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THE PRIMARY SOLVATION OF THE PROTON AND THE SOLVENT EXTRACTION OF MINERAL ACIDS

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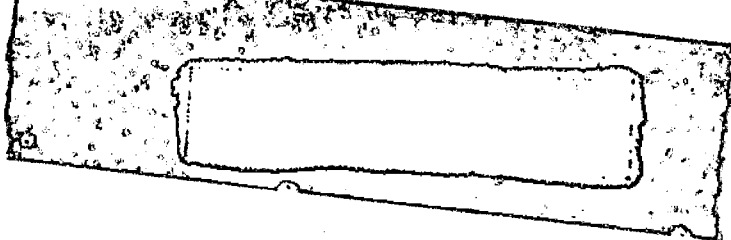
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September 1959

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AND THE SOLVENT EXTRACTION OF MINERAL ACIDS

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ABSTRACT

Evidence is presented for the presence of the trihydrated hydronium ion,  $\text{H}_3\text{O}(\text{H}_2\text{O})_3^+$ , in extracts from aqueous solutions into basic organic solvents of the strong acids,  $\text{HClO}_4$ ,  $\text{HBr}$ ,  $\text{HCl}$ ,  $\text{HInCl}_4$ , and  $\text{HAuCl}_4$ . In the organic phase, this species is further solvated by (hydrogen-bonded) coordination to the basic organic molecules, and so the degree of extraction depends partly upon the coordinating ability of the solvent molecules. With the somewhat weaker acids,  $\text{HNO}_3$  and  $\text{CCl}_3\text{CO}_2\text{H}$ , the proton coordinates preferentially in the low-dielectric-constant organic phase with the more basic (charged) anion than with water. The molecule formed is solvated by water and (or) organic solvent molecules, depending upon the solvent basicity. For solvents, such as the ethers and ketones, the resulting species is  $\text{HNO}_3 \cdot \text{H}_2\text{O}_{(sol)}$ , and with the more basic tributyl phosphate, an anhydrous species,  $\text{HNO}_3 \cdot \text{TBP}_{(sol)}$ , results.

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INTRODUCTION

Since the early years of the ionic theory, attempts have been made to measure the number of water molecules associated with an ion in aqueous solution. Various properties of solvated ions have been studied with this end in view, but the measurements do not give concordant results because they are concerned with different aspects of solvation. Much of the progress made in recent years can be ascribed to the differentiation now made between primary, i.e., first-shell or coordinate, and secondary solvation.<sup>1--5</sup> A review by Bockris discusses the various experimental techniques that have been employed,<sup>6</sup> and Stokes and Robinson give a more recent survey.<sup>2</sup>

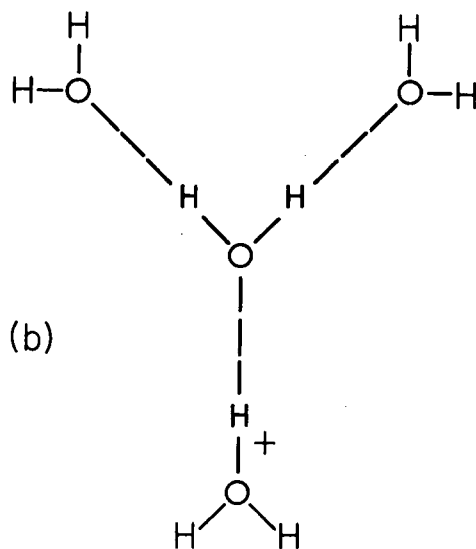
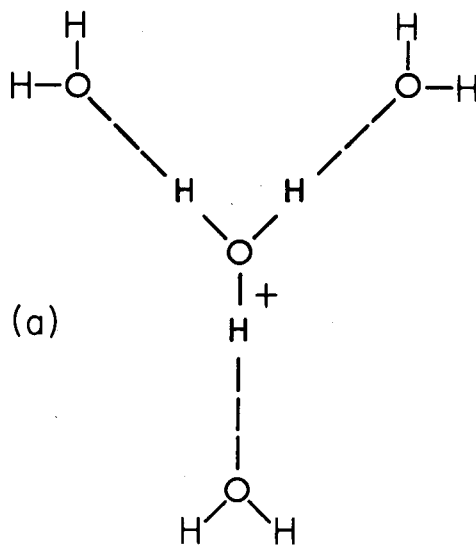
A great deal of attention has been directed to the hydration of the hydrogen ion. Because of its size (it is approximately  $10^4$  times smaller than, for example, the lithium ion), the bare proton has a much higher charge density than any other ion. This charge density makes the existence of the free proton in any solvating medium very improbable and, in particular, explains the strong

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binding of the proton to a water molecule to form the hydronium ion,  $\text{H}_3\text{O}^+$ . There is already evidence from X-ray,<sup>7</sup> nuclear-magnetic-resonance,<sup>8</sup> infrared,<sup>9</sup> and Raman<sup>10</sup> studies for the existence of this species in the solid state. An accumulation of indirect evidence now available suggests that in aqueous solution the  $\text{H}_3\text{O}^+$  group behaves as an ion that can be further solvated by a "primary" shell of three water molecules to give the symmetrical species shown in Fig. 1(a). Because of the unique structure of the  $\text{H}_3\text{O}^+$  ion, with approximately 1/3 of the positive charge concentrated on each proton, the hydrogen bonding of the three water molecules to the hydronium ion yields much stronger coordinate solvation than exists for other univalent positive ions of the same size, e.g.,  $\text{K}^+$ . With the latter ion, the charge can be regarded as being spread over the whole surface of the ion, and hydrogen bonding to the hydrating molecules is not possible.<sup>11,12</sup> A number of studies suggests the existence of this trihydrated hydronium ion in solution. For example, Robinson and Stokes have calculated hydration numbers from activity coefficient data,<sup>13</sup> and a more refined treatment by Glueckauf<sup>14</sup> leads to a value of 3.9 for the primary hydration number of the proton. Isopiestic measurements of the water vapor pressure over ion-exchange resins give a similar result.<sup>15,16</sup