	22.5	5.0×10^{10}	0.007	---------	0.1284	------	0.033	0	0.033	0	0.128	0	-----
12.5	12.4	26.3	1.0×10^{12}	0.001	---------	0.1413	------	0.015	0	0.015	0	0.128	0	-----

Table VII. Extraction of $HClO_4$ by 0.366 M TBP in CCl_4.

M_o	M	m	a	a_{H_2O}	a'	$\overline{H}^+$	$\overline{H}^{+'}$	H_2O_{KF}	H_2O_{IR}	$\overline{H_2O}$	TBP_{H_2O}	TBP_{H^+}	$\overline{TBP}$	$\overline{TBP}'$
0.52	0.52	0.52	1.6×10^{-1}	0.982	1.5×10^{-1}	0.0002	0.0002	0.060	0.059	0.001	0.047	0.0006	0.318	0.319
0.77	0.77	0.80	4.0×10^{-1}	0.971	3.7×10^{-1}	0.0003	0.0003	0.059	0.058	0.001	0.046	0.0009	0.319	0.319
1.02	1.02	1.06	7.7×10^{-1}	0.961	7.0×10^{-1}	0.0006	0.0006	0.063	0.059	0.004	0.046	0.0018	0.318	0.319
1.14	1.14	1.20	1.1×10^{0}	0.954	9.8×10^{-1}	0.0008	0.0008	0.059	0.057	0.002	0.045	0.0024	0.318	0.319
1.69	1.69	1.85	5.6×10^{0}	0.923	4.6×10^{0}	0.0032	0.0034	0.069	0.065	0.004	0.043	0.0096	0.313	0.319
2.04	2.04	2.24	6.8×10^{0}	0.903	5.3×10^{0}	0.0039	0.0042	0.068	0.059	0.009	0.042	0.0117	0.312	0.319
2.09	2.09	2.30	7.4×10^{0}	0.900	5.7×10^{0}	0.0044	0.0048	0.068	0.056	0.008	0.042	0.0132	0.311	0.319
2.64	2.63	2.96	1.8×10^{1}	0.861	1.2×10^{1}	0.0094	0.0114	0.081	0.065	0.016	0.039	0.0282	0.299	0.319
3.40	3.38	3.92	6.5×10^{1}	0.810	3.8×10^{1}	0.0212	0.0320	0.112	0.050	0.062	0.033	0.0636	0.269	0.319
4.07	4.03	4.85	2.1×10^{2}	0.726	1.0×10^{2}	0.0413	0.1288	0.156	0.048	0.108	0.024	0.1239	0.218	0.319
4.69	4.63	5.75	6.2×10^{2}	0.652	2.1×10^{2}	0.0630	0.4890	0.199	0.047	0.152	0.016	0.1890	0.161	0.319
5.05	4.97	6.25	1.1×10^{3}	0.612	3.2×10^{2}	0.0803	------	0.212	0.033	0.179	0.010	0.2409	0.115	0.319
5.22	5.14	6.6	1.7×10^{3}	0.582	4.4×10^{2}	0.0843	------	0.234	0.027	0.207	0.009	0.2529	0.104	0.319
6.08	5.97	8.0	9.0×10^{3}	0.469	---------	0.1137	------	0.287	0.010	0.277	0.002	0.3411	0.023	0.319
6.08	5.97	8.0	9.0×10^{3}	0.469	---------	0.1140	------	0.274	0.010	0.264	0.002	0.3420	0.022	0.319
6.39	6.25	8.5	1.9×10^{4}	0.428	---------	0.1356	------	0.274	0.008	0.266	0	0.366	0	-----
6.50	6.37	8.8	2.3×10^{4}	0.406	---------	0.1325	------	0.293	0.007	0.286	0	0.366	0	-----
6.94	6.79	9.5	6.0×10^{4}	0.356	---------	0.1535	------	0.292	0.003	0.289	0	0.366	0	-----
6.94	6.78	9.5	6.0×10^{4}	0.356	---------	0.1561	------	0.289	0.003	0.286	0	0.366	0	-----
7.47	7.29	10.4	1.5×10^{5}	0.295	---------	0.1757	------	0.292	0	0.292	0	0.366	0	-----
8.15	7.95	11.9	8.0×10^{5}	0.210	---------	0.1953	------	0.288	0	0.288	0	0.366	0	-----
8.15	7.95	11.9	8.0×10^{5}	0.210	---------	0.1951	------	0.291	0	0.291	0	0.366	0	-----
8.76	8.55	13.4	4.0×10^{6}	0.143	---------	0.2095	------	0.305	0	0.305	0	0.366	0	-----
8.92	8.70	13.7	6.0×10^{6}	0.133	---------	0.2209	------	0.283	0	0.283	0	0.366	0	-----
9.73	9.48	15.6	5.0×10^{7}	0.079	---------	0.2507	------	0.254	0	0.254	0	0.366	0	-----
10.5	10.2	17.8	4.5×10^{8}	0.040	---------	0.3051	------	0.250	0	0.250	0	0.366	0	-----
10.8	10.5	18.8	1.3×10^{9}	0.029	---------	0.3163	------	0.240	0	0.240	0	0.366	0	-----
11.2	10.9	20.2	6.0×10^{9}	0.018	---------	0.3491	------	0.195	0	0.195	0	0.366	0	-----
11.6	11.2	21.2	1.6×10^{10}	0.012	---------	0.3779	------	0.140	0	0.140	0	0.366	0	-----
11.7	11.3	21.6	2.0×10^{10}	0.010	---------	0.3671	------	0.156	0	0.156	0	0.366	0	-----
12.5	12.1	25.3	7.0×10^{11}	0.002	---------	0.4311	------	0.078	0	0.078	0	0.366	0	-----

Table VIII. Extraction of HBr by various solutions of TBP in CCl_4.

$\overline{TBP}$	M_o	M	m	a	a_{H_2O}	a'	$\bar{H}^+$	$\bar{H}^{+\prime}$	H_2O_{KF}	H_2O_{IR}	$\overline{H_2O}$	TBP_{H_2O}	TBP_{H^+}	$\overline{TBP}$	$\overline{TBP}'$
0.0366	6.483	6.483	7.74	6.5×10^3	0.491	2.6×10^3	0.0001	0.0001	0.0051	0.0025	0.003	0.0025	0.0003	0.0338	0.0338
	7.125	7.125	8.70	2.1×10^4	0.413	6.6×10^3	0.0004	0.0004	0.0059	0.0023	0.004	0.0022	0.0012	0.0332	0.0338
	7.500	7.499	9.26	3.8×10^4	0.369	1.0×10^4	0.0007	0.0008	0.0052	0.0019	0.003	0.0019	0.0021	0.0326	0.0338
	8.085	8.084	10.17	1.2×10^5	0.310	2.6×10^4	0.0014	0.0018	0.0068	0.0018	0.005	0.0015	0.0042	0.0309	0.0338
	8.530	8.528	10.90	2.7×10^5	0.268	4.9×10^4	0.0022	0.0035	0.0084	0.0019	0.007	0.0011	0.0066	0.0289	0.0338
0.0915	5.167	5.167	5.93	8.0×10^2	0.637	3.9×10^2	0.00015	0.00015	0.0096	0.0092	0.000	0.0092	0.0005	0.0818	0.0825
	5.567	5.567	6.46	1.5×10^3	0.595	6.6×10^2	0.0003	0.0003	0.0086	0.0081	0.001	0.0081	0.0009	0.0825	0.0825
	6.070	6.069	7.15	3.4×10^3	0.539	1.3×10^3	0.0007	0.0007	0.0085	0.0074	0.001	0.0074	0.0021	0.0820	0.0825
	6.483	6.482	7.74	6.5×10^3	0.491	2.1×10^3	0.0011	0.0011	0.0088	0.0067	0.002	0.0067	0.0033	0.0815	0.0825
	7.125	7.123	8.70	2.1×10^4	0.413	5.0×10^3	0.0023	0.0027	0.0107	0.0060	0.005	0.0059	0.0069	0.0787	0.0825
	7.500	7.495	9.26	3.8×10^4	0.369	7.6×10^3	0.0045	0.0065	0.0128	0.0056	0.007	0.0048	0.0135	0.0732	0.0825
	8.085	8.076	10.16	1.2×10^5	0.311	1.9×10^4	0.0089	0.0217	0.0168	0.0051	0.012	0.0035	0.0267	0.0613	0.0825
	8.530	8.516	10.88	2.6×10^5	0.269	3.2×10^4	0.0143	0.0813	0.0221	0.0045	0.018	0.0023	0.0429	0.0463	0.0825
	8.530	8.516	10.88	2.6×10^5	0.269	3.2×10^4	0.140	0.0730	0.0223	0.0045	0.018	0.0018	0.0420	0.0477	0.0825
0.183	3.212	3.212	3.49	3.9×10^1	0.830	2.7×10^1	0.00014	0.00014	0.0196	0.0200	0.000	0.0200	0.0004	0.1626	0.1637
	4.280	4.280	4.78	2.0×10^2	0.732	1.1×10^2	0.0004	0.0004	0.0173	0.0184	0.000	0.0184	0.0012	0.1634	0.1637
	5.167	5.166	5.93	8.1×10^2	0.638	3.5×10^2	0.0011	0.0011	0.0176	0.0161	0.002	0.0161	0.0033	0.1636	0.1637
	5.567	5.565	6.46	1.5×10^3	0.595	5.7×10^2	0.0017	0.017	0.0175	0.0151	0.003	0.0146	0.0051	0.1633	0.1637
	6.070	6.067	7.15	3.4×10^3	0.539	1.1×10^3	0.0034	0.0037	0.0194	0.0133	0.006	0.0134	0.0102	0.1594	0.1637
	6.483	6.477	7.74	6.5×10^3	0.491	2.1×10^3	0.0063	0.0079	0.0236	0.0122	0.011	0.0120	0.0189	0.1521	0.1637
	7.125	7.112	8.69	2.0×10^4	0.414	4.2×10^3	0.0134	0.0251	0.0286	0.0109	0.018	0.0101	0.0402	0.1327	0.1637
	7.500	7.478	9.25	3.9×10^4	0.370	5.8×10^3	0.0216	0.0698	0.0395	0.0084	0.031	0.0074	0.0648	0.1108	0.1637
	8.085	8.048	10.11	1.1×10^5	0.313	1.4×10^4	0.0368	0.4760	0.0608	0.0050	0.056	0.0030	0.1104	0.0696	0.1637
	8.530	8.480	10.81	2.4×10^5	0.271	2.3×10^4	0.0503	------	0.0777	0.0035	0.074	0.0017	0.1509	0.0304	0.1637
0.366	1.075	1.075	1.12	8.9×10^{-1}	0.958	8.2×10^{-1}	0.0001	0.0001	0.052	0.052	0.000	0.0494	0.0003	0.3163	0.3198
	2.145	2.145	2.30	7.4×10^0	0.900	6.0×10^0	0.0001	0.0001	0.049	0.048	0.001	0.0477	0.0004	0.3179	0.3198
	3.212	3.212	3.49	3.9×10^1	0.830	2.7×10^1	0.0005	0.0005	0.047	0.044	0.003	0.0454	0.0015	0.3191	0.3198
	4.280	4.278	4.78	2.0×10^2	0.732	1.1×10^2	0.0022	0.0022	0.047	0.040	0.007	0.0396	0.0066	0.3198	0.3198
	5.167	5.161	5.92	8.0×10^2	0.638	3.3×10^2	0.0058	0.0058	0.049	0.032	0.017	0.0341	0.0174	0.3145	0.3198
	5.567	5.558	6.45	1.4×10^3	0.597	5.0×10^2	0.0091	0.0101	0.057	0.030	0.027	0.0299	0.0273	0.3088	0.3198
	6.070	6.049	7.12	3.3×10^3	0.541	9.7×10^2	0.0210	0.0320	0.070	0.030	0.040	0.0253	0.0630	0.2777	0.3198
	6.483	6.449	7.70	6.3×10^3	0.495	1.6×10^3	0.0338	0.766	0.097	0.028	0.069	0.0205	0.1014	0.2441	0.3198
	7.125	7.062	8.59	1.8×10^4	0.420	3.3×10^3	0.0632	0.4720	0.142	0.028	0.114	0.0124	0.1896	0.1640	0.3198
	7.500	7.415	9.13	3.6×10^4	0.378	5.1×10^3	0.0854	------	0.189	0.026	0.163	0.0069	0.2562	0.1029	0.3198
	8.085	7.963	9.98	9.3×10^4	0.322	---------	0.1223	------	0.241	0.023	0.218	0	0.3660	0	------
	8.530	8.380	10.63	2.0×10^5	0.282	---------	0.1504	------	0.288	0.014	0.274	0	0.3660	0	------

Table VIII (Continued)

$\overline{TBP}$	M_o	M	m	a	a_{H_2O}	a'	$\overline{H}^+$	$\overline{H}^{+\prime}$	H_2O_{KF}	H_2O_{IR}	$\overline{H_2O}$	TBP_{H_2O}	TBP_{H^+}	$\overline{TBP}$	$\overline{TBP}'$
0.183	1.075	1.075	1.12	8.9×10^{-1}	0.958	8.2×10^{-1}	0.00006	0.00007	------	------	------	0.0230	0.0002	0.1598	0.1637
	2.145	2.145	2.30	7.4×10^{0}	0.900	6.0×10^{0}	0.00009	0.00010	------	------	------	0.0220	0.0003	0.1607	0.1637
	3.212	3.212	3.49	3.9×10^{1}	0.830	2.7×10^{1}	0.00013	0.00013	------	------	------	0.0200	0.0004	0.1626	0.1637
	4.280	4.280	4.78	2.0×10^{2}	0.732	1.1×10^{2}	0.0003	0.0003	------	------	------	0.0184	0.0009	0.1637	0.1637
	5.167	5.166	5.93	8.1×10^{2}	0.638	3.5×10^{2}	0.0012	0.0012	------	------	------	0.0161	0.0036	0.1633	0.1637
	5.567	5.565	6.46	1.5×10^{3}	0.595	5.7×10^{2}	0.0021	0.0022	------	------	------	0.0146	0.0063	0.1621	0.1637
	5.567	5.565	6.46	1.5×10^{3}	0.595	5.7×10^{2}	0.0022	0.0022	------	------	------	0.0134	0.0066	0.1630	0.1637
	6.070	6.066	7.15	3.4×10^{3}	0.539	1.1×10^{3}	0.0035	0.0037	------	------	------	0.0120	0.0105	0.1605	0.1637
	6.483	6.476	7.74	6.5×10^{3}	0.491	2.0×10^{3}	0.0068	0.0084	------	------	------	0.0101	0.0204	0.1525	0.1637
	7.125	7.110	8.69	2.1×10^{4}	0.414	4.2×10^{3}	0.0152	0.0301	------	------	------	0.0074	0.0456	0.1300	0.1637
	8.085	8.046	10.11	1.1×10^{5}	0.313	1.4×10^{4}	0.0388	0.6360	------	------	------	0.0030	0.1164	0.0636	0.1637
	8.530	8.484	10.82	2.4×10^{5}	0.271	2.3×10^{4}	0.0455	------	------	------	------	0.0017	0.1365	0.0448	0.1637
0.366	1.075	1.075	1.12	8.9×10^{-1}	0.958	8.2×10^{-1}	0.0002	0.0002	------	------	------	0.0494	0.0006	0.3160	0.3198
	2.145	2.145	2.30	7.4×10^{0}	0.900	6.0×10^{0}	0.0003	0.0003	------	------	------	0.0477	0.0009	0.3174	0.3198
	3.212	3.211	3.49	3.9×10^{1}	0.830	2.7×10^{1}	0.0007	0.0007	------	------	------	0.0454	0.0021	0.3185	0.3198
	4.280	4.278	4.78	2.0×10^{2}	0.732	1.1×10^{2}	0.0024	0.0024	------	------	------	0.0396	0.0072	0.3192	0.3198
	5.167	5.160	5.92	8.0×10^{2}	0.638	3.3×10^{2}	0.0066	0.0072	------	------	------	0.0341	0.0198	0.3121	0.3198
	5.567	5.555	6.45	1.4×10^{3}	0.597	5.0×10^{2}	0.0115	0.0131	------	------	------	0.0299	0.0345	0.3016	0.3198
	6.070	6.049	7.12	3.3×10^{3}	0.541	9.7×10^{2}	0.0207	0.0312	------	------	------	0.0253	0.0621	0.2786	0.3198
	6.483	6.450	7.70	6.3×10^{3}	0.495	1.6×10^{3}	0.0328	0.0712	------	------	------	0.0205	0.0984	0.2471	0.3198
	7.125	7.064	8.59	1.8×10^{4}	0.420	3.3×10^{3}	0.0605	0.3820	------	------	------	0.0124	0.1815	0.1721	0.3198
	7.500	7.418	9.13	3.6×10^{4}	0.378	5.1×10^{3}	0.0825	------	------	------	------	0.0069	0.2475	0.1116	0.3198
	8.085	7.968	9.99	9.4×10^{4}	0.321	---------	0.1172	------	------	------	------	0	0.3660	0	------
	8.530	8.382	10.63	2.0×10^{5}	0.282	---------	0.1481	------	------	------	------	0	0.3660	0	------

Table IX. Extraction of HNO_3 by various solutions of TBP in CCl_4.

TBP	M_o	M	m	a	a_{H_2O}	$\overline{H}^+$	$\overline{H}^{+\prime}$	H_2O_{KF}	H_2O_{IR}	$\overline{H_2O}$	TBP_{H_2O}	TBP_{H^+}	$\overline{TBP}$	$\overline{TBP}'$
0	3.95	3.95	4.48	2.1×10^1	0.820	0.0002	------	------	------	-----	-------	-------	-------	-------
	8.07	8.07	10.87	2.9×10^2	0.590	0.0012	------	------	------	-----	-------	-------	-------	-------
	12.10	12.09	20.25	1.4×10^3	0.360	0.0071	------	------	------	-----	-------	-------	-------	-------
	15.80	15.77	35.6	1.4×10^4	0.160	0.0291	------	------	------	-----	-------	-------	-------	-------
0.00013	3.95	3.95	4.48	2.1×10^1	0.820	0.0000	0.0000	------	------	-----	0.00001	0.00001	0.00011	0.00011
0.00037	3.95	3.95	4.48	2.1×10^1	0.820	0.0002	0.0002	------	------	-----	0.00002	0.00018	0.00017	0.00017
0.00128	3.95	3.95	4.48	2.1×10^1	0.820	0.0008	0.0008	------	------	-----	0.00005	0.00081	0.00042	0.00042
0.00366	3.95	3.95	4.48	2.1×10^1	0.820	0.0023	0.0023	------	------	-----	0.00015	0.00231	0.00120	0.00120
0.0128	3.95	3.94	4.46	2.1×10^1	0.821	0.0084	0.0084	------	------	-----	0.00047	0.00845	0.0039	0.0039
0.0366	0.202	0.202	0.20	2.3×10^{-2}	0.993	0.0001	0.0001	------	------	-----	0.0046	0.0001	0.0319	0.0302
	0.501	0.500	0.50	1.4×10^{-1}	0.983	0.0005	0.0005	------	------	-----	0.0045	0.0005	0.0316	0.0302
	1.003	1.001	1.05	5.8×10^{-1}	0.965	0.0020	0.0020	0.0071	0.0044	0.003	0.0044	0.0020	0.0302	0.0302
	2.016	2.009	2.16	2.9×10^0	0.925	0.0072	0.0084	0.0059	0.0040	0.002	0.0036	0.0072	0.0258	0.0302
	2.93	2.91	3.22	8.5×10^0	0.879	0.0151	0.0240	0.0047	0.0034	0.001	0.0025	0.0151	0.0190	0.0302
	3.95	3.93	4.45	2.1×10^1	0.822	0.0231	0.0581	0.0041	0.0025	0.002	0.0015	0.0231	0.0120	0.0302
	4.96	4.93	5.78	4.3×10^1	0.762	0.0286	0.1200	0.0055	0.0025	0.003	0.0008	0.0286	0.0072	0.0302
	6.05	6.02	7.36	8.9×10^1	0.703	0.0329	0.300	0.0046	0.0018	0.003	0.0004	0.0329	0.0033	0.0302
	8.07	8.03	10.80	2.8×10^2	0.589	0.0352	0.887	0.0054	0.0019	0.004	0.0002	0.0352	0.0012	0.0302
	10.08	10.04	15.00	8.0×10^2	0.472	0.0381	-----	0.0060	0.0035	0.003	0	0.0366	0	------
	12.10	12.05	20.17	2.1×10^3	0.361	0.0417	-----	0.0067	0.0057	0.001	0	0.0366	0	------
	14.04	13.98	26.6	4.8×10^3	0.258	0.0498	-----	0.0103	0.0088	0.002	0	0.0366	0	------
	15.80	15.71	35.5	1.2×10^4	0.161	0.0593	-----	0.0112	0.0128	0.000	0	0.0366	0	------

Table IX (Continued)

TBP	M_o	M	m	a	a_{H_2O}	$\overline{H}^+$	$\overline{H}^{+\prime}$	H_2O_{KF}	H_2O_{IR}	$\overline{H_2O}$	TBP_{H_2O}	TBP_{H^+}	$\overline{TBP}$	$\overline{TBP}'$
0.128	0.202	0.202	0.20	2.3×10^{-2}	0.993	0.0004	0.0004	------	------	-----	0.0161	0.0004	0.112	0.106
	0.501	0.499	0.50	1.4×10^{-1}	0.983	0.0019	0.0019	------	------	-----	0.0158	0.0019	0.110	0.106
	1.003	0.996	1.04	5.6×10^{-1}	0.965	0.0069	0.0069	0.0196	0.0156	0.004	0.0155	0.0069	0.1056	0.106
	2.016	1.998	2.14	2.8×10^{0}	0.927	0.0277	0.0332	0.0186	0.0138	0.005	0.0123	0.0277	0.880	0.106
	2.93	2.87	3.18	8.2×10^{0}	0.880	0.0558	0.0923	0.0173	0.0123	0.005	0.0084	0.0558	0.0638	0.106
	3.95	3.86	4.36	2.0×10^{1}	0.826	0.0853	0.237	0.0168	0.0100	0.007	0.0047	0.0853	0.0380	0.106
	4.96	4.86	5.68	4.1×10^{1}	0.771	0.1033	0.487	0.0133	0.0090	0.004	0.0025	0.1033	0.0272	0.106
	6.05	5.93	7.22	8.4×10^{1}	0.711	0.1148	1.033	0.0113	0.0077	0.004	0.0015	0.1148	0.0117	0.106
	8.07	7.94	10.60	2.7×10^{2}	0.596	0.1271	-----	0.0131	0.0096	0.004	0.0001	0.1271	0.0008	0.106
	10.08	9.94	14.77	7.6×10^{2}	0.479	0.1367	-----	0.0137	0.0129	0.001	0	0.128	0	-----
	12.10	11.94	19.81	2.0×10^{3}	0.367	0.1540	-----	0.0182	0.0179	0.000	0	0.128	0	-----
	14.04	13.85	26.0	4.5×10^{3}	0.266	0.1782	-----	0.0206	0.0252	0	0	0.128	0	-----
	15.80	15.56	33.5	9.9×10^{3}	0.178	0.2152	-----	0.0257	0.0345	0	0	0.128	0	-----
0.366	0.202	0.201	0.20	2.3×10^{-2}	0.993	0.0014	0.0013	------	------	-----	0.0488	0.0014	0.316	0.293
	0.501	0.494	0.50	1.3×10^{-1}	0.983	0.0067	0.0063	------	------	-----	0.0478	0.0067	0.311	0.293
	1.003	0.977	1.03	5.5×10^{-1}	0.965	0.0264	0.0264	0.0624	0.051	0.011	0.0468	0.264	0.293	0.293
	2.016	1.936	2.08	2.6×10^{0}	0.929	0.0900	0.1102	0.0644	0.048	0.016	0.0367	0.0900	0.239	0.293
	2.93	2.76	3.03	7.1×10^{0}	0.886	0.1663	0.2795	0.0592	0.042	0.017	0.0251	0.1663	0.175	0.293
	3.95	3.71	4.18	1.7×10^{1}	0.836	0.2414	0.644	0.0536	0.036	0.018	0.0148	0.2414	0.110	0.293
	4.96	4.66	5.41	3.6×10^{1}	0.782	0.2959	1.39	0.0440	0.028	0.016	0.0079	0.2959	0.062	0.293
	6.05	5.72	6.91	7.3×10^{1}	0.721	0.3339	3.42	0.0398	0.022	0.018	0.0035	0.3339	0.029	0.293
	8.07	7.70	10.18	2.4×10^{2}	0.610	0.3688	------	0.0284	0.022	0.006	0	0.366	0	-----
	10.08	9.68	14.20	6.7×10^{2}	0.493	0.3964	------	0.0324	0.028	0.004	0	0.366	0	-----
	12.10	11.54	18.80	1.7×10^{3}	0.387	0.4485	------	0.0438	0.046	0	0	0.366	0	-----
	14.04	13.50	24.7	3.8×10^{3}	0.288	0.5147	------	0.0503	0.072	0	0	0.366	0	-----
	15.80	15.13	31.5	8.2×10^{3}	0.198	0.6404	------	0.0691	0.104	0	0	0.366	0	-----

Table X. Extraction of $HReO_4$ by solutions of TBP in iso-octane.

TBP	M_o	M	org	aq	D	$\overline{H}^+$	$\overline{H}^{+\prime}$	TBP_{H_2O}	TBP_{H^+}	$\overline{TBP}$	$\overline{TBP}'$
0	0.109	0.109	2.0×10^{-1}	7.3×10^4	0.00000	0.00000	-------	0	0	0	-----
	0.109	0.109	-3.1×10^0	1.2×10^5	0.00000	0.00000	-------	0	0	0	------
	0.435	0.435	-3.0×10^{-1}	6.9×10^4	0.00000	0.00000	-------	0	0	0	------
	1.74	1.74	-1.3×10^0	7.1×10^4	0.00000	0.00000	-------	0	0	0	------
	1.63[a]	1.63	-1.7×10^0	7.0×10^4	0.00000	0.00000	-------	0	0	0	-----
0.0366	0.87	0.87	7.6×10^0	9.2×10^4	0.00008	0.00007	0.00011	0.0046	0.0002	0.0318	0.0342
	1.74	1.74	7.0×10^0	6.5×10^4	0.00012	0.00021	0.00032	0.0044	0.0006	0.0316	0.0342
	1.63[a]	1.63	8.0×10^0	9.4×10^4	0.00011	0.00018	0.00027	0.0044	0.0005	0.0317	0.0342
0.0732	0.217	0.217	9.2×10^0	8.3×10^4	0.00011	0.00002	0.00002	0.0095	0.0001	0.0636	0.0637
	0.435	0.435	9.1×10^0	8.9×10^4	0.00010	0.00004	0.00004	0.0094	0.0001	0.0637	0.0637
	0.87	0.87	1.7×10^1	7.2×10^4	0.00023	0.00020	0.00020	0.0092	0.0006	0.0634	0.0637
	1.74	1.74	2.8×10^1	7.3×10^4	0.00038	0.00066	0.00068	0.0086	0.0020	0.0626	0.0637
	1.63[a]	1.63	3.5×10^1	8.3×10^4	0.00044	0.00072	0.00074	0.0086	0.0022	0.0624	0.0637
0.128	0.109	0.109	1.1×10^1	7.5×10^4	0.00016	0.00002	0.00002	0.016	0.000	0.112	0.113
	0.109	0.109	1.9×10^1	1.2×10^5	0.00015	0.00002	0.00002	0.016	0.000	0.112	0.113
	0.217	0.217	2.2×10^1	7.8×10^4	0.00028	0.00006	0.00006	0.016	0.000	0.112	0.113
	0.435	0.435	3.3×10^1	8.8×10^4	0.00038	0.00016	0.00017	0.016	0.001	0.111	0.113
	0.87	0.87	6.0×10^2	7.2×10^4	0.00077	0.00067	0.00078	0.016	0.002	0.110	0.113
	1.74	1.74	1.2×10^3	7.0×10^4	0.00175	0.00305	0.00385	0.014	0.009	0.105	0.113
	1.63[a]	1.63	1.4×10^3	8.5×10^4	0.00171	0.00279	0.00340	0.014	0.008	0.106	0.113
0.219	0.109	0.109	1.1×10^2	1.2×10^5	0.00092	0.00010	0.00054	0.028	0.000	0.191	0.319
0.366	0.109	0.109	6.6×10^2	1.2×10^5	0.00424	0.00046	0.00046	0.047	0.001	0.318	0.319
	0.109	0.108	3.7×10^1	8.8×10^4	0.00528	0.00058	0.00058	0.047	0.002	0.317	0.319
	0.217	0.215	6.0×10^2	8.1×10^4	0.00745	0.00161	0.00176	0.047	0.005	0.314	0.319
	0.435	0.430	1.2×10^3	9.5×10^4	0.0122	0.00522	0.00584	0.045	0.016	0.305	0.319
	0.87	0.85	1.4×10^3	7.2×10^4	0.0180	0.0156	0.0229	0.040	0.046	0.280	0.319
	1.74	1.69	2.1×10^3	7.0×10^4	0.0303	0.0528	0.2633	0.026	0.153	0.187	0.319
	1.63[a]	1.58	3.0×10^3	9.0×10^4	0.0336	0.0571	0.3020	0.025	0.162	0.179	0.319

[a] $HClO_4$ solution containing $HReO_4$ tracer.

Table XI. Extraction of $HAuCl_4$ into TBP from HCl solutions, iso-octane diluent.

Au	HCl	TBP	org	aq	D
1×10^{-6}	6.0	0	4.0×10^{0}	2.1×10^{5}	2.0×10^{-5}
		0.0037	1.5×10^{2}	2.1×10^{5}	8.6×10^{-4}
		0.0073	1.1×10^{3}	2.1×10^{5}	5.3×10^{-3}
		0.0146	1.6×10^{4}	3.4×10^{5}	4.6×10^{-2}
		0.0220	3.0×10^{4}	2.0×10^{5}	1.5×10^{-1}
		0.037	8.2×10^{4}	1.3×10^{5}	6.2×10^{-1}
		0.073	1.8×10^{5}	4.3×10^{4}	4.3×10^{0}
		0.128	6.7×10^{4}	3.5×10^{3}	1.9×10^{1}
		0.146	2.1×10^{5}	5.7×10^{3}	3.6×10^{1}
		0.220	2.1×10^{5}	2.0×10^{3}	1.0×10^{2}
		0.37	2.1×10^{5}	6.6×10^{2}	3.2×10^{2}
8×10^{-6}	2.0	0	5.0×10^{0}	1.4×10^{5}	4.0×10^{-5}
		0.0037	2.3×10^{1}	1.5×10^{5}	1.2×10^{-4}
		0.0128	3.7×10^{2}	2.8×10^{5}	1.3×10^{-3}
		0.0220	1.0×10^{3}	1.6×10^{5}	6.4×10^{-3}
		0.037	5.9×10^{3}	1.8×10^{5}	3.2×10^{-2}
		0.073	3.5×10^{4}	1.4×10^{5}	2.5×10^{-1}
		0.0073	9.8×10^{1}	1.5×10^{5}	6.2×10^{-4}
		0.128	7.9×10^{4}	9.8×10^{4}	8.1×10^{-1}
		0.220	1.2×10^{5}	4.8×10^{4}	2.5×10^{0}
		0.37	1.7×10^{5}	1.7×10^{4}	9.9×10^{0}
		0.73	1.6×10^{5}	1.6×10^{3}	9.8×10^{1}
		1.28	1.6×10^{5}	3.2×10^{2}	4.9×10^{2}
1×10^{-5}	2.0	0	5.1×10^{0}	8.4×10^{4}	6.1×10^{-5}
		0.0128	1.1×10^{2}	7.2×10^{4}	1.4×10^{-3}
		0.0220	5.1×10^{2}	8.1×10^{4}	6.3×10^{-3}
		0.037	2.4×10^{3}	7.3×10^{4}	3.3×10^{-2}
		0.073	1.7×10^{4}	6.0×10^{4}	2.9×10^{-1}
		0.128	4.5×10^{4}	2.9×10^{4}	1.6×10^{0}
		0.220	6.4×10^{4}	1.3×10^{4}	4.9×10^{0}
		0.37	6.5×10^{4}	2.9×10^{3}	2.3×10^{1}
	6.0	0	1.2×10^{1}	1.2×10^{5}	9.8×10^{-5}
		0.0073	7.8×10^{2}	9.4×10^{4}	8.2×10^{-3}
		0.0128	4.5×10^{3}	1.1×10^{5}	4.2×10^{-2}
		0.0220	1.3×10^{4}	6.7×10^{4}	2.0×10^{-1}
		0.037	9.4×10^{4}	1.9×10^{5}	4.9×10^{-1}
		0.073	1.0×10^{5}	1.5×10^{4}	7.0×10^{0}
		0.128	8.9×10^{4}	3.2×10^{3}	2.8×10^{1}
		0.220	1.1×10^{5}	7.0×10^{2}	1.6×10^{2}
		0.37	8.9×10^{4}	1.8×10^{4}	5.0×10^{2}
	10.	0	9.8×10^{0}	1.1×10^{5}	8.7×10^{-5}
		0.0073	4.1×10^{3}	1.5×10^{5}	2.7×10^{-2}
		0.0128	1.3×10^{4}	1.3×10^{5}	1.0×10^{-1}
		0.0220	3.9×10^{4}	7.4×10^{4}	5.2×10^{-1}
		0.037	1.0×10^{5}	5.3×10^{4}	2.0×10^{0}
		0.073	1.2×10^{5}	1.3×10^{4}	9.8×10^{0}
		0.128	1.3×10^{5}	4.4×10^{3}	3.0×10^{1}
		0.220	1.4×10^{5}	1.5×10^{3}	9.1×10^{1}

Table XII. Extraction of $HAuCl_4$ into TBP from HCl solutions, xylene diluent

Au	HCl	TBP	org	aq	D
2×10^{-7}	6.0	0	7.4×10^{-1}	3.1×10^{2}	2.4×10^{-3}
		0	1.2×10^{3}	3.1×10^{5}	4.0×10^{-3}
		0	8.4×10^{2}	2.7×10^{5}	3.0×10^{-3}
		0.0183	2.3×10^{1}	2.8×10^{2}	5.8×10^{-2}
		0.0183	1.5×10^{4}	2.6×10^{5}	5.4×10^{-2}
		0.0183	1.5×10^{4}	2.4×10^{5}	5.9×10^{-2}
		0.037	9.7×10^{1}	2.0×10^{2}	4.9×10^{-1}
		0.073	1.8×10^{5}	8.5×10^{4}	2.2×10^{0}
		0.110	9.9×10^{0}	1.1×10^{0}	8.7×10^{0}
		0.110	1.3×10^{2}	2.0×10^{1}	6.3×10^{0}
		0.110	2.4×10^{5}	4.2×10^{4}	5.8×10^{0}
		0.146	2.7×10^{5}	2.2×10^{4}	1.2×10^{1}
		0.183	1.9×10^{2}	7.5×10^{0}	2.6×10^{1}
		0.183	2.8×10^{5}	1.6×10^{4}	1.8×10^{1}
1×10^{-6}	6.0	0	9.0×10^{2}	2.6×10^{5}	3.4×10^{-3}
		0	8.8×10^{2}	2.3×10^{5}	3.4×10^{-3}
		0.0183	2.1×10^{4}	2.7×10^{5}	7.3×10^{-2}
		0.0183	1.7×10^{4}	2.2×10^{5}	7.2×10^{-2}
		0.037	6.8×10^{4}	2.3×10^{5}	7.3×10^{-2}
		0.073	1.8×10^{5}	5.6×10^{4}	3.3×10^{0}
		0.110	2.2×10^{5}	2.1×10^{4}	1.1×10^{1}
		0.146	2.2×10^{5}	8.3×10^{3}	2.6×10^{1}
		0.183	2.3×10^{5}	5.1×10^{3}	4.5×10^{1}
		0.183	2.3×10^{5}	5.1×10^{3}	4.6×10^{1}
1×10^{-5}	2.0	0	1.3×10^{1}	4.6×10^{2}	2.9×10^{-2}
		0	1.5×10^{1}	4.8×10^{2}	3.0×10^{-2}
		0	4.3×10^{0}	3.0×10^{2}	1.4×10^{-2}
		0	4.2×10^{0}	2.9×10^{2}	1.4×10^{-2}
		0.0183	8.5×10^{0}	4.7×10^{2}	6.0×10^{-3}
		0.0183	5.1×10^{0}	3.0×10^{2}	3.0×10^{-3}
		0.0183	7.5×10^{0}	4.7×10^{2}	2.0×10^{-3}
		0.0183	8.5×10^{0}	4.7×10^{2}	3.0×10^{-3}
		0.037	8.3×10^{0}	2.9×10^{2}	1.4×10^{-2}
		0.073	4.5×10^{1}	4.4×10^{2}	7.2×10^{-2}
		0.110	1.1×10^{2}	3.9×10^{2}	2.4×10^{-1}
		0.146	1.7×10^{2}	3.3×10^{2}	5.0×10^{-1}
		0.183	1.5×10^{2}	1.7×10^{2}	9.1×10^{-1}
		0.183	2.5×10^{2}	2.7×10^{2}	8.8×10^{-1}
1×10^{-5}	6.0	0	1.2×10^{0}	2.6×10^{2}	4.6×10^{-3}
		0	1.2×10^{0}	2.6×10^{2}	4.7×10^{-3}
		0	1.5×10^{0}	2.9×10^{2}	4.9×10^{-3}
		0	1.5×10^{0}	2.9×10^{2}	5.0×10^{-3}
		0	6.8×10^{-1}	1.4×10^{2}	5.0×10^{-3}
		0	6.6×10^{-1}	1.4×10^{2}	4.8×10^{-3}
		0.0183	8.0×10^{0}	2.7×10^{2}	2.5×10^{-2}
		0.0183	2.4×10^{0}	8.2×10^{1}	2.3×10^{-2}
		0.0183	4.0×10^{0}	1.3×10^{2}	2.5×10^{-2}
		0.037	2.8×10^{1}	2.5×10^{2}	1.1×10^{-1}
		0.037	1.4×10^{1}	1.2×10^{2}	1.1×10^{-1}
		0.073	1.3×10^{2}	1.7×10^{2}	7.4×10^{-1}
		0.073	6.2×10^{1}	8.3×10^{1}	7.4×10^{-1}
		0.110	2.1×10^{2}	8.4×10^{1}	2.5×10^{0}
		0.110	1.0×10^{2}	4.1×10^{1}	2.5×10^{0}
		0.146	2.5×10^{2}	4.9×10^{1}	5.1×10^{0}
		0.146	1.2×10^{2}	2.5×10^{1}	5.0×10^{0}
		0.183	2.5×10^{2}	3.3×10^{1}	7.8×10^{0}
		0.183	7.6×10^{1}	9.8×10^{0}	7.8×10^{0}
		0.183	1.3×10^{2}	1.6×10^{1}	7.9×10^{0}
	10.	0	6.0×10^{-1}	2.4×10^{2}	2.4×10^{-3}
		0.0183	3.9×10^{1}	2.5×10^{2}	1.6×10^{-1}
		0.037	1.1×10^{2}	1.6×10^{2}	6.7×10^{-1}
		0.037	1.1×10^{2}	1.7×10^{2}	6.6×10^{-1}
		0.073	2.1×10^{2}	7.4×10^{1}	2.9×10^{0}
		0.110	2.5×10^{2}	3.9×10^{1}	6.5×10^{0}
		0.146	2.8×10^{2}	1.6×10^{1}	1.8×10^{1}
		0.183	1.8×10^{2}	6.8×10^{0}	2.7×10^{1}
		0.183	1.8×10^{2}	6.7×10^{0}	2.6×10^{1}

Table XII. (Continued)

Au	HCl	TBP	org	aq	D
1×10^{-4}	2.0	0	1.3×10^{0}	2.9×10^{2}	4.4×10^{-3}
		0.0183	1.6×10^{0}	2.7×10^{2}	1.4×10^{-3}
		0.037	4.0×10^{0}	3.1×10^{2}	8.4×10^{-3}
		0.073	2.1×10^{1}	2.7×10^{2}	7.6×10^{-2}
		0.110	5.2×10^{1}	2.2×10^{2}	2.0×10^{-1}
		0.146	9.4×10^{1}	2.2×10^{2}	3.8×10^{-1}
		0.183	1.3×10^{2}	1.9×10^{2}	6.4×10^{-1}
	6.0	0	6.0×10^{-1}	3.0×10^{2}	2.0×10^{-3}
		0.0183	1.3×10^{1}	2.5×10^{2}	4.8×10^{-2}
		0.037	6.1×10^{1}	2.0×10^{2}	3.0×10^{-1}
		0.073	1.6×10^{2}	1.0×10^{2}	1.6×10^{0}
		0.110	2.2×10^{2}	5.2×10^{1}	4.1×10^{0}
		0.146	2.4×10^{2}	3.0×10^{1}	8.0×10^{0}
		0.183	2.5×10^{2}	1.8×10^{1}	1.4×10^{1}
	10.	0	4.8×10^{-1}	2.4×10^{2}	2.0×10^{-3}
		0.0183	5.2×10^{1}	2.0×10^{2}	2.6×10^{-1}
		0.037	1.4×10^{2}	1.1×10^{2}	1.3×10^{0}
		0.073	2.3×10^{2}	3.0×10^{1}	7.6×10^{0}
		0.110	2.4×10^{2}	1.3×10^{1}	2.1×10^{1}
		0.146	2.5×10^{2}	5.4×10^{0}	4.7×10^{1}
		0.183	2.6×10^{2}	3.2×10^{0}	7.9×10^{1}
1×10^{-3}	2.0	0	2.3×10^{-1}	2.3×10^{2}	1.0×10^{-3}
		0.0183	6.3×10^{-1}	2.0×10^{2}	2.2×10^{-3}
		0.037	2.4×10^{0}	2.0×10^{2}	1.2×10^{-2}
		0.073	1.8×10^{1}	1.8×10^{2}	9.6×10^{-2}
		0.110	5.4×10^{1}	1.6×10^{2}	3.3×10^{-1}
		0.146	9.4×10^{1}	1.2×10^{2}	7.9×10^{-1}
		0.183	1.3×10^{2}	8.4×10^{1}	1.6×10^{0}
1×10^{-3}	6.0	0	1.1×10^{-1}	2.0×10^{2}	5.5×10^{-4}
		0.0183	9.0×10^{0}	1.6×10^{2}	4.9×10^{-2}
		0.037	5.0×10^{1}	1.4×10^{2}	3.5×10^{-1}
		0.073	1.2×10^{2}	5.1×10^{1}	2.4×10^{0}
		0.110	1.7×10^{2}	2.4×10^{1}	7.1×10^{0}
		0.146	5.5×10^{1}	3.6×10^{0}	1.4×10^{1}
		0.183	2.0×10^{2}	8.3×10^{0}	2.4×10^{1}
	10.	0	9.0×10^{-2}	1.7×10^{2}	6.8×10^{-4}
		0.0183	3.2×10^{1}	1.3×10^{2}	2.3×10^{-1}
		0.037	9.1×10^{1}	7.3×10^{1}	1.3×10^{0}
		0.073	1.5×10^{2}	2.3×10^{1}	6.5×10^{0}
		0.110	1.4×10^{2}	7.2×10^{0}	1.9×10^{1}
		0.146	1.8×10^{2}	4.4×10^{0}	4.2×10^{1}
		0.183	1.8×10^{2}	2.9×10^{0}	6.2×10^{1}
1×10^{-2}	2.0	0	2.9×10^{-2}	2.3×10^{2}	1.2×10^{-4}
		0.0183	4.5×10^{-1}	1.9×10^{2}	2.1×10^{-3}
		0.037	3.0×10^{0}	2.2×10^{2}	1.4×10^{-2}
		0.073	1.9×10^{1}	2.0×10^{2}	9.4×10^{-2}
		0.110	4.7×10^{1}	1.5×10^{2}	3.1×10^{-1}
		0.146	7.3×10^{1}	1.0×10^{2}	7.4×10^{-1}
		0.183	1.4×10^{2}	9.1×10^{1}	1.5×10^{0}
	6.0	0	4.4×10^{-2}	2.0×10^{2}	2.2×10^{-4}
		0.037	4.3×10^{1}	1.6×10^{2}	2.7×10^{-1}
		0.073	8.0×10^{1}	5.0×10^{1}	1.6×10^{0}
		0.110	1.7×10^{2}	2.9×10^{1}	5.7×10^{0}
		0.146	1.9×10^{2}	1.4×10^{1}	1.4×10^{1}
		0.183	1.8×10^{2}	5.7×10^{0}	3.1×10^{1}
	10.	0	9.0×10^{-2}	1.7×10^{2}	5.2×10^{-4}
		0.037	8.3×10^{1}	1.2×10^{2}	7.1×10^{-1}
		0.073	1.6×10^{2}	3.9×10^{1}	4.1×10^{0}
		0.110	2.1×10^{2}	1.6×10^{1}	1.3×10^{1}
		0.146	2.2×10^{2}	6.8×10^{0}	3.2×10^{1}
		0.183	2.3×10^{2}	4.2×10^{0}	5.5×10^{1}

Table XIII. Extraction of $HAuCl_4$ into TBP from HCl solutions, CCl_4 diluent.

Au	HCl	TBP	org	aq	D
1×10^{-6}	6.0	0	1.1×10^{1}	7.7×10^{4}	1.5×10^{-4}
		0	1.0×10^{1}	1.2×10^{5}	8.0×10^{-5}
		0.037	3.1×10^{3}	7.9×10^{4}	4.6×10^{-2}
		0.037	5.2×10^{3}	9.6×10^{4}	5.4×10^{-2}
		0.055	1.4×10^{4}	1.1×10^{5}	1.3×10^{-1}
		0.092	2.3×10^{4}	5.9×10^{4}	3.8×10^{-1}
		0.128	4.3×10^{4}	2.7×10^{4}	1.6×10^{0}
		0.146	6.7×10^{4}	3.5×10^{4}	1.9×10^{0}
		0.220	6.7×10^{4}	1.0×10^{4}	6.7×10^{0}
		0.220	9.1×10^{4}	1.2×10^{4}	7.3×10^{0}
		0.37	7.7×10^{4}	2.8×10^{3}	2.7×10^{1}
		0.37	8.7×10^{4}	2.6×10^{3}	3.3×10^{1}
2×10^{-6}	2.0	0	2.0×10^{1}	5.8×10^{4}	3.4×10^{-4}
		0.037	1.7×10^{2}	5.9×10^{4}	2.5×10^{-3}
		0.037	1.4×10^{2}	6.1×10^{4}	2.0×10^{-3}
		0.055	2.2×10^{2}	5.7×10^{4}	5.5×10^{-3}
		0.055	3.3×10^{2}	5.8×10^{4}	3.7×10^{-3}
		0.092	9.9×10^{2}	5.6×10^{4}	1.7×10^{-2}
		0.146	3.2×10^{3}	4.9×10^{4}	6.4×10^{-2}
		0.220	8.8×10^{3}	4.6×10^{4}	1.9×10^{-1}
		0.37	6.8×10^{4}	3.5×10^{4}	1.9×10^{0}
		0.37	3.8×10^{4}	2.1×10^{4}	1.9×10^{0}
8×10^{-6}	10.	0	8.0×10^{0}	8.0×10^{4}	1.0×10^{-4}
		0.037	2.0×10^{4}	5.1×10^{4}	4.0×10^{-1}
		0.073	5.2×10^{4}	3.3×10^{4}	1.6×10^{0}
		0.128	7.2×10^{4}	9.1×10^{3}	7.9×10^{0}
		0.220	5.9×10^{4}	1.1×10^{3}	5.4×10^{1}
		0.37	6.9×10^{4}	4.6×10^{2}	1.5×10^{2}
1×10^{-5}	2.0	0	2.6×10^{1}	1.2×10^{5}	2.3×10^{-4}
		0.037	2.0×10^{2}	7.4×10^{4}	2.5×10^{-3}
		0.073	1.1×10^{3}	8.6×10^{4}	1.3×10^{-2}
		0.128	4.8×10^{3}	7.3×10^{4}	6.5×10^{-2}
		0.220	2.2×10^{4}	5.5×10^{4}	3.9×10^{-1}
		0.37	5.3×10^{4}	2.6×10^{4}	2.0×10^{0}
	6.0	0	2.6×10^{1}	1.2×10^{5}	2.3×10^{-4}
		0.0220	1.3×10^{3}	8.7×10^{4}	1.5×10^{-2}
		0.037	5.1×10^{3}	9.5×10^{4}	5.3×10^{-2}
		0.073	2.7×10^{4}	7.2×10^{4}	3.8×10^{-1}
		0.128	6.6×10^{4}	3.3×10^{4}	2.0×10^{0}
		0.220	8.9×10^{4}	9.4×10^{3}	9.5×10^{0}
		0.37	9.2×10^{4}	4.0×10^{3}	2.3×10^{1}
	10.	0	1.6×10^{2}	1.2×10^{5}	1.3×10^{-3}
		0.0073	1.9×10^{3}	1.6×10^{5}	1.1×10^{-2}
		0.0128	5.0×10^{3}	1.6×10^{5}	1.1×10^{-2}
		0.0220	2.0×10^{4}	1.3×10^{5}	1.5×10^{-1}
		0.037	4.6×10^{4}	9.7×10^{4}	4.7×10^{-1}
		0.073	8.6×10^{4}	3.0×10^{4}	2.8×10^{0}
		0.128	1.1×10^{5}	8.2×10^{3}	4.6×10^{1}
		0.220	1.2×10^{5}	2.5×10^{3}	4.6×10^{1}
		0.37	1.4×10^{5}	6.8×10^{3}	2.0×10^{2}

Table XTV. Extraction of $HAuBr_4$ into TBP from HBr solutions, xylene diluent.

Au	HBr	TBP	org	aq	D
1×10^{-6}	2.0	0	6.0×10^{-1}	8.5×10^{1}	7.1×10^{-3}
		0	9.1×10^{-1}	1.4×10^{2}	6.5×10^{-3}
		0.0183	1.3×10^{0}	1.4×10^{2}	2.0×10^{-3}
		0.037	2.5×10^{0}	1.4×10^{2}	6.0×10^{-3}
		0.073	5.0×10^{0}	1.1×10^{2}	3.9×10^{-2}
		0.110	1.7×10^{1}	1.4×10^{2}	1.2×10^{-1}
		0.146	3.3×10^{1}	1.3×10^{2}	5.3×10^{-1}
		0.183	6.7×10^{1}	1.3×10^{2}	5.3×10^{-1}
		0.183	5.3×10^{1}	1.1×10^{2}	4.9×10^{-1}
1×10^{-5}	1.1	0	9.5×10^{2}	4.4×10^{5}	2.2×10^{-3}
		0	6.8×10^{2}	2.5×10^{5}	2.6×10^{-3}
		0.0183	1.9×10^{3}	2.4×10^{5}	5.0×10^{-3}
		0.0183	2.0×10^{3}	2.8×10^{5}	5.2×10^{-3}
		0.037	9.8×10^{3}	4.5×10^{5}	1.9×10^{-2}
		0.110	8.2×10^{4}	1.4×10^{5}	5.8×10^{-1}
		0.110	8.2×10^{4}	1.5×10^{5}	5.3×10^{-1}
		0.146	1.4×10^{5}	1.0×10^{5}	1.4×10^{0}
		0.183	1.5×10^{5}	5.9×10^{4}	2.6×10^{0}
		0.183	1.7×10^{5}	6.2×10^{4}	2.7×10^{0}
1×10^{-5}	4.1	0	6.5×10^{2}	2.5×10^{5}	3.1×10^{-3}
		0	7.0×10^{2}	2.7×10^{5}	2.6×10^{-3}
		0.0183	3.7×10^{4}	2.1×10^{5}	1.7×10^{-1}
		0.0183	4.4×10^{4}	2.5×10^{5}	1.7×10^{-1}
		0.037	1.3×10^{5}	1.4×10^{5}	9.5×10^{-1}
		0.073	2.1×10^{5}	2.4×10^{4}	8.6×10^{0}
		0.110	2.2×10^{5}	6.8×10^{3}	3.2×10^{1}
		0.146	2.5×10^{5}	3.0×10^{3}	8.3×10^{1}
		0.183	2.5×10^{5}	1.5×10^{3}	1.7×10^{2}
		0.183	2.6×10^{5}	1.5×10^{3}	1.6×10^{2}
	6.3	0	2.4×10^{-1}	1.6×10^{2}	1.5×10^{-3}
		0	2.9×10^{-1}	1.9×10^{2}	1.7×10^{-3}
		0.0183	9.6×10^{1}	1.1×10^{2}	8.7×10^{-1}
		0.0183	1.0×10^{2}	1.1×10^{2}	8.6×10^{-1}
		0.0183	7.6×10^{1}	7.1×10^{1}	1.1×10^{0}
		0.037	1.5×10^{2}	3.1×10^{1}	4.0×10^{0}
		0.073	[illegible].0 × 10^{2}	6.5×10^{0}	3.1×10^{1}
		0.073	1.0×10^{2}	2.5×10^{0}	4.0×10^{1}
		0.110	2.0×10^{2}	3.1×10^{0}	6.5×10^{1}
		0.146	1.9×10^{2}	1.7×10^{0}	1.1×10^{2}
		0.183	1.5×10^{2}	1.1×10^{0}	1.4×10^{2}
		0.183	2.1×10^{2}	2.1×10^{0}	1.0×10^{2}
		0.183	2.0×10^{2}	1.8×10^{0}	1.1×10^{2}

Table XV. Extraction of $HAuCl_4$ into TBP from 6 M LiCl-0.1 M HCl solutions, Au = 1×10^{-5} M

iso-octane diluent				CCl_4 diluent			
TBP	org	aq	D	TBP	org	aq	D
0	5.0×10^{-1}	9.0×10^{4}	5.5×10^{-6}	0	8.3×10^{1}	9.7×10^{4}	8.5×10^{-4}
0.0013	5.0×10^{-1}	7.1×10^{4}	1.5×10^{-6}	0.0220	1.1×10^{3}	9.3×10^{4}	1.1×10^{-2}
0.0022	1.3×10^{0}	6.9×10^{4}	1.2×10^{-5}	0.0220	1.0×10^{3}	1.1×10^{4}	8.5×10^{-3}
0.0037	2.7×10^{0}	6.1×10^{4}	3.9×10^{-5}	0.037	3.3×10^{3}	1.1×10^{5}	2.9×10^{-2}
0.0073	1.7×10^{1}	5.8×10^{4}	2.9×10^{-4}	0.037	2.6×10^{3}	9.9×10^{4}	2.6×10^{-2}
0.0128	1.3×10^{2}	7.1×10^{4}	1.8×10^{-3}	0.073	1.8×10^{4}	9.9×10^{4}	1.8×10^{-1}
0.0220	6.7×10^{2}	7.7×10^{4}	8.7×10^{-3}	0.073	1.8×10^{4}	9.9×10^{4}	1.8×10^{-1}
0.037	4.4×10^{3}	6.8×10^{4}	6.5×10^{-2}	0.128	3.9×10^{4}	6.3×10^{4}	6.4×10^{-1}
0.073	2.9×10^{4}	3.9×10^{4}	7.4×10^{-1}	0.128	3.8×10^{4}	5.8×10^{4}	6.6×10^{-1}
0.128	5.6×10^{4}	1.2×10^{4}	5.0×10^{0}	0.220	7.8×10^{4}	2.9×10^{4}	2.7×10^{0}
0.220	6.1×10^{4}	1.8×10^{3}	3.5×10^{1}	0.220	7.2×10^{4}	3.4×10^{4}	2.2×10^{0}
0.37	7.2×10^{4}	3.5×10^{2}	2.0×10^{2}	0.37	8.8×10^{4}	1.2×10^{4}	7.6×10^{0}
				0.37	9.2×10^{4}	7.5×10^{3}	1.3×10^{1}

Table XVI. Extraction of $HReO_4$ into TBP and TOPO from HCl solutions, $HReO_4$ = 1 X 10^{-6} M, iso-octane duluent

HCl	TBP	org	aq	D	HCl	TOPO	org	aq	D
2.0	0	2.0×10^{-1}	8.4×10^{4}	2.2×10^{-6}	0.20	0	-9.0×10^{-1}	1.6×10^{5}	-6.0×10^{-6}
	0.0220	3.1×10^{0}	9.3×10^{4}	3.1×10^{-5}		0.0010	2.8×10^{1}	1.6×10^{5}	1.8×10^{-4}
	0.037	6.4×10^{0}	8.2×10^{4}	7.6×10^{-5}		0.0020	1.4×10^{2}	1.8×10^{5}	8.0×10^{-4}
	0.073	4.4×10^{1}	8.2×10^{4}	5.4×10^{-4}		0.0035	1.0×10^{3}	1.8×10^{5}	5.5×10^{-3}
	0.073	9.7×10^{1}	1.6×10^{5}	6.1×10^{-4}		0.0060	1.2×10^{3}	1.3×10^{5}	8.9×10^{-3}
	0.128	2.5×10^{2}	8.0×10^{4}	3.1×10^{-3}		0.0060	4.7×10^{3}	1.2×10^{5}	3.8×10^{-2}
	0.128	8.1×10^{2}	1.8×10^{5}	4.6×10^{-3}		0.0100	3.9×10^{4}	1.2×10^{5}	3.2×10^{-1}
	0.220	1.7×10^{3}	8.1×10^{4}	2.1×10^{-2}		0.0200	1.0×10^{5}	8.0×10^{4}	1.3×10^{0}
	0.37	9.8×10^{3}	7.9×10^{4}	1.2×10^{-1}		0.035	1.6×10^{5}	2.7×10^{4}	6.2×10^{0}
						0.060	1.7×10^{5}	7.6×10^{3}	2.2×10^{1}
6.0	0	-5.0×10^{-1}	6.7×10^{4}	-7.0×10^{-6}					
	0.0220	3.1×10^{1}	6.5×10^{4}	4.8×10^{-4}					
	0.037	1.0×10^{2}	6.6×10^{4}	1.6×10^{-3}					
	0.073	7.0×10^{2}	6.5×10^{4}	1.1×10^{-2}					
	0.128	3.7×10^{3}	6.0×10^{4}	6.1×10^{-2}					
	0.220	1.2×10^{4}	3.9×10^{4}	3.1×10^{-1}					
	0.37	2.3×10^{4}	1.5×10^{4}	1.5×10^{0}					
	0.73	1.1×10^{5}	1.1×10^{4}	1.1×10^{1}					

Table XVII. Extraction of $HAuCl_4$ into TOPO from HCl solutions, CCl_4 diluent.

Au	HCl	TOPO	org	aq	D
1×10^{-6}	0.20	0	2.4×10^{1}	7.4×10^{4}	3.2×10^{-4}
		0	3.8×10^{1}	1.4×10^{5}	2.7×10^{-4}
		0.020	8.6×10^{4}	1.8×10^{4}	4.7×10^{0}
		0.020	7.4×10^{4}	2.0×10^{4}	3.7×10^{0}
		0.035	9.5×10^{4}	3.8×10^{3}	2.5×10^{1}
		0.060	7.0×10^{4}	1.0×10^{3}	7.0×10^{1}
		0.060	1.0×10^{5}	9.4×10^{2}	1.1×10^{2}
		0.100	1.0×10^{5}	3.7×10^{2}	2.8×10^{2}
		0.100	1.1×10^{5}	4.3×10^{2}	2.5×10^{2}
2×10^{-6}	0.05	0	6.8×10^{1}	3.7×10^{4}	1.8×10^{-3}
		0.0050	1.1×10^{4}	6.3×10^{4}	1.7×10^{-1}
		0.0050	8.0×10^{3}	6.2×10^{4}	1.3×10^{-1}
		0.0100	2.4×10^{4}	4.0×10^{4}	6.1×10^{-1}
		0.020	4.9×10^{4}	1.9×10^{4}	2.5×10^{0}
		0.050	6.8×10^{4}	3.3×10^{3}	2.1×10^{1}
		0.100	7.2×10^{4}	3.8×10^{2}	1.9×10^{2}
		0.200	7.0×10^{4}	3.0×10^{1}	2.3×10^{3}
		0.400	7.5×10^{4}	1.3×10^{1}	5.8×10^{3}
	0.20	0	7.0×10^{1}	9.5×10^{4}	7.1×10^{-4}
		0.0100	6.2×10^{4}	3.9×10^{4}	1.6×10^{0}
		0.020	8.8×10^{4}	1.1×10^{4}	7.9×10^{0}
		0.050	1.0×10^{5}	1.0×10^{3}	1.0×10^{2}
		0.100	8.1×10^{4}	1.1×10^{2}	7.8×10^{2}
		0.100	7.7×10^{4}	1.0×10^{2}	7.7×10^{2}
1×10^{-5}	0.05	0	4.5×10^{0}	4.6×10^{4}	1.0×10^{-4}
		0.020	1.2×10^{4}	2.7×10^{4}	4.5×10^{-1}
		0.035	2.8×10^{4}	1.6×10^{4}	1.7×10^{0}
		0.060	2.5×10^{4}	2.7×10^{3}	9.3×10^{0}
		0.100	4.1×10^{4}	1.5×10^{3}	2.7×10^{1}
		0.200	4.1×10^{4}	1.9×10^{2}	2.1×10^{2}
		0.400	4.3×10^{4}	1.8×10^{1}	2.4×10^{3}
	0.20	0	1.9×10^{1}	5.0×10^{4}	3.8×10^{-4}
		0	7.1×10^{1}	1.2×10^{5}	6.1×10^{-4}
		0.0100	3.2×10^{4}	1.0×10^{4}	3.2×10^{-1}
		0.020	7.2×10^{4}	3.2×10^{4}	2.3×10^{0}
		0.020	7.9×10^{4}	3.6×10^{4}	2.2×10^{0}
		0.020	1.4×10^{4}	7.1×10^{3}	2.0×10^{0}
		0.020	6.5×10^{4}	4.3×10^{4}	1.5×10^{0}
		0.035	1.2×10^{5}	2.5×10^{4}	4.8×10^{0}
		0.035	3.6×10^{4}	6.6×10^{3}	5.4×10^{0}
		0.050	1.3×10^{5}	9.6×10^{3}	1.4×10^{1}
		0.060	4.6×10^{4}	2.0×10^{3}	2.3×10^{1}
		0.100	1.1×10^{5}	1.2×10^{3}	8.8×10^{1}
		0.100	1.1×10^{5}	1.2×10^{3}	9.0×10^{1}
		0.100	4.9×10^{4}	5.7×10^{2}	8.6×10^{1}
		0.200	5.3×10^{4}	7.8×10^{1}	6.8×10^{2}
		0.400	4.8×10^{4}	1.4×10^{1}	3.4×10^{3}

Table XVIII. Distribution of fatty - acid anions between Dowex -1 and aqueous solutions.

Anion	M	[Cl]	[$\bar{A}$]	[A]	[$\overline{Cl}$]	Q	D	X_{Cl}
Acetate	1.095	0.129	1.225	0.966	1.467	0.112	1.27	0.545
	0.547	0.0993	0.995	0.448	1.737	0.122	2.13	0.645
	0.219	0.0645	0.613	0.155	2.079	0.123	3.98	0.772
	0.1095	0.0443	0.421	0.0652	2.271	0.126	6.46	0.844
	0.0547	0.0293	0.278	0.0254	2.414	0.133	10.9	0.897
	0.0219	0.0150	0.143	0.0069	2.549	0.122	21	0.947
Formate	1.054	0.1455	1.382	0.909	1.310	0.170	1.53	0.487
	0.527	0.1135	1.078	0.413	1.614	0.184	2.62	0.600
	0.211	0.0720	0.684	0.139	2.008	0.175	4.96	0.746
	0.105	0.0510	0.487	0.054	2.207	0.208	9.0	0.820
	0.0527	0.0326	0.309	0.0201	2.382	0.210	15.4	0.885
	0.0211	0.0162	0.153	0.0049	2.538	0.20	31	0.943
Butyrate	1.074	0.161	1.530	0.913	1.162	0.232	1.68	0.432
	0.537	0.123	1.169	0.414	1.523	0.228	2.82	0.566
	0.215	0.0798	0.758	0.135	1.934	0.231	5.61	0.718
	0.1074	0.0543	0.516	0.0531	2.176	0.243	9.72	0.808
	0.0537	0.0345	0.328	0.0192	2.364	0.249	17.1	0.878
	0.0215	0.0173	0.164	0.0042	2.528	0.27	39	0.937
Trimethylacetate	1.116	0.180	1.710	0.936	0.982	0.335	1.83	0.365
	0.558	0.142	1.349	0.416	1.343	0.341	3.24	0.499
	0.223	0.0915	0.869	0.132	1.823	0.332	6.61	0.677
	0.1116	0.0623	0.592	0.0493	2.100	0.356	12.0	0.780
	0.0558	0.0390	0.371	0.0168	2.321	0.371	22.1	0.862
	0.0223	0.0185	0.176	0.0038	2.516	0.34	46	0.935
Trimethylacetate	1.116	0.1742	1.655	0.946	1.037	0.293	1.75	0.385
(repeat run)	0.558	0.1355	1.287	0.422	1.405	0.295	3.06	0.522
	0.223	0.0902	0.857	0.133	0.1835	0.318	6.47	0.682
	0.1116	0.0612	0.575	0.0504	2.111	0.327	11.3	0.784
	0.0558	0.0388	0.368	0.0170	2.323	0.362	21.7	0.863
	0.0223	0.0185	0.176	0.0038	2.516	0.34	46	0.935

Table XVIII (Continued)

Anion	M	[Cl]	$[\bar{A}]$	[A]	$[\overline{Cl}]$	Q	D	X_{Cl}
Valerate	1.158	0.193	1.834	0.965	0.858	0.427	1.90	0.319
	0.579	0.155	1.473	0.424	1.219	0.442	3.47	0.453
	0.232	0.1005	0.955	0.132	1.737	0.420	7.26	0.645
	0.1158	0.0685	0.651	0.0473	2.041	0.462	13.8	0.758
	0.0579	0.0433	0.411	0.0146	2.281	0.534	28.2	0.847
	0.0232	0.0198	0.188	0.0034	2.504	0.44	55	0.930
Caproate	1.063	0.207	1.966	0.856	0.726	0.654	2.30	0.270
	0.532	0.175	1.662	0.357	1.030	0.792	4.66	0.383
	0.213	0.117	1.111	0.096	1.581	0.86	11.6	0.587
	0.1063	0.0777	0.738	0.286	1.954	1.03	25.8	0.726
	0.0532	0.0450	0.427	0.0082	2.265	1.03	52	0.841
	0.0213	0.0193	0.183	0.0020	2.509	0.70	92	0.932
Methyldichloroacetate	1.068	0.212	2.014	0.854	0.678	0.74	2.36	0.252
	0.533	0.203	1.928	0.330	0.764	1.55	5.84	0.284
	0.213	0.144	1.370	0.069	1.322	2.17	19.9	0.491
	0.1068	0.0877	0.833	0.0189	1.859	2.08	44	0.691
	0.0533	0.0478	0.454	0.0055	2.238	1.76	83	0.831
	0.0213	0.0197	0.187	0.0016	2.505	0.9	120	0.931
Trichloroacetate	1.071	0.277	2.631	0.794	0.061	15.1	3.3	0.023
	0.536	0.266	2.527	0.270	0.165	15.1	9.4	0.061
	0.214	0.179	1.700	0.035	0.992	8.8	49	0.369
	0.1071	0.0947	0.900	0.0124	1.792	3.8	73	0.666
	0.0536	0.0485	0.461	0.0051	2.231	2.0	90	0.829
	0.0214	0.0201	0.191	0.0013	2.501	1.2	150	0.929

Table XIX. Preparation of radiochemical tracers.

Tracer	$T_{\frac{1}{2}}$[a]		Chemical form	Source	Processing
H^3 (T)	12.26	y	T_xH_yO	LRL B-O	dissolved in distilled H_2O
Be^7	53	d	$BeCl_2$ in HCl	NSEC	none
Na^{22}	2.6	y	NaCl in H_2O[c]	NSEC	none
Na^{24}	15.0	h	$NaHCO_3$	LPTR	dissolved in distilled H_2O
Sc^{46}	85	d	$ScCl_3$ in HCl	ORNL	evaporated to dryness and dissolved in $HClO_4$
Cr^{51}	27	d	$CrCl_3$ in HCl	ORNL	evaporated to dryness with $HClO_4$ and dissolved in $HClO_4$, allowed to stand for two weeks before use to permit Cl-H_2O exchange
			$Cr(ClO_4)_3$	GETR	dissolved in $HClO_4$, treated with H_2O_2 to reduce $Cr_2O_7^=$, and boiled to remove excess H_2O_2
			CrO_3	GETR	same as above
Fe^{59}	45	d	Fe filings	GETR	dissolved in $HClO_4$, evaporated to dryness, and redissolved in $HClO_4$
			$Fe_2(SO_4)_3$	GETR	dissolved in $HClO_4$, treated with $K_2S_2O_8$ to oxidize Fe(II), and boiled to decompose excess $K_2S_2O_8$
Rb^{86}	19.6	d	$RbNO_3$	LPTR GETR	dissolved in distilled H_2O
I^{131}	8.05	d	NaI in H_2O[c]	ORNL	none
Cs^{137}	30	y	CsCl in H_2O[c] Cs_2SO_4 in H_2O[c]	LRL HC	none

[a] Ref. 62.

[b] LRL B-O - Lawrence Radiation Laboratory, Bio-Organic Group
NSEC - Nuclear Science and Engineering Corporation, Pittsburgh, Pa.
LPTR - Material irradiated at Livermore Pool-Type Reactor, Lawrence Radiation Laboratory, Livermore, Calif.
ORNL - Oak Ridge National Laboratory, Oak Ridge, Tenn.
GETR - Material irradiated at General Electric Test Reactor (Vallecitos), Pleasanton, Calif.
LRL HC - Lawrence Radiation Laboratory Health Chemistry Source Preparation Department.

[c] Carrier-free isotope

Table XX. Description of Ion-exchange columns.

Column	Resin	Length	Diam.	Volume	Weight	Wt_{H_2O}	Vol_{I^-}	Vol_{T_2O}	Cap	N
1	Dowex-50W	28.5	3.0	2.0	1.10	1.38	0.55	1.39	2.3	2.4
1a	Dowex-50W	31.0	3.5	3.0	1.64	----	0.82	----	2.3	1.9
2	Dowex-50W	34.1	4.2	4.7	2.64	----	1.31	----	2.3	1.0
3	Dowex-50W	91.0	3.3	7.8	4.8	----	2.2	----	2.3	0.55
4	Dowex-50W	111.8	3.3	9.5	5.5	----	2.7	----	2.3	0.48
5	Dowex-50W	117.8	3.3	10.1	5.9	----	2.9	----	2.3	0.45
6	Bio-Rex	34.1	4.0	4.28	1.07	3.63	1.65	3.49	4.6	1.0

Table XXI. Limiting equivalent conductivities of anions and dissociation constants of parent acids.

Anion	λ^{o}[a]	K_a of parent acid[a]
F^-	55.4	6.7×10^{-4}[c]
Cl^-	76.4	strong
Br^-	78.1	strong
I^-	76.8	strong
ClO_4^-	67.4	strong
HCO_2^-	54.6	1.77×10^{-4}
$CH_3CO_2^-$	40.9	1.76×10^{-5}
$CH_3CH_2CO_2^-$	35.8	1.34×10^{-5}
$CH_3(CH_2)_2CO_2^-$	32.6	1.51×10^{-5}
$CH_3(CH_2)_3CO_2^-$	----	1.38×10^{-5}
$CClH_2CO_2^-$	39^{145}[b]	1.38×10^{-3}
$CCl_2HCO_2^-$	38.5^{145}[b]	
$CCl_3CO_2^-$	37^{145}[b]	strong
ClO_3^-	64.6	strong
BrO_3^-	55.7	
IO_3^-	39.4[b]	1.67×10^{-1}[d]
NO_2^-	62.[b]	4.5×10^{146}[d]
NO_3^-	71.5	strong
ClO^-		3.2×10^{-8}
BrO^-		2.1×10^{-9}
IO^-		10^{-11}

[a] Ref. 144

[b] Ref. 145

[c] Ref. 146

[d] Ref. 147

Table XXII. Resin: Dowex-50W. Eluting solution: $LiClO_4$. Column 1.

Tracer	M	m	vol	vol_{cor}	vol_{H_2O}	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Na	0.108	0.109	71.9	70.5	69.8	169	168	64	64
	0.222	0.227	34.0	32.8	32.1	79	77	29.9	29.2
	0.400	0.407	19.3	18.2	17.9	44	43	16.7	16.3
	0.443	0.450	17.0	15.9	15.6	38	37	14.4	14.0
	0.443	0.450	16.5	15.4	15.2	37	36	14.0	13.6
	0.886	0.920	7.6	6.6	6.4	15.8	15.4	6.0	5.8
	0.886	0.920	8.1	7.1	6.8	17.0	16.3	6.4	6.2
	1.77	1.92	3.7	3.9	3.6	9.4	8.6	3.6	3.3
	1.77	1.92	3.7	3.8	3.5	9.1	8.4	3.4	3.2
	3.54	4.20	2.3	1.5	1.3	3.6	3.1	1.4	1.2
	3.54	4.20	2.1	1.4	1.2	3.4	2.9	1.3	1.1
Rb	0.108	0.109	275	274	271	660	650	250	246
	0.222	0.227	137	136	133	330	320	125	121
	0.400	0.407	69.0	67.9	66.7	163	160	62	61
Cs	0.108	0.109	420	419	415	1010	1000	380	380
	0.400	0.407	87.6	86.5	85.0	208	204	79	77
	0.443	0.450	76.0	74.9	73.7	180	177	68	67
	0.443	0.450	68.0	66.9	65.8	161	158	61	60
	0.886	0.920	21.4	20.4	19.6	49	47	18.6	17.8
	0.886	0.920	22.4	21.4	20.6	51	49	19.3	18.6
	1.77	1.92	5.2	5.3	4.9	12.7	11.8	4.8	4.5
	1.77	1.92	5.2	5.4	5.0	13.0	12.0	4.9	4.5
	3.54	4.20	1.6	0.8	0.7	1.9	1.7	0.7	0.6
	3.54	4.20	1.5	0.8	0.7	1.9	1.7	0.7	0.6

Table XXIII. Resin: Dowex-50W. Eluting solution: $HClO_4$. Column 1

Tracer	M	m	vol	vol_{cor}	vol_{H_2O}	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Na	0.100	0.100	63.4	62.0	62.0	149	149	56	56
	0.400	0.407	16.9	15.8	15.5	38	37	14.4	14.0
	0.400	0.407	17.8	16.7	16.4	40	39	15.2	14.8
	0.420	0.427	17.6	16.5	16.2	40	39	15.2	14.8
	0.630	0.647	11.6	10.6	10.3	25.4	24.7	9.6	9.4
	0.630	0.647	12.0	11.0	10.7	26.4	25.7	10.0	9.7
	1.05	1.10	6.9	6.0	5.7	14.4	13.7	5.5	5.2
	1.05	1.10	6.7	5.8	5.5	13.9	13.2	5.3	5.0
	2.10	2.31	3.4	2.6	2.4	6.2	5.8	2.3	2.2
	2.10	2.31	3.4	2.6	2.4	6.2	5.8	2.3	2.2
Rb	0.100	0.100	224	223	223	540	540	205	205
	0.400	0.407	52.4	51.3	50.4	123	121	47	46
	0.400	0.407	53.3	52.2	51.3	125	123	47	47
	0.420	0.427	52.0	50.9	50.1	122	120	46	45
	0.630	0.647	29.6	28.6	27.8	69	67	26.2	25.4
	0.630	0.647	29.6	28.6	27.8	69	67	26.2	25.4
	1.05	1.10	12.3	11.3	10.8	27.1	25.9	10.3	9.8
	1.05	1.10	12.2	11.3	10.8	27.1	25.9	10.3	9.8
Cs	0.100	0.100	420	419	419	980	980	370	370
	0.400	0.400	64.9	63.8	62.7	153	150	58	57
	0.400	0.407	67.6	66.5	65.4	160	157	61	60
	0.420	0.427	66.5	65.4	64.3	157	154	60	58
	0.630	0.647	35.5	34.5	33.6	83	81	31	31
	1.05	1.10	13.3	12.4	11.8	29.9	28.3	11.3	10.7
	2.10	2.31	3.0	2.2	2.0	5.3	4.8	2.0	1.8

Table XXIII. (Continued) Column 5.

Tracer	M	m	vol	vol_{cor}	vol_{H_2O}	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Na	2.10	2.31	18.1	13.9	12.6	6.3	5.7	2.4	2.2
	2.10	2.31	18.2	14.0	12.7	6.3	5.7	2.4	2.2
	4.20	5.08	8.8	5.1	4.2	2.3	1.9	0.9	0.7
	4.20	5.08	8.8	5.1	4.2	2.3	1.9	0.9	0.7
	6.30	8.56	7.1	3.7	2.7	1.7	1.2	0.6	0.5
	6.30	8.56	7.2	3.7	2.7	1.7	1.2	0.6	0.5
	8.40	12.9	5.4	2.1	1.4	0.9	0.6	0.3	0.2
	8.40	12.9	5.2	1.9	1.2	0.9	0.5	0.3	0.2
	10.5	18.8	4.7	1.5	0.8	0.7	0.4	0.3	0.2
Cs	2.10	2.31	16.8	12.6	11.4	5.7	5.1	2.2	1.9
	2.10	2.31	17.1	12.9	11.7	5.8	5.3	2.2	2.0
	4.20	5.08	5.3	1.6	1.3	0.7	0.6	0.3	0.2
	4.20	5.08	5.3	1.6	1.3	0.7	0.7	0.3	0.2
	6.30	8.56	4.6	1.1	0.8	0.5	0.4	0.2	0.2
	6.30	8.56	4.6	1.2	0.9	0.5	0.4	0.2	0.2
	8.40	12.9	3.5	0.2	0.1	0.1	0.1	0.0	0.0
	8.40	12.9	3.4	0.1	0.1	0.1	0.1	0.0	0.0
	10.5	18.8	3.3	0.1	0.1	0.1	0.1	0.0	0.0

Table XXIV. Resin: Dowex-50W. Eluting solution: $LiNO_3$. Column 1.

Tracer	M	m	vol	vol_{cor}	vol_{H_2O}	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Na	0.100	0.100	71.4	70.0	70.0	168	168	64	64
	0.400	0.406	17.6	16.5	16.2	40	39	15.2	14.8
	0.830	0.852	7.8	6.8	6.6	16.3	15.8	6.2	6.0
	0.830	0.852	7.7	6.7	6.5	16.1	15.6	6.1	5.9
	1.63	1.75	4.41	3.5	3.3	8.4	7.9	3.2	3.0
	1.63	1.75	4.32	3.5	3.3	8.4	7.9	3.2	3.0
Rb	0.100	0.100	308	307	307	740	740	280	280
Cs	0.100	0.100	502	501	501	1200	1200	450	450
	0.400	0.406	102	101	100	242	239	92	91
	0.830	0.852	34.9	33.9	33.0	81	79	31	30
	0.830	0.852	35.6	34.1	33.7	83	81	31	31
	1.63	1.75	14.4	13.5	12.6	32	30	12.1	11.4
	1.63	1.75	14.2	13.3	12.4	32	30	12.1	11.4
				Column 5					
Na	1.63	1.75	26.4	22.1	20.6	9.9	9.3	3.8	3.5
	1.63	1.75	25.6	21.3	19.8	9.6	8.9	3.6	3.4
	3.25	3.63	11.0	7.1	6.4	3.2	2.9	1.2	1.1
	3.25	3.63	11.0	7.1	6.4	3.2	2.9	1.2	1.1
	6.12	7.56	6.37	2.9	2.3	1.3	1.0	0.5	0.4
	6.12	7.56	6.61	3.1	2.5	1.4	1.1	0.5	0.4
	8.18	11.1	6.03	2.7	2.0	1.2	0.9	0.5	0.3
	8.16	11.1	5.71	2.4	1.8	1.1	0.8	0.4	0.3
Cs	1.63	1.75	90.2	85.9	80.0	39	36	14.8	14.6
	1.63	1.75	92.9	88.6	82.5	40	37	15.2	14.0
	3.25	3.63	21.8	17.9	16.0	8.1	7.2	3.1	2.8
	3.25	3.63	22.0	18.1	16.2	8.1	7.3	3.1	2.8
	6.12	7.56	7.26	3.8	3.1	1.7	1.4	0.6	0.5
	6.12	7.56	7.58	4.1	3.3	1.8	1.5	0.7	0.6
	8.16	11.1	6.35	3.1	2.3	1.4	1.0	0.5	0.4
	8.16	11.1	6.19	2.9	2.1	1.3	0.9	0.5	0.3

Table XXV. Resin: Dowex-50W. Eluting solution: HNO_3. Column 1.

Tracer	M	m	vol	vol_{cor}	vol_{H_2O}	$\overline{\text{vol}}_{cor}$	$\overline{\text{vol}}_{H_2O}$	D(M)	D(m)
Na	0.100	0.100	61.2	59.8	59.8	144	144	55	55
	0.400	0.405	18.1	17.0	16.8	41	40	15.5	15.2
	0.400	0.405	17.6	16.5	16.3	40	39	15.2	14.8
	0.495	0.503	13.7	12.6	12.4	30	30	11.4	11.1
	0.496	0.504	16.8	15.7	15.4	38	37	14.4	14.0
	0.496	0.504	16.8	15.7	15.4	38	37	14.4	14.0
	0.992	1.03	7.9	7.0	6.7	16.8	16.1	6.4	6.1
	0.992	1.03	8.7	7.7	7.4	18.5	17.8	7.0	6.7
	1.00	1.04	6.68	5.7	5.5	13.7	13.2	5.2	5.0
	1.00	1.04	6.52	5.6	5.4	13.4	13.0	5.1	4.9
	1.92	2.07	2.80	2.0	1.9	4.8	4.6	1.8	1.7
	1.92	2.07	2.80	2.0	1.9	4.8	4.6	1.8	1.7
	2.02	2.18	3.52	2.6	2.4	6.2	5.8	2.3	2.2
	2.02	2.18	3.56	2.6	2.4	6.2	5.8	2.3	2.2
	2.93	3.25	2.60	1.8	1.6	4.3	3.8	1.6	1.4
	6.05	7.40	1.60	0.9	0.7	2.2	1.7	0.8	0.6
	6.05	7.40	1.67	1.0	0.8	2.4	1.9	0.9	0.7
	8.05	10.8	1.64	1.0	0.7	2.4	1.7	0.9	0.6
	8.05	10.8	1.55	0.9	0.7	2.2	1.7	0.8	0.6
	10.1	15.2	1.74	1.1	0.7	2.6	1.7	1.0	0.6
	10.1	15.2	1.74	1.1	0.7	2.6	1.7	1.0	0.6
	14.0	26.5	2.25	1.6	0.8	3.8	1.9	1.4	0.7
	14.0	26.5	2.23	1.6	0.8	3.8	1.9	1.4	0.7
Rb	0.100	0.100	246.0	245.0	245.0	590.0	590.0	224.0	224.0
	0.400	0.405	63.8	62.7	61.9	150.0	149.0	57.0	56.0
	0.400	0.405	63.8	62.7	61.9	150.0	149.0	57.0	56.0

Table XXV. (Continued)

Tracer	M	m	vol	vol_{cor}	vol_{H_2O}	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Cs	0.100	0.100	350	349	349	840	840	320	320
	0.400	0.405	85.7	84.6	83.6	203	201	320	320
	0.400	0.405	86.2	85.1	84.1	204	202	77	77
	0.495	0.503	61.5	60.4	59.4	145	143	55	54
	0.496	0.504	59.5	58.4	57.5	140	138	53	52
	0.496	0.504	59.5	58.4	57.5	140	138	53	52
	0.992	1.03	23.4	22.4	21.6	54	52	20.4	19.7
	0.992	1.03	24.4	23.4	22.5	56	54	21.2	10.4
	1.00	1.04	22.9	21.9	21.1	53	51	20.1	19.3
	1.00	1.04	22.8	21.9	21.1	53	51	20.1	19.3
	1.92	2.07	5.4	4.6	4.3	11.0	10.3	4.2	3.9
	1.92	2.07	5.4	4.6	4.3	11.0	10.3	4.2	3.9
	2.02	2.18	7.44	6.6	6.1	15.8	14.6	6.0	5.5
	2.02	2.18	7.32	6.5	6.0	15.6	14.4	5.9	5.5
	2.93	3.25	4.24	3.5	3.2	8.4	7.7	3.2	2.9
	2.93	3.25	4.28	3.5	3.2	8.4	7.7	3.2	2.9
	6.05	7.40	1.60	0.9	0.7	2.2	1.7	0.8	0.6
	6.05	7.40	1.60	0.9	0.7	2.2	1.7	0.8	0.6
	8.05	10.8	1.29	0.6	0.4	1.4	1.0	0.5	0.4
	8.05	10.8	1.36	0.7	0.5	1.7	1.2	0.8	0.5
	10.1	15.2	1.31	0.7	0.5	1.7	1.2	0.8	0.5
	10.1	15.2	1.31	0.6	0.4	1.4	1.0	0.5	0.4
	14.0	26.5	1.09	0.5	0.3	1.2	0.7	0.5	0.3
	14.0	26.5	1.14	0.5	0.3	1.2	0.7	0.5	0.3

Table XXV (Continued) Column 5.

Tracer	M	m	vol	vol_{cor}	vol_{H_2O}	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Na	1.92	2.07	19.1	14.9	13.6	6.7	6.1	2.5	2.3
	1.92	2.07	19.8	15.6	14.5	7.0	6.5	2.6	2.5
	3.84	4.55	11.5	7.7	6.5	3.5	2.9	1.3	1.1
	3.84	4.55	11.9	8.1	6.9	3.6	3.1	1.4	1.2
	4.96	5.83	10.2	6.6	5.6	3.0	2.5	1.2	0.9
	4.96	5.83	9.5	5.9	5.0	2.7	2.2	1.0	0.8
	6.05	7.40	8.9	5.4	4.4	2.4	2.0	0.9	0.8
	6.05	7.40	8.9	5.4	4.4	2.4	2.0	0.9	0.8
	8.07	10.9	8.4	5.1	3.8	2.3	1.7	0.9	0.6
	8.07	10.9	8.6	5.3	4.0	2.4	1.8	0.9	0.7
	10.1	15.2	8.9	5.7	3.8	2.6	1.7	1.0	0.6
	10.1	15.2	9.0	5.8	3.9	2.6	1.8	1.0	0.7
	14.0	26.5	14.1	11.1	5.9	5.0	2.7	1.9	1.0
Rb	1.92	2.07	39.7	35.5	32.9	16.0	14.8	6.1	5.6
	1.92	2.07	40.4	36.2	33.6	16.3	15.1	6.2	5.7
	3.84	4.55	14.0	10.2	8.6	4.6	3.9	1.7	1.5
	3.84	4.55	14.4	10.6	8.9	4.8	4.0	1.8	1.5
	4.96	5.83	10.6	7.0	6.0	3.2	2.7	1.2	1.0
	4.96	5.83	10.2	6.6	5.6	3.0	2.5	1.1	0.9
	6.05	7.40	8.5	5.0	4.1	2.2	1.8	0.8	0.7
	6.05	6.40	8.3	4.8	3.9	2.2	1.8	0.8	0.7
	8.07	10.9	7.1	3.8	2.8	1.7	1.3	0.6	0.5
	8.07	10.9	7.3	4.0	3.0	1.8	1.3	0.7	0.5
	10.1	15.2	6.5	3.3	2.2	1.5	1.0	0.6	0.4
	10.1	15.2	6.4	3.2	2.1	1.4	0.9	0.5	0.3
	14.1	26.5	7.2	4.2	2.2	1.9	1.0	0.7	0.3

Table XXVI. Resin: Dowex-50W. Eluting solution: LiCl. Column 1.

Tracer	M	m	vol	vol_{cor}	vol_{H_2O}	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Na	0.100	0.100	75.9	72.4	72.4	174	174	66	66
	0.318	0.320	28.6	27.5	27.3	66	66	25.0	25.0
	0.318	0.320	24.6	23.5	23.3	56	56	21.2	21.2
	0.400	0.402	19.5	18.4	18.3	44	44	16.7	16.7
	0.400	0.402	20.0	18.9	18.8	45	45	17.1	17.1
	1.06	1.07	8.8	7.8	7.7	18.7	18.5	7.1	7.0
	1.06	1.07	8.3	7.4	7.3	17.8	17.5	6.7	6.6
	3.18	3.36	3.20	2.4	2.3	5.8	5.5	2.2	2.1
	3.18	3.36	3.30	2.5	2.4	6.0	5.8	2.3	2.2
	3.53	3.77	2.97	2.2	2.1	5.3	5.0	2.0	1.9
	3.53	3.77	2.73	2.0	1.9	4.8	4.6	1.8	1.7
	3.53	3.77	2.84	2.1	2.0	5.0	4.8	1.9	1.8
	7.06	8.29	1.80	1.1	0.9	2.6	2.2	1.0	0.8
	7.06	8.29	1.70	1.0	0.8	2.4	1.9	0.9	0.7
	7.06	8.29	1.75	1.1	0.9	2.6	2.2	1.0	0.8
	9.41	11.7	1.47	0.8	0.6	1.9	1.4	0.7	0.5
	9.41	11.7	1.53	0.9	0.7	2.2	1.7	0.8	0.6
	9.41	11.7	1.53	0.9	0.7	2.2	1.7	0.8	0.6
	11.3	15.2	1.32	0.7	0.5	1.7	1.2	0.6	0.5
	11.3	15.2	1.32	0.7	0.5	1.7	1.2	0.6	0.5
	11.3	15.2	1.26	0.6	0.4	1.4	1.0	0.5	0.4
Rb	0.100	0.100	337	336	336	810	810	307	307
	0.318	0.320	131.6	130	129	310	310	117	117
	0.318	0.320	117.6	116	115	278	276	105	105
	0.400	0.402	94.0	92.9	92.6	223	222	85	84
	0.400	0.402	96.2	95.1	94.8	228	228	86	86
	1.06	1.07	32.5	31.6	31.3	76	75	28.8	28.4
	1.06	1.07	33.5	32.6	32.3	78	78	29.6	29.2
	3.18	3.36	7.9	7.1	6.7	17.0	16.1	6.4	6.1
	3.18	3.36	7.9	7.1	6.7	17.0	16.1	6.4	6.1

Table XXVI. (Continued).

Tracer	M	m	vol	vol_{cor}	vol_{H_2O}	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Cs	0.100	0.100	521	520	520	1250	1250	474	474
	0.400	0.402	126	125	124	300	300	114	114
	0.400	0.402	123	122	121	293	290	111	110
	11.3	15.2	1.26	0.6	0.4	1.4	1.0	0.5	0.4
	11.3	15.2	1.32	0.7	0.5	1.7	1.2	0.6	0.5
	11.3	15.2	1.32	0.7	0.5	1.7	1.2	0.6	0.5
				Column 4					
Na	3.18	3.36	15.9	12.3	11.6	5.9	5.6	2.2	2.1
	3.18	3.36	15.9	12.3	11.6	5.9	5.6	2.2	2.1
	3.18	3.36	16.4	12.8	12.1	6.1	5.8	2.3	2.2
	6.36	7.34	9.3	6.1	5.3	2.9	2.5	1.1	0.9
	6.36	7.34	9.3	6.1	5.3	2.9	2.5	1.1	0.9
	6.36	7.34	9.3	6.1	5.3	2.9	2.5	1.1	0.9
	10.6	13.8	6.9	4.0	3.1	1.9	1.5	0.7	0.6
	10.6	13.8	6.8	3.9	3.0	1.9	1.4	0.7	0.5
	10.6	13.8	6.8	3.9	3.0	1.9	1.4	0.7	0.5
	13.2	20.3	5.6	2.8	1.8	1.3	0.9	0.5	0.3
	13.2	20.3	5.5	2.7	1.8	1.3	0.9	0.5	0.3
	13.2	20.3	5.5	2.7	1.8	1.3	0.9	0.5	0.3
Rb	3.18	3.36	41.3	37.7	35.7	18.1	17.1	6.9	6.5
	3.18	3.36	41.7	38.1	36.1	18.3	17.3	6.9	6.6
	3.18	3.36	43.0	39.4	37.3	18.9	17.9	7.2	6.8
	6.36	7.34	13.5	10.3	8.9	4.9	4.3	1.9	1.6
	6.36	7.34	13.7	10.5	9.1	5.0	4.4	1.9	1.7
	6.36	7.34	13.8	10.6	9.2	5.1	4.4	1.9	1.7
	10.6	13.8	6.8	3.9	3.0	1.9	1.4	0.7	0.5
	10.6	13.8	6.8	3.9	3.0	1.9	1.4	0.7	0.5
	10.6	13.8	6.6	3.7	2.8	1.8	1.3	0.7	0.5
	13.2	20.3	5.4	2.6	1.7	1.2	0.8	0.5	0.3
	13.2	20.3	5.4	2.6	1.7	1.2	0.8	0.5	0.3
	13.2	20.3	5.4	2.6	1.7	1.2	0.8	0.5	0.3

Table XXVII. Resin: Dowex-50W. Eluting solution: HCl. Column 1.

Tracer	M	m	vol	vol_{cor}	vol_{H_2O}	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Na	0.100	0.100	68.7	67.3	67.3	162	162	61	61
	0.350	0.352	22.1	21.0	20.9	50	50	19.0	19.0
	0.350	0.352	21.6	20.5	20.4	49	49	18.6	18.6
	0.400	0.402	18.7	17.6	17.5	42	42	15.9	15.9
	1.00	1.01	7.3	6.4	6.3	15.4	15.3	5.8	5.8
	1.00	1.01	7.4	6.4	6.3	15.4	15.3	5.8	5.8
	2.00	2.06	4.10	3.2	3.1	7.7	7.4	2.9	2.8
	2.00	2.06	4.20	3.3	3.2	7.9	7.7	3.0	2.9
	5.74	6.45	2.23	1.5	1.3	3.6	3.1	1.4	1.2
	5.74	6.45	2.18	1.5	1.3	3.6	3.1	1.4	1.2
	11.2	14.8	3.04	2.4	1.8	5.8	4.3	2.2	1.6
	11.2	14.8	2.96	2.4	1.8	5.8	4.3	2.2	1.6
	11.2	14.8	2.96	2.4	1.8	5.8	4.3	2.2	1.6
Na[a]	2.00	2.06	4.30	3.4	3.3	8.2	7.9	3.1	3.0
	2.00	2.06	4.15	3.3	3.2	7.9	7.7	3.0	2.9
	5.74	6.45	2.27	1.6	1.4	3.8	3.4	1.4	1.3
	5.74	6.45	2.27	1.6	1.4	3.8	3.4	1.4	1.3
	11.2	14.8	3.19	2.6	2.0	6.2	4.8	2.3	1.8
	11.2	14.8	3.23	2.6	2.0	6.2	4.8	2.3	1.8
	11.2	14.8	3.23	2.6	2.0	6.2	4.8	2.3	1.8
Rb	0.100	0.100	240	239	239	570	570	216	216
	0.350	0.352	78.0	76.9	76.5	185	184	70	70
	0.350	0.352	80.6	79.5	79.0	191	190	72	72
	0.400	0.402	69.3	68.2	67.9	164	163	62	62
	1.00	1.01	24.0	23.0	22.8	55	55	20.8	20.6
	1.00	1.01	24.6	23.6	23.4	57	56	21.6	21.4
Cs	0.100	0.100	353	352	352	840	840	320	320
	0.400	0.402	96	95	95	228	228	86	86

Table XXVII. (Continued) Column 2

Tracer	M	m	vol	vol_{cor}	vol_{H_2O}	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Cs	1.00	1.01	93.8	91.6	90.7	92	91	35	35
	1.00	1.01	94.4	92.2	91.3	92	91	35	35
	1.00	1.01	81.9	79.7	78.9	80	79	30	30
	4.15	4.49	10.8	9.1	8.4	9.1	8.4	3.4	3.2
	4.15	4.49	11.1	9.4	8.7	9.4	8.7	3.6	3.3
	4.15	4.49	13.0	11.7	10.8	11.7	10.8	4.4	4.1
	6.92	8.02	4.94	3.4	2.9	3.4	2.9	1.3	1.1
	6.92	8.02	4.94	3.4	2.9	3.4	2.9	1.3	1.1
	8.95	11.0	4.11	2.6	2.1	2.6	2.1	1.0	0.8
	8.95	11.0	4.35	2.8	2.3	2.8	2.3	1.1	0.9
	8.95	11.0	4.35	2.9	2.4	2.9	2.4	1.1	0.9
	11.2	14.8	3.15	1.9	1.4	1.9	1.4	0.7	0.5
	11.2	14.8	3.02	1.7	1.3	1.7	1.3	0.6	0.5
	11.2	14.8	3.05	1.7	1.3	1.7	1.3	0.6	0.5
	11.2	14.8	3.2	1.8	1.4	1.8	1.4	0.7	0.5
	11.2	14.8	3.3	1.9	1.4	1.9	1.4	0.7	0.5
	11.2	14.8	3.1	1.7	1.3	1.7	1.3	0.6	0.5

[a] Tracer Na dissolved in 11.2 M HCl saturated with carrier NaCl; sample for elution was a total of 2×10^{-5} mmole NaCl.

Table XXVII. (Continued) Column 2

Tracer	M	m	vol	vol_{cor}	vol_{H_2O}	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Na	1.00	1.01	17.2	15.0	14.9	15.0	14.9	5.7	5.6
	1.00	1.01	17.9	15.7	15.6	15.7	15.6	6.0	5.9
	1.00	1.01	17.3	15.1	15.0	15.1	15.0	5.7	5.7
	4.15	4.49	5.6	3.9	3.6	3.9	3.6	1.5	1.4
	4.15	4.49	5.9	4.2	3.9	4.2	3.9	1.6	1.5
	4.15	4.49	5.6	3.9	3.6	3.9	3.6	1.5	1.4
	6.92	8.02	5.27	3.7	3.2	3.7	3.2	1.4	1.2
	6.92	8.02	5.51	3.9	3.4	3.9	3.4	1.5	1.3
	6.92	8.02	5.51	3.9	3.4	3.9	3.4	1.5	1.3
	6.92	8.02	5.40	3.8	3.3	3.8	3.3	1.4	1.3
	8.95	11.0	6.48	5.0	4.1	5.0	4.1	1.9	1.6
	8.95	11.0	6.48	5.0	4.1	5.0	4.1	1.9	1.6
	8.95	11.0	6.48	5.0	4.1	5.0	4.1	1.9	1.6
	11.2	14.8	7.08	5.7	4.4	5.7	4.4	2.2	1.7
	11.2	14.8	6.71	5.3	4.0	5.3	4.0	2.0	1.5
	11.2	14.8	6.90	5.5	4.2	5.5	4.2	2.1	1.6
	11.2	14.8	7.8	6.4	4.8	6.4	4.8	2.4	1.8
	11.2	14.8	7.4	6.0	4.5	6.0	4.5	2.3	1.7
	11.2	14.8	7.7	6.3	4.8	6.3	4.8	2.4	1.8
Rb	4.15	4.49	11.0	9.3	8.6	9.3	8.6	3.5	3.3
	4.15	4.49	11.4	9.7	9.0	9.7	9.0	3.7	3.4
	4.15	4.49	11.3	9.6	8.9	9.6	8.9	3.6	3.4
	6.92	8.02	6.64	5.1	4.4	5.1	4.4	1.9	1.7
	6.92	8.02	7.07	5.5	4.7	5.5	4.7	2.1	1.8
	6.92	8.02	7.07	5.5	4.7	5.5	4.7	2.1	1.8
	8.95	11.0	5.54	4.0	3.3	4.0	3.3	1.5	1.3
	8.95	11.0	6.00	4.5	3.7	4.5	3.7	1.7	1.4
	8.95	11.0	5.76	4.3	3.5	4.3	3.5	1.6	1.3
	11.2	14.8	4.34	3.0	2.2	3.0	2.2	1.1	0.8
	11.2	14.8	4.34	3.0	2.2	3.0	2.2	1.1	0.8
	11.2	14.8	4.56	3.2	2.4	3.2	2.4	1.2	0.9

Table XXVIII. Resin: Dowex-50W. Eluting Solution: CsCl. Column 1.

Tracer	M	m	vol	$\mathrm{vol}_{\mathrm{cor}}$	$\mathrm{vol}_{\mathrm{H_2O}}$	$\overline{\mathrm{vol}}_{\mathrm{cor}}$	$\overline{\mathrm{vol}}_{\mathrm{H_2O}}$	D(M)	D(m)
Na	0.100	0.100	44.2	42.8	42.8	103	103	39	39
	0.279	0.282	17.2	16.0	15.8	38	38	14.4	14.4
	0.279	0.282	16.7	15.5	15.3	37	37	14.0	14.0
	0.279	0.282	16.7	15.5	15.3	37	37	14.0	14.0
	0.400	0.410	10.9	9.8	9.6	23.5	23.0	8.9	8.7
	0.400	0.410	11.2	10.1	9.8	24.2	23.5	9.2	8.9
	1.11	1.16	4.9	4.0	3.8	9.6	9.1	3.6	3.4
	1.11	1.16	4.9	4.0	3.8	9.6	9.1	3.6	3.4
Rb	0.100	0.100	51.0	49.6	49.6	119	119	45	45
	0.279	0.282	18.5	17.3	17.1	42	41	15.9	15.5
	0.279	0.282	17.5	16.3	16.1	39	39	14.8	14.8
	0.279	0.282	17.5	16.3	16.1	39	39	14.8	14.8
	0.400	0.410	12.9	11.8	11.5	28.3	27.6	10.7	10.5
	0.400	0.410	12.8	11.7	11.4	28.0	27.4	10.6	10.4
	1.11	1.16	5.1	4.2	4.0	10.1	9.6	3.8	3.6
	1.11	1.16	5.1	4.2	4.0	10.1	9.6	3.8	3.6
Cs	0.100	0.100	60.4	59.0	59.0	142	142	54	54
				Column 2					
Na	6.92	10.0	3.7	2.1	1.4	2.1	1.4	0.8	0.5
	6.92	10.0	3.7	2.1	1.4	2.1	1.4	0.8	0.5
	6.92	10.0	3.7	2.1	1.4	2.1	1.4	0.8	0.5
	6.92	10.0	3.6	2.0	1.4	2.0	1.4	0.8	0.5
	6.92	10.0	3.6	2.0	1.4	2.0	1.4	0.8	0.5
Rb	6.92	10.0	4.2	2.6	1.8	2.6	1.8	1.0	0.7
	6.92	10.0	4.0	2.4	1.7	2.4	1.7	0.9	0.6
	6.92	10.0	4.1	2.5	1.7	2.5	1.7	0.9	0.6
	6.92	10.0	4.0	2.4	1.7	2.4	1.7	0.9	0.6
	6.92	10.0	4.0	2.4	1.7	2.4	1.7	0.9	0.6
	6.92	10.0	3.8	2.2	1.5	2.2	1.5	0.8	0.6
	6.92	10.0	3.9	2.3	1.6	2.3	1.6	0.9	0.6
	6.92	10.0	3.9	2.3	1.6	2.3	1.6	0.9	0.6

Table XXVIII. (Continued) Column 3

Tracer	M	m	vol	vol_{cor}	vol_{H_2O}	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Na	1.11	1.16	19.2	15.7	15.0	8.6	8.3	3.3	3.1
	1.11	1.16	18.9	15.4	14.7	8.5	8.1	3.2	3.1
	1.11	1.16	20.5	17.0	16.3	9.4	9.0	3.6	3.4
	2.79	3.16	9.26	6.2	5.5	3.4	3.0	1.3	1.1
	2.79	3.16	9.19	6.2	5.5	3.4	3.0	1.3	1.1
	4.65	5.83	7.07	4.4	3.5	2.4	1.9	0.9	0.7
	4.65	5.83	7.00	4.3	3.4	2.4	1.9	0.9	0.7
	5.81	7.80	6.88	4.3	3.2	2.4	1.8	0.9	0.7
	5.81	7.80	6.50	3.9	2.9	2.1	1.6	0.8	0.6
	7.26	10.1	6.77	4.3	3.1	2.4	1.7	0.9	0.6
	7.26	10.1	6.83	4.3	3.1	2.4	1.7	0.9	0.6
Rb	1.11	1.16	20.6	17.1	16.4	9.4	9.0	3.6	2.4
	1.11	1.16	20.4	16.9	16.2	9.3	8.9	3.5	3.4
	1.11	1.16	22.3	18.8	18.0	10.3	9.9	3.9	3.8
	2.79	3.16	9.85	6.8	6.0	3.7	3.3	1.4	1.3
	2.79	3.16	9.78	6.8	6.0	3.7	3.3	1.4	1.3
	4.65	5.83	7.64	4.9	3.9	2.7	2.1	1.0	0.8
	5.81	7.80	7.44	4.8	3.6	2.6	2.0	0.9	0.8
	5.81	7.80	7.13	4.3	3.4	2.5	1.9	0.9	0.7
	7.26	10.1	7.42	4.9	3.5	2.7	1.9	1.0	0.7
	7.26	10.1	7.42	4.9	3.5	2.7	1.9	1.0	0.7

Table XXIX. Resin: Dowex-50W. Eluting solution: LiAc. Column 1a.

Tracer	M	m	vol	vol_{cor}	vol_{H_2O}	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Na	0.104	0.104	—	—	—	216	216	82	82
	0.314	0.317	—	—	—	74	73	28.0	27.7
	0.664	0.674	—	—	—	29.7	29.3	11.3	11.1
	1.36	1.44	—	—	—	13.7	12.9	5.2	4.9
	1.36	1.44	9.50	8.60	8.12	16.3	15.4	6.2	5.8
	1.36	1.44	9.50	8.60	8.12	16.3	15.4	6.2	5.8
	2.76	2.98	6.19	5.39	4.99	10.2	9.5	3.9	3.6
	2.76	2.98	6.19	5.39	4.99	10.2	9.5	3.9	3.6
	4.16	4.65	5.09	4.34	3.88	8.2	7.4	3.1	2.8
	4.16	4.65	5.13	4.38	3.92	8.3	7.4	3.2	2.8
	5.56	6.70	4.74	4.02	3.34	7.6	6.3	2.9	2.4
	5.56	6.70	4.78	4.06	3.38	7.7	6.4	2.9	2.4
Cs	0.104	0.104	—	—	—	1610	1610	610	610
	0.314	0.317	—	—	—	500	500	190	188
	0.664	0.674	—	—	—	234	231	89	88
	1.36	1.44	—	—	—	116	110	44	42
	1.36	1.44	65.5	65.4	61.8	124	117	47	44
	1.36	1.44	67.5	67.4	63.7	128	121	49	46
	2.76	2.98	38.3	38.2	25.4	73	67	27.7	25.5
	2.76	2.98	28.9	28.8	26.0	74	58	28.1	25.9
	4.16	4.65	28.6	28.5	25.5	54	48	20.5	18.2
	4.16	4.65	28.6	28.5	25.5	54	48	20.5	18.2
	5.56	6.70	26.5	26.4	21.9	50	42	19.0	16.0
	5.56	6.70	26.5	26.4	21.9	50	42	19.0	16.0

Table XXX. Distribution of alkali tracers between Dowex-50W and LiAc and HAc solutions.

		Na tracer				Cs tracer			
BX	M	C_o	C_{aq}	C_{res}	D	C_o	C_{aq}	C_{res}	D
LiAc	0.104	1.4×10^5	7.9×10^4	6.2×10^4	8.2×10^1	4.9×10^5	6.9×10^4	4.2×10^5	6.1×10^2
	0.314	1.4×10^5	1.1×10^5	3.1×10^4	2.8×10^1	4.8×10^5	1.6×10^5	3.2×10^5	1.9×10^2
	0.664	1.3×10^5	1.1×10^5	1.3×10^4	1.1×10^1	8.0×10^5	4.2×10^5	3.8×10^5	8.9×10^1
	1.36	1.5×10^5	1.4×10^5	7.3×10^3	5.2×10^0	5.5×10^5	3.8×10^5	1.7×10^5	4.4×10^1
HAc	0.174	1.6×10^5	5.2×10^3	1.6×10^5	3.1×10^3	4.3×10^5	2.0×10^3	4.3×10^5	2.1×10^4
	0.435	1.4×10^5	6.1×10^3	1.4×10^5	2.2×10^3	4.8×10^5	3.8×10^3	4.8×10^5	1.3×10^4
	0.870	1.4×10^5	7.6×10^3	1.3×10^5	1.7×10^3	5.2×10^5	5.6×10^3	5.2×10^5	9.2×10^3
	1.74	1.6×10^5	1.0×10^4	1.5×10^5	1.4×10^3	5.4×10^5	7.4×10^3	5.3×10^5	7.2×10^3
	4.35	1.1×10^5	8.1×10^3	1.0×10^5	1.3×10^3	4.8×10^5	9.8×10^3	4.7×10^5	4.8×10^3
	8.70	1.6×10^5	9.9×10^3	1.5×10^5	1.5×10^3	5.3×10^5	1.2×10^4	5.2×10^5	4.3×10^3
	13.0	1.3×10^5	4.6×10^3	1.3×10^5	2.7×10^3	5.1×10^5	9.0×10^3	5.0×10^5	5.5×10^3
	17.4	1.1×10^5	1.3×10^2	1.1×10^5	8.4×10^4	3.1×10^5	2.1×10^2	3.1×10^5	1.5×10^5

Table XXXI. Distribution of alkali tracers between Dowex-50W and 0.1 M salt and acid solutions.

		Na tracer				Rb tracer				Cs tracer			
BX	M	C_o	C_{aq}	C_{res}	D	C_o	C_{aq}	C_{res}	D	C_o	C_{aq}	C_{res}	D
CsCl	0.100	1.7×10^6	1.4×10^6	3.1×10^5	23	7.1×10^4	5.4×10^4	1.7×10^4	31	5.1×10^4	3.7×10^4	1.4×10^4	37
$HClO_4$	0.100	1.6×10^6	1.1×10^6	5.7×10^5	53	6.2×10^4	2.2×10^4	4.0×10^4	188	5.9×10^4	1.5×10^4	4.4×10^4	297
HNO_3	0.100	1.9×10^6	1.3×10^6	6.4×10^5	51	4.9×10^4	1.6×10^4	3.3×10^4	207	6.2×10^4	1.6×10^4	4.6×10^4	294
HCl	0.100	1.7×10^6	1.1×10^6	6.4×10^5	58	6.9×10^4	2.3×10^4	4.6×10^4	202	5.2×10^4	1.1×10^4	4.1×10^4	353
$LiClO_4$	0.108	1.9×10^6	1.2×10^6	7.3×10^5	60	5.9×10^4	1.8×10^4	4.1×10^4	231	5.3×10^4	1.2×10^4	4.1×10^4	359
$LiNO_3$	0.100	2.1×10^6	1.3×10^6	7.9×10^5	60	4.7×10^4	1.3×10^4	3.4×10^4	259	6.6×10^4	1.3×10^4	5.3×10^4	422
LiCl	0.100	1.7×10^6	1.0×10^6	6.7×10^5	64	5.9×10^4	1.5×10^4	4.4×10^4	283	5.5×10^4	1.0×10^4	4.5×10^4	438

Table XXXII. Resin: BioRex 70. Eluting Solution: $LiClO_4$. Column 6

tracer	M	m	vol	vol_{cor}	vol_{H_2O}	D(M)	D(m)
Na	0.103	0.103	72.2	68.7	68.7	64.2	64.2
	0.103	0.103	72.0	68.5	68.5	64.0	64.0
	0.207	0.210	36.9	33.6	33.1	31.4	30.9
	0.207	0.210	36.2	32.9	32.4	30.8	30.3
	0.414	0.428	18.3	15.1	14.6	14.1	13.7
	0.414	0.428	18.1	14.9	14.4	13.9	13.5
	1.03	1.08	7.37	4.4	4.2	4.1	3.9
	1.03	1.08	7.36	4.4	4.2	4.1	3.9
	2.07	2.27	4.26	1.4	1.3	1.3	1.2
	2.07	2.27	4.20	1.3	1.2	1.2	1.1
	4.14	5.07	3.32	0.5	0.4	0.5	0.4
	4.14	5.07	3.42	0.6	0.5	0.6	0.5
Cs	0.103	0.103	120	117	117	109	109
	0.103	0.103	120	117	117	109	109
	0.207	0.210	52.4	49.1	48.4	45.9	45.3
	0.207	0.210	50.0	46.7	46.0	43.6	43.0
	0.414	0.428	20.3	17.1	16.5	16.0	15.4
	1.03	1.08	5.80	2.6	2.5	2.4	2.3
	1.03	1.08	5.70	2.5	2.4	2.3	2.2
	2.07	2.27	2.97	0.1	0.1	0.1	0.1
	2.07	2.27	2.94	0.0	0.0	0.0	0.0
	4.14	5.07	2.74	0.0	0.0	0.0	0.0
	4.14	5.07	2.93	0.1	0.1	0.1	0.1

Table XXXIII. Resin: BioRex 70. Eluting Solution: $LiNO_3$. Column 6

tracer	M	m	vol	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Na	0.106	0.106	71.0	67.5	67.5	63.1	63.1
	0.106	0.106	70.5	67.0	67.0	62.6	62.6
	0.213	0.217	37.1	33.8	33.2	31.6	31.0
	0.213	0.217	36.3	32.0	31.4	29.9	29.4
	0.520	0.530	13.6	10.5	10.3	9.8	9.6
	0.520	0.530	13.0	9.9	9.7	9.3	9.1
	1.06	1.11	6.97	4.0	3.8	3.7	3.6
	1.06	1.11	6.95	3.9	3.7	3.6	3.5
	2.13	2.31	4.32	1.4	1.3	1.3	1.2
	2.13	2.31	4.29	1.4	1.3	1.3	1.2
	4.25	4.86	3.16	0.4	0.3	0.4	0.3
	4.25	4.86	3.10	0.3	0.3	0.3	0.2
	8.51	11.8	3.06	0.3	0.2	0.3	0.2
	8.51	11.8	3.00	0.3	0.2	0.3	0.2
Cs	0.106	0.106	125	122	122	114	114
	0.106	0.106	124	121	121	113	113
	0.213	0.217	58.6	55.3	54.5	51.7	51.0
	0.213	0.217	59.6	56.3	55.3	52.6	51.7
	0.520	0.530	18.2	15.1	14.8	14.1	13.8
	0.520	0.530	17.8	14.7	14.4	13.7	13.5
	1.06	1.11	7.47	4.5	4.3	4.2	4.0
	1.06	1.11	7.50	4.5	4.3	4.2	4.0
	2.13	2.31	4.11	1.2	1.1	1.1	1.0
	2.13	2.31	4.00	1.1	1.0	1.0	0.9
	4.25	4.86	2.79	0.0	0.0	0.0	0.0
	4.25	4.86	2.76	0.0	0.0	0.0	0.0
	8.51	11.8	2.87	0.2	0.1	0.2	0.1
	8.51	11.8	2.84	0.1	0.1	0.1	0.1

Table XXXIV. Resin: BioRex 70. Eluting Solution: LiCl. Column 6

tracer	M	m	vol	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Na	0.135	0.136	59.4	56.0	55.6	52.4	52.0
	0.270	0.272	29.5	29.5	26.0	24.5	24.3
	0.270	0.272	29.5	26.2	26.0	24.5	24.3
	0.625	0.630	12.8	9.7	9.6	9.1	9.0
	0.625	0.530	12.8	9.7	9.6	9.1	9.1
	1.35	1.38	7.2	4.2	4.1	3.9	3.8
	1.35	1.38	7.2	4.2	4.1	3.9	3.8
	2.70	2.83	4.77	1.9	1.8	1.8	1.7
	2.70	2.83	4.79	1.9	1.8	1.8	1.7
	5.90	6.72	3.75	1.0	0.9	0.9	0.8
	5.90	6.72	3.72	1.0	0.9	0.9	0.8
	9.40	11.7	2.92	0.2	0.2	0.2	0.2
	9.40	11.7	3.27	0.6	0.5	0.6	0.5
	13.5	21.2	3.00	0.4	0.3	0.4	0.3
	13.5	21.2	2.94	0.3	0.2	0.3	0.2
Cs	0.135	0.136	105	102	101	95.4	94.4
	0.270	0.272	50.1	46.8	46.4	43.8	43.4
	0.270	0.272	50.5	47.2	46.8	44.1	43.8
	0.625	0.630	18.6	15.5	15.4	14.5	14.4
	0.625	0.630	18.6	15.5	15.4	14.5	14.4
	1.35	1.38	8.7	5.7	5.6	5.3	5.2
	1.35	1.38	8.7	5.7	5.6	5.3	5.2
	2.70	2.83	4.76	1.9	1.8	1.8	1.7
	2.70	2.83	4.76	1.9	1.8	1.8	1.7
	5.90	6.72	3.39	0.6	0.5	0.6	0.5
	5.90	6.72	2.28	0.6	0.5	0.6	0.5
	9.40	11.7	2.83	0.1	0.1	0.1	0.1
	9.40	11.7	3.06	0.4	0.3	0.4	0.3
	13.5	21.2	2.89	0.3	0.2	0.3	0.2
	13.5	21.2	2.78	0.2	0.1	0.2	0.2

Table XXXV. Resin: BioRex 70. Eluting Solution: LiAc. Column 6.

tracer	M	m	vol	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
Na	0.111	0.111	70.4	66.9	66.9	62.6	62.6
	0.111	0.111	71.0	67.5	67.5	63.1	63.1
	0.112	0.227	34.4	31.1	30.4	29.1	28.4
	0.222	0.237	34.5	31.2	30.5	29.2	28.5
	0.556	0.566	15.6	12.5	12.3	11.7	11.5
	0.556	0.566	15.8	12.7	12.5	11.9	11.7
	1.11	1.16	10.1	7.1	6.8	6.6	6.4
	1.11	1.16	9.9	6.9	6.6	6.5	6.2
	2.22	2.41	6.93	4.0	3.7	3.7	3.5
	2.22	2.41	6.91	4.0	3.7	3.7	3.5
	3.34	3.74	5.83	3.0	2.7	2.8	2.5
	3.34	3.74	5.86	3.0	2.7	2.8	2.5
	5.56	6.72	4.95	2.2	1.8	2.1	1.7
	5.56	6.72	4.85	2.1	1.7	2.0	1.6
Cs	0.111	0.111	134	131	131	122	122
	0.111	0.111	135	132	132	123	123
	0.222	0.227	64.4	61.1	59.8	57.1	55.9
	0.222	0.227	64.3	61.0	59.7	57.0	55.8
	0.556	0.566	27.4	24.1	23.7	22.5	22.2
	0.556	0.566	28.2	24.9	24.5	23.3	22.9
	1.11	1.16	17.1	14.1	13.5	13.2	12.6
	1.11	1.16	16.4	13.4	12.8	12.5	13.0
	2.22	2.41	10.2	7.3	6.7	6.8	6.3
	2.22	2.41	10.2	7.3	6.7	6.8	6.3
	3.34	3.74	8.95	5.6	5.0	5.2	4.7
	3.34	3.74	8.52	5.7	5.1	5.2	4.8
	5.56	6.72	6.54	3.8	3.1	3.6	2.9
	5.56	6.72	6.70	3.9	3.2	3.6	3.0

Table XXXVI. Resin: Dowex-50W. Tracer: Be. Column 1

eluant	M	m	vol	vol_{cor}	vol_{H_2O}	$\overline{vol}_{cor}$	$\overline{vol}_{H_2O}$	D(M)	D(m)
$HClO_4$	0.400	0.407	110	109	107	262	257	99	97
	0.400	0.407	114	113	111	271	266	103	101
	0.633	0.647	52.6	51.6	50.2	124	120	47	45
	0.630	0.647	49.0	48.0	46.7	115	112	44	42
	1.05	1.10	18.4	17.4	16.6	42	40	15.9	15.2
	1.05	1.10	18.3	18.4	16.6	42	40	15.9	15.2
	2.10	2.31	6.4	5.5	5.0	13.2	12.0	5.0	4.5
	2.10	2.31	6.1	5.3	4.8	12.7	11.5	4.8	4.4
HNO_3	0.400	0.407	103	102	100	245	240	93	91
	0.400	0.407	103	102	100	245	240	93	91
	0.496	0.508	82.2	81.1	79.2	195	190	74	72
	0.496	0.508	83.4	82.3	80.4	198	193	75	73
	0.992	1.03	21.8	20.8	20.0	50	48	19.0	18.2
	0.992	1.03	23.4	22.4	21.6	54	52	20.5	19.7
	1.92	2.07	4.6	3.7	3.4	8.9	8.2	3.4	3.1
	1.92	2.07	4.6	3.7	3.4	8.9	8.2	3.4	3.1

Table XXXVI. (Continued) Column 5.

eluant	M	m	vol	vol_{cor}	$\overline{\text{vol}}_{H_2O}$	$\overline{\text{vol}}_{cor}$	$\overline{\text{vol}}_{H_2O}$	D(M)	D(m)
$HClO_4$	2.10	2.31	32.8	32.0	29.1	14.4	13.1	5.5	5.0
	2.10	2.31	33.1	32.2	29.3	14.5	13.2	5.5	5.0
	4.20	5.08	16.1	15.4	12.7	6.9	5.7	2.6	2.2
	4.20	5.08	15.9	15.2	12.5	6.8	5.6	2.6	2.1
	6.30	8.56	13.7	13.0	9.6	5.9	4.3	2.2	1.6
	6.30	8.56	14.1	13.4	10.0	6.0	4.5	2.3	1.7
	8.40	12.9	12.2	11.6	7.6	5.2	2.3	2.0	1.3
	8.40	12.9	11.3	10.4	6.8	4.7	3.1	1.8	1.2
	10.5	18.8	12.1	11.5	6.4	5.2	2.9	2.0	1.1
HNO_3	1.92	2.07	47.5	46.7	43.3	21.0	19.5	8.0	7.4
	1.92	2.07	50.0	48.1	45.5	22.1	20.5	8.4	7.8
	3.84	4.55	14.7	14.0	11.8	6.3	5.3	2.4	2.0
	3.84	4.55	15.2	14.4	12.2	6.5	5.5	2.5	2.1
	4.96	5.83	13.3	12.6	10.7	5.7	4.8	2.2	1.8
	4.96	5.83	13.1	12.4	10.5	5.6	4.7	2.1	1.8
	6.05	7.40	11.8	11.1	9.1	5.0	4.1	1.9	1.6
	6.05	7.40	11.7	11.0	9.0	5.0	4.1	1.9	1.6
	8.07	10.9	11.9	11.2	8.3	5.0	3.7	1.9	1.4
	8.07	10.9	11.9	11.2	8.3	5.0	3.7	1.9	1.4
	10.1	15.2	13.2	12.6	8.4	5.7	3.8	2.2	1.4
	10.1	15.2	13.4	12.8	8.5	5.8	3.8	2.2	1.4

Table XXXVII. Distribution of trivalent tracers between Dowex-50W and $HClO_4$ solutions.

	Sc tracer				Fe tracer				Cr tracer			
M	C_o	C_{aq}	C_{res}	D	C_o	C_{aq}	C_{res}	D	C_o	C_{aq}	C_{res}	D
0.226	1.0×10^5	1.5×10^2	1.0×10^5	6.7×10^4	1.1×10^5	1.9×10^3	1.1×10^5	5.3×10^3	3.1×10^5	2.2×10^3	3.1×10^5	1.4×10^4
0.418	1.1×10^5	4.3×10^2	1.1×10^5	2.6×10^4	1.1×10^5	6.5×10^3	1.0×10^5	1.6×10^3	3.0×10^5	1.0×10^4	2.9×10^5	2.8×10^3
0.818	1.0×10^5	2.9×10^3	9.7×10^4	3.4×10^3	1.2×10^5	3.4×10^4	8.7×10^4	2.5×10^2	3.3×10^5	8.3×10^4	2.5×10^5	3.0×10^2
1.63	8.7×10^4	1.4×10^4	7.3×10^4	5.4×10^2	1.1×10^5	7.0×10^4	3.7×10^4	5.2×10^1	3.1×10^5	2.1×10^5	9.9×10^4	4.8×10^1
2.62	1.1×10^5	3.5×10^4	7.1×10^4	2.0×10^2	1.0×10^5	8.8×10^4	1.4×10^4	1.5×10^1	2.7×10^5	2.4×10^5	2.8×10^4	1.2×10^1
3.42	1.1×10^5	3.5×10^4	7.7×10^4	2.2×10^2	1.1×10^5	9.9×10^4	1.2×10^4	1.2×10^1	2.6×10^5	2.5×10^5	1.8×10^4	7.2×10^0
4.48	1.0×10^5	2.3×10^4	7.8×10^4	3.5×10^2	1.1×10^5	9.9×10^4	1.3×10^4	1.3×10^1	2.8×10^5	2.7×10^5	1.8×10^4	6.7×10^0
5.80	9.8×10^4	9.6×10^3	8.9×10^4	9.3×10^2	1.1×10^5	9.3×10^4	1.8×10^4	2.0×10^1	3.2×10^5	3.0×10^5	1.[illegible] $\times 10^4$	5.5×10^0
7.47	1.1×10^5	1.4×10^3	1.1×10^5	7.6×10^3	1.1×10^5	6.1×10^4	5.0×10^4	8.2×10^1	2.9×10^5	2.7×10^5	1.8×10^4	6.7×10^0
9.83	1.0×10^5	1.6×10^2	1.0×10^5	6.2×10^4	1.1×10^5	6.7×10^4	4.6×10^4	6.8×10^1	2.6×10^5	2.5×10^5	1.6×10^4	6.4×10^0

Table XXXVIII. Distribution of trivalent tracers between 0.0697 M DNNS and $HClO_4$ solutions.

M	Sc tracer			Fe tracer			Cr tracer		
	org	aq	D	org	aq	D	org	aq	D
0.226	5.9×10^{4}	2.8×10^{2}	2.1×10^{2}	6.7×10^{3}	2.0×10^{2}	3.3×10^{1}	1.8×10^{5}	2.4×10^{3}	7.5×10^{1}
0.418	5.1×10^{4}	1.5×10^{5}	3.4×10^{1}	6.1×10^{3}	7.2×10^{2}	8.4×10^{0}	1.3×10^{5}	1.0×10^{4}	1.3×10^{1}
0.818	5.2×10^{4}	1.2×10^{4}	4.4×10^{0}	4.0×10^{3}	2.7×10^{3}	1.5×10^{0}	1.1×10^{5}	7.3×10^{4}	1.5×10^{0}
1.63	5.0×10^{4}	6.0×10^{4}	8.2×10^{-1}	1.6×10^{3}	5.8×10^{3}	2.8×10^{-1}	2.9×10^{4}	1.1×10^{5}	2.6×10^{-1}
2.63	1.3×10^{4}	4.1×10^{4}	3.1×10^{-1}	6.7×10^{2}	6.8×10^{3}	9.5×10^{-2}	1.3×10^{4}	1.7×10^{5}	7.4×10^{-2}
3.88	1.3×10^{4}	4.3×10^{4}	3.1×10^{-1}	5.3×10^{2}	7.4×10^{3}	6.9×10^{-2}	4.6×10^{3}	1.4×10^{5}	3.1×10^{-2}
5.08	1.9×10^{4}	4.2×10^{4}	4.6×10^{-1}	5.5×10^{2}	7.4×10^{3}	7.0×10^{-2}	5.7×10^{3}	1.5×10^{5}	3.8×10^{-2}
6.27	3.3×10^{4}	2.6×10^{4}	1.2×10^{0}	7.4×10^{2}	6.8×10^{3}	1.1×10^{-1}	2.7×10^{3}	1.7×10^{5}	1.6×10^{-2}
7.47	4.8×10^{4}	8.0×10^{3}	6.0×10^{0}	1.4×10^{3}	5.9×10^{3}	2.3×10^{-1}	1.7×10^{3}	1.5×10^{3}	1.1×10^{-2}
8.92	5.7×10^{4}	9.8×10^{2}	6.4×10^{1}	4.5×10^{3}	4.3×10^{3}	1.0×10^{0}	5.4×10^{2}	1.4×10^{5}	3.8×10^{-3}
11.2	5.9×10^{4}	4.1×10^{1}	1.5×10^{3}	6.1×10^{3}	2.7×10^{3}	2.2×10^{0}	6.8×10^{1}	1.5×10^{5}	4.5×10^{-4}

Table XXXIX. Time studies of the distribution of trivalent tracers between Dowex-50W and $HClO_4$.

Tracer	T	M	C_0	C_{aq}	C_{res}	D
Sc	4 h	0.226	1.0×10^5	1.5×10^2	1.0×10^5	6.7×10^4
	7 d	0.226	9.9×10^4	2.0×10^2	9.9×10^4	5.0×10^4
	4 h	7.47	1.1×10^5	1.4×10^3	1.1×10^5	7.5×10^3
	7 d	7.47	9.8×10^4	7.5×10^2	9.8×10^4	1.3×10^4
Fe	15 m	0.226	9.5×10^4	1.7×10^3	9.3×10^4	5.5×10^3
	4 h	0.226	1.1×10^5	1.9×10^3	1.1×10^5	5.7×10^3
	7 d	0.226	7.2×10^4	1.8×10^3	7.1×10^4	4.0×10^3
	15 m	1.63	9.6×10^4	6.6×10^4	3.1×10^4	4.6×10^1
	4 h	1.63	1.1×10^5	7.1×10^4	3.7×10^4	5.2×10^1
	7 d	1.63	7.1×10^4	5.1×10^4	2.0×10^4	3.9×10^1
	4 h	7.47	1.1×10^5	6.1×10^4	5.0×10^4	8.2×10^1
	7 d	7.47	7.3×10^4	4.2×10^4	3.1×10^4	7.4×10^1
Cr	15 m	0.226	2.0×10^5	1.2×10^3	1.9×10^5	1.6×10^4
	4 h	0.226	3.1×10^5	2.2×10^3	3.1×10^5	1.4×10^4
	7 d	0.226	1.9×10^5	1.1×10^3	1.9×10^5	1.7×10^4
	15 m	1.63	2.0×10^5	1.4×10^5	6.7×10^4	4.8×10^1
	4 h	1.63	3.1×10^5	2.1×10^5	9.9×10^4	4.8×10^1
	7 d	1.63	2.0×10^5	1.3×10^5	6.4×10^4	4.9×10^1
	15 m	7.47	2.4×10^5	2.3×10^5	1.2×10^4	5.2×10^0
	4 h	7.47	2.9×10^5	2.7×10^5	1.8×10^4	6.7×10^0
	24 h	7.47	2.9×10^5	2.7×10^5	2.4×10^4	8.9×10^0
	4 d	7.47	2.4×10^5	2.1×10^5	2.8×10^4	1.3×10^1
	5 d	7.47	2.7×10^5	2.3×10^5	3.5×10^4	1.5×10^1
	7 d	7.47	2.4×10^5	2.0×10^5	3.7×10^4	1.8×10^1
	14 d	7.47	1.7×10^5	1.4×10^5	2.8×10^4	2.0×10^1
	28 d	7.47	7.5×10^4	6.2×10^4	1.3×10^4	2.1×10^1

Table XL. Time studies on the distribution of trivalent tracers between 0.0697 M DNNS and 7.47 M $HClO_4$.

Tracer	T	org	sq	D
Sc	30 m	4.8×10^4	8.0×10^3	6.0×10^0
	7 d	6.8×10^4	1.1×10^4	6.2×10^0
Cr	30 m	1.7×10^3	1.5×10^5	1.1×10^{-2}
	2 d	3.6×10^3	1.9×10^5	1.9×10^{-2}
	5 d	4.3×10^3	1.6×10^5	2.6×10^{-2}
	8 d	6.1×10^3	1.7×10^5	3.5×10^{-2}
	15 d	5.1×10^3	1.3×10^5	3.9×10^{-2}

REFERENCES

1. G. H. Morrison and H. Freiser, Solvent Extraction in Analytical Chemistry (John Wiley and Sons, Inc., New York, 1957).
2. G. H. Morrison and H. Freiser, Anal. Chem. 30, 632 (1958).
3. G. H. Morrison and H. Freiser, Anal. Chem. 32, 37R (1960).
4. G. H. Morrison and H. Freiser, Anal. Chem. 34, 65R (1962).
5. H. M. Irving, Quart. Rev. (London) 5, 200 (1951).
6. V. I. Kusnetsov, Usp. Khim. 23,654 (1954).
7. F. S. Martin and R. J. W. Holt, Quart. Rev. (London) 13, 327 (1959).
8. R. M. Diamond and D. G. Tuck, in Progress in Inorganic Chemistry Vol. II, F. A. Cotton, Ed. (Interscience Publishers, Inc., New York, 1960).
9. L. Pauling, Nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1960), p. 468: G. H. Haggis, J. B. Hasted, and T. J. Buchanan, J. Chem. Phys. 20, 1452 (1952); P. Cross, J. Burnham, and P. Leighton, J. Am. Chem. Soc. 59, 1134 (1937); J. Morgan and B. E. Warren, J. Chem. Phys. 6, 666 (1938).
10. M. Gwynne and E. Davies, J. Am. Chem. Soc. 74, 2748 (1952).
11. H. J. Vogt and C. J. Geaukpolis, Ind. Eng. Chem. 45, 2119 (1953)
12. H. A. Pagel and F. W. McLaffetry, Anal. Chem. 20, 272 (1948).
13. R. M. Diamond, J. Phys. Chem. 63, 659 (1959).
14. S. Tribalat, Anal. Chem. Acta 3, 113 (1948); 4, 228 (1950); 5,115 (1951); 6, 96 (1952); 8,22 (1953).
15. R. C. Fix and J. W. Irvine, Jr., in Massachusetts Institute of Technology Laboratory of Nuclear Science, Progress Reports, Nov. 30, 1955; May, 1956.
16. F. J. Welcher, Organic Analytical Reagents (D. Van Nostrand Company, Inc., New York, 1947).
17. E. B. Sandell, Calorimetric Determination of Transition Metals, 3rd. ed. (Interscience Publishers, Inc., New York, 1959).

18. D. G. Tuck and R. M. Diamond, J. Phys. Chem. 65, 193 (1961).

19. W. H. Baldwin, C. E. Higgins, and B. A. Soldano, J. Phys. Chem. 63, 118 (1959).

20. K. Alcock, S. S. Grimley, T. V. Healy, J. Kennedy, and H. A. C. McKay, Trans. Faraday Soc. 52, 39 (1956).

21. D. G. Tuck, J. Chem. Soc. 1957, 3202; 1958, 2783.

22. D. R. Olander, L. Donadieu, and M. Benedict, A. I. Ch. E. J. 7, 152 (1961).

23. J. Sutton, Distribution of Nitric Acid between Water and Ether, AERE C/R 438 (1949).

24. W. W. Wendlandt and J. M. Bryant, J. Phys. Chem. 60, 1145 (1956).

25. T. V. Healy and H. A. C. McKay, Trans. Faraday Soc. 52, 633 (1956).

26. S. M. Karpacheva, L. P. Khorkhorina, and A. M. Rozen, Zh. Neorgan. Khim. 2, 1441 (1957).

27. R. P. Bell, *The Proton in Chemistry* (Cornell University Press, Ithaca, New York, 1960).

28. F. S. Lee and G. B. Carpenter, J. Phys. Chem. 63, 279 (1959).

29. Y. K. Yoon and G. B. Carpenter, Acta Cryst. 12, 17 (1959).

30. R. E. Richards and J. A. S. Smith, Trans. Faraday. Soc. 47, 1261 (1951); Y. Kakinchi, H. Shono, H. Komatsu, and K. Kigoshi, J. Chem. Phys. 19, 1069 (1951).

31. D. E. Bethell and N. Sheppard, J. Chem. Phys. 21, 1421 (1953).

32. R. C. Taylor and G. S. Vidale, J. Am. Chem. Soc. 78, 5999 (1956).

33. M. Falk and P. A. Giguère, Can. J. Chem. 35, 1195 (1957); W. J. Biermann and J. B. Gilmour, Can. J. Chem. 37, 1249 (1959).

34. R. H. Stokes and R. A. Robinson, J. Am. Chem. Soc. 70, 1870 (1948).

35. E. Glueckauf, Trans. Faraday Soc. 51, 1235 (1955).

36. D. G. Miller, J. Phys. Chem. 60, 1296 (1956).

37. E. Glueckauf and G. P. Kitt, Proc. Royal Soc. (London) A328 (1955); Nature 171, 1010 (1953).

38. K. W. Pepper and D. Reichenberg, Z. Electrochem. 57, 183 (1953).

39. M. H. Waxman, Thesis, Brooklyn Polytechnic Institute, 1952.

40. K. N. Bascombe and R. P. Bell, Discussions Faraday Soc. 24, 158 (1957).

41. P. A. H. Wyatt, Discussions Faraday Soc. 24, 162 (1957).

42. E. Wicke, M. Eigen, and Th. Ackermann, Z. Phys. Chem. (Frankfurt) 1, 340 (1954).

43. Th. Ackermann, Discussions Faraday Soc. 24, 180 (1957).

44. D. Reichenberg and W. F. Wall, J. Chem. Soc. 1956, 3364.

45. R. Grahn, Arkiv Fysik 19, 147 (1960).

46. R. Grahn, Arkiv Fysik 21, 1 (1962).

47. R. Grahn, Arkiv Fysik 21, 13 (1962).

48. M. Eigen and L. De Maeyer, Proc. Royal Soc. (London) A247, 505 (1958).

49. M. Eigen and L. De Maeyer, in The Structure of Electrolytic Solutions, W. J. Hamer, Ed. (John Wiley and Sons, Inc., New York, 1959).

50. H. D. Beckey, Z. Naturforsch. 14A, 712 (1959).

51. S. Kato and R. Ishii, Sci. Papers Inst. Phys. Chem. Research (Tokyo) 36, 82 (1939); J. Axelrod and E. H. Smith, J. Am. Chem. Soc. 62, 33 (1940); R. J. Myers, D. E. Metzler, and E. M. Swift, J. Am. Chem. Soc. 72, 3767 (1950); A. H. Laurence, D. E. Campbell, S. E. Wiberley, and H. M. Clark, J. Phys. Chem. 60, 901 (156).

52. V. V. Fomin and A. F. Morgunov, Russ. J. Inorg. Chem. (English Transl.) 5, 670 (1960).

53. K. Naito and T. Suzuki, J. Phys. Chem. 66, 983 (1962).

54. A. S. Kertes and V. Kertes, J. Appl. Chem. 10, 287 (1960).

55. S. Siekierski and R. Gwóźdź, Nukleonika 5, 205 (1960).

56. A. S. Kertes, J. Inorg. Nuclear Chem. 14, 104 (1960).

57. H. Irving and D. N. Edgington, J. Inorg. Nucl. Chem. 10, 306 (1959).

58. A. S. Kertes and V. Kertes, Can. J. Chem. 38, 612 (1960).

59. R. A. Horne, J. Chem. Eng. Data 7, 1 (1962).

60. M. I. Tocher, T. J. Conocchioli, and R. M. Diamond (Lawrence Radiation Laboratory), unpublished data.

61. E. Hesford, H. A. C. McKay, and D. Scargill, J. Inorg. Nucl. Chem. 4, 321 (1957); E. Hesford and H. A. C. McKay, Trans. Faraday Soc. 54, 573 (1958); E. Hesford, H. A. C. McKay, and E. E. Jackson, J. Inorg. Nucl. Chem. 9, 229 (1959).

62. All half-lives taken from the "General Electric Chart of the Nuclides", Fifth Ed., Knolls Atomic Power Laboratory, April, 1956.

63. A. G. Maddock, W. Smulek, and A. J. Tench, Trans. Faraday Soc. 58, 923 (1962).

64. W. Korpak, "Alkyl Sulfoxides as Solvents for the Extraction of Mineral Acids and Urangl Nitrate," PAN-191/IV, 1960.

65. J. Mitchell, Jr., and D. M. Smith, *Aquametry*, (Interscience Publishers, Inc., New York, 1948), p. 235.

66. G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, (D. Van Nostrand Co., Inc., New York, 1950), pp. 282-3.

67. M. Desnoyer, "Dosage de L'Eau dans les Solvants Organiques par Absorption Infra-Rouge et Mesure des Constantes Diélectriques" CEA-1254, 1959.

68. L. P. Kuhn, J. Am. Chem. Soc. 74, 2492 (1952).

69. L. L. Ingraham, J. Corse, G. F. Bailey, and F. Stitt, J. Am. Chem. Soc. 74, 2297 (1952).

70. E. Hesford and H. A. C. McKay, J. Inorg, Nucl. Chem. 13, 156 (1960).

71. M. I. Tocher, T. J. Conocchioli and R. M. Diamond, "Extraction of Strong Acids into Tri-n-octyl Phosphine Oxide", to be submitted.

72. R. J. Allen and M. A. DeSesa, Nucleonics 15, 88 (Oct. 1957).

73. T. J. Collopy "The tributyl Phosphate-Nitric Acid Complex and its Role in Uranium Extraction", NLCO-749, 1958.

74. T. J. Collopy and J. F. Blum, J. Phys. Chem. 64, 1324 (1960).

75. T. J. Collopy and J. H. Cavendish, J. Phys. Chem. 64, 1328 (1960).

76. L. Damiani and V. Fattore, Energia Nucl. (Milan) 6, 793 (1959) [Nucl. Sci. Abstr. 14:5268 (1960)].

77. V. V. Fomin and E. P. Maiorova, Russ. J. Inorg. Chem. (English Transl.) 3, No. 2, 404 (1958).

78. V. V. Fomin, R. E. Kartushova, and E. P. Maiorova, Russ. J. Inorg. Chem (English Transl.) 5, 645 (1960).
79. W. Korpak and C. Deptuła, Nukleonika 5, 63 (1960)[Nucl. Sci. Abs. 14:18836 (1960)].
80. K. Naito, Bull. Chem. Soc. Japan 33, 363 (1960).
81. K. Nukeda, K. Naito, and U. Maeda, Bull. Chem. Soc. Japan 33, 894 (1960).
82. D. F. Peppard and J. R. Ferraro, J. Inorg. Nucl. Chem. 15, 365 (1960).
83. C. J. Hardy, B. F. Greenfield and D. Scargill, J. Chem. Soc. 1961, 90.
84. A. M. Rozen and L. P. Khorkhorina, Russ. J. Inorg. Chem. (English Transl.) 2, No. 8, 389 (1957).
85. Z. A. Sheka and E. E. Kriss, Russ. J. Inorg. Chem. (English Transl.) 4, 2505 (1959).
86. D. G. Tuck, Trans. Faraday Soc. 57, 1297 (1961).
87. F. L. Moore "Liquid-Liquid Extraction with High-molecular-weight Amines" NAS-NS-3101, 1960.
88. I. Newman and P. Klotz, J. Phys. Chem. 65, 796 (1961).
89. K. A. Allen, J. Phys. Chem. 60, 239 (1956).
90. J. T. Way, J. Roy. Agr. Soc. Engl. 11, 313 (1850); 13, 123 (1852); H. S. Thompson, J. Roy. Agr. Soc. Engl. 11, 68 (1850).
91. B. A. Adams and E. L. Holmes, U. S. Patent 2104501, Jan. 4, 1938.
92. C. D. Coryell and N. Sugarman, Eds., Radiochemical Studies: The Fission Products (McGraw-Hill Book Co., New York, 1951).
93. Many papers by many authors, J. Am. Chem. Soc. 69, 2769-2881 (1947).
94. J. F. Duncan and B. A. J. Lister, Quart. Rev. (London) 2, 307 (1948).
95. R. Kunin. Anal. Chem. 21, 87 (1949).
96. E. R. Tompkins, Anal. Chem. 22, 1352 (1950).
97. G. E. Boyd, in Annual Reviews of Physical Chemistry, Vol. 2, G. K. Rollefson and R. E. Powell, Eds. (Annual Reviews, Inc., Stanford, California, 1951).

98. R. W. Miner, Ed., Ion Exchange Resins in Medical and Biological Research (Symposium), Ann. N. Y. Acad. Sci. 57, 61-324 (1953).

99. Various Authors in Annual Reviews of Physical Chemistry Vols. 3-5, 7-10, 12 (Annual Reviews, Inc., Palo Alto, California, 1952-1962).

100. R. Kunin et al. Anal. Chem. 22-24, 26, 28, 30, 32 (1950-1962).

101. O. Samuelson, Ion Exchangers in Analytical Chemistry (John Wiley and Sons, Inc., New York, 1958).

102. R. Kunin, Ion Exchange Resins (John Wiley and Sons, Inc., New York, 1958).

103. F. C. Nachod and J. Schubert, Eds., Ion Exchange Technology (Academic Press, Inc., New York 1956).

104. C. Calmon and T. R. E. Kressman, Eds., Ion Exchangers in Organic and Bio-chemistry (Interscience Publishers, Inc., New York, 1957).

105. G. H. Osborn, Synthetic Ion Exchangers (Chapman and Hall, Ltd, London, 1961).

106. F. Helfferich, Ion Exchange (McGraw-Hill Book Co., Inc., New York, 1962).

107. G. Wiegner, J. Landw. 60, 111 (1912); Rothmund and Kornfeld, Z. Anorg. Allgem. Chem. 103, 129 (1918).

108. G. Weigner and H. Jenny, Kolloid-Z. 43, 268 (1927); H. Jenny, J. Phys. Chem. 36, 2217 (1932).

109. F. G. Donnan, Chem. Rev. 1, 73 (1924).

110. E. Ekedahl, E. Högfeldt, and L. Sillén, Acta Chem. Scand. 4, 556 (1950).

111. S. W. Mayer, J. Am. Chem. Soc. 72, 2293 (1950).

112. W. J. Argersinger, Jr., and A. W. Davidson, J. Phys. Chem. 56, 92 (1952).

113. J. F. Duncan, Proc. Roy. Soc. (London) 214A, 344 (1952); Austral. J. Chem. 8, 293 (1955).

114. E. Glueckauf, Proc. Roy. Soc. (London) 214A, 207 (1952).

115. C. W. Davies and G. D. Yeoman, Trans. Farday Soc. 49, 968, 975 (1953).

116. H. P. Gregor and M. H. Gottlieb, J. Am. Chem. Soc. 75, 3539 (1953); 76, 4639 (1954).
117. L. W. Holm, Arkiv Kemi 10, 151 (1956).
118. H. Sobue and Y. Tabata, Bull. Chem. Soc. Japan 29, 527 (1956).
119. G. E. Myers and G. E. Boyd, J. Phys. Chem. 60, 521 (1956).
120. G. E. Boyd, J. Lindenbaum, and G. E. Myers, J. Phys. Chem. 65, 577 (1961).
121. D. H. Freeman, J. Chem. Phys. 35, 189 (1961).
122. A. Jász, T. Lengyel, and G. Schay, Acta Chem. Acad. Sci. Hungary 30, 49 (1961).
123. H. P. Gregor, J. Am. Chem. Soc. 70, 1293 (1948); 73, 642 (1951).
124. G. E. Boyd and B. A. Soldano, Z. Electrochem. 57, 163 (1953).
125. G. H. Haggis, J. B. Hasted, and T. J. Buchanan, J. Chem. Phys. 20, 1452 (1952).
126. F. E. Harris and C. T. O'Konski, J. Phys. Chem. 61, 310 (1957).
127. S. A. Rice and F. E. Harris, Z. Physik. Chem. (Frankfurt) 8, 207 (1956); J. Chem. Phys. 24, 1258 (1956); J. Phys. Chem. 61, 1360 (1957).
128. J. L. Pauley, J. Am. Chem. Soc. 76, 1422 (1954).
129. H. F. Walton, D. E. Jordan, S. R. Samedy, and N. W. McKay, J. Phys. Chem. 65, 1477 (1961).
130. O. D. Bonner and L. L. Smith, J. Phys. Chem. 61, 326 (1959), give a list for uni- and divalent cations; see also references 101-106.
131. H. P. Gregor and J. I. Bregman, J. Colloid Sci. 6, 323 (1951); T. R. E. Kressman and J. A. Kitchener, J. Chem. Soc. 1949, 1208.
132. B. Chu and R. M. Diamond, Cornell University, unpublished data.
133. R. M. Wheaton and W. C. Bauman, Ind. Eng. Chem. 43, 1088 (1951).
134. R. Kunin and F. X. McCarthy, Ind. Eng. Chem. 41, 12 (1949).
135. K. A. Kraus and F. Nelson, J. Am. Chem. Soc. 76, 984 (1954).
136. S. Peterson, Ann. N. Y. Acad. Sci. 57, 144 (1953).

137. J. Bregman and Y. Murata, J. Am. Chem. Soc. 74, 1867 (1952).
138. H. P. Gregor, J. Belle, and R. A. Marcus, J. Am. Chem. Soc. 73, 2713 (1955).
139. J. Aveston, D. A. Everest, and R. H. Wells, J. Chem. Soc. 1958, 231.
140. C. B. Amphlett and J. Kennedy, Chem. and Ind. (London) 1958, 1200.
141. G. E. Boyd and B. A. Soldano, J. Am. Chem. Soc. 75, 6105 (1953).
142. R. M. Wheaton and W. C. Bauman, Ind. Eng. Chem. 45, 228 (1953); Ann. N. Y. Acad. Sci. 57, 159 (1953).
143. S. W. Mayer and E. R. Thompkins, J. Am. Chem. Soc. 69, 2866 (1947).
144. R. A. Robinson and R. H. Stokes, Electrolyte Solutions (Butterworths Scientific Publications, London, 1955).
145. W. M. Latimer, Oxidation Potentials (Prentice-Hall, Inc., New York, 1952).
146. International Critical Tables, Vol. VI (McGraw-Hill Book Co., Inc., New York, 1929).
147. H. V. Halban and J. Brüll, Helv. Chim. Acta 27, 1719 (1944).
148. J. J. Bucher and R. M. Diamond (Lawrence Radiation Laboratory) unpublished data.
149. G. R. Choppin and R. M. Dinius, Progress Report on Research in Nuclear Chemistry, Florida State University, 19 (1961).
150. H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, 3rd Ed. (Reinhold Publishing Corp., New York, 1958), p. 300.
151. R. Vandoni and M. Laudy, J. Chim. Phys. 49, 99 (1952); Landolt-Börnstein Tables (Springer-Verlag, Berlin, 1923) Supplement 3, Part 3, 2145.
152. H. P. Gregor and J. I. Bregman, J. Am. Chem. Soc. 70, 2370 (1948).
153. G. R. Choppin and R. H. Dinius, Inorg. Chem. 1, 140 (1962).
154. J. E. Gordon, Chem. and Ind. (London) 1962, 267.
155. R. H. Dinins and G. R. Choppin, J. Phys. Chem. 66, 268 (1962).

156. L. Kotin and M. Nagasawa, J. Am. Chem. Soc. 83, 1026 (1961).

157. R.M. Diamond, J. Am. Chem. Soc. 80, 4808 (1958).

158. H. Kakihana, N. Maruichi, and N. Namasaki, J. Phys. Chem. 60, 36 (1956).

159. W.A. Plateck and J. A. Marinsky, J. Phys. Chem 65, 2113 (1961).

160. R.M. Diamond, J. Am. Chem. Soc. 77, 2978 (1955).

161. "Dowex Chelating Resin A-1", Dow Chemical Co., Technical Services and Development Department, Midland, Mich.

162. "Ion Exchange Materials", Price List O, Bio-Rad Laboratories, Richmond, California, July 1, 1961.

163. H. Ohtaki and K. Yamasaki, Bull. Chem. Soc. Japan 31, 6 (1958).

164. C.J. Hardy, B.F. Greenfield, and D. Seargill, J. Chem. Soc. 1961, 174.

165. R.M. Diamond, K. Street, Jr., and G. T. Seaborg, J. Am. Chem. Soc. 76, 1461 (1954).

166. G.R. Choppin and A. Chetham-Strode, J. Inorg. Nucl. Chem. 15, 377 (1960).

167. J.P. Hunt and H. Taube, J. Chem. Phys. 19, 602 (1951).

168. T. Moeller, Inorganic Chemistry (John Wiley and Sons, Inc. New York, 1952), p. 140.

169. J. P. Surls, Jr., "Ion Exchange Behavior of Actinides and Lanthanides," Thesis, UCRL-3209 (1956).

170. J.P. Surls, Jr., and G. R. Choppin, J. Am. Chem. Soc. 79, 855 (1957).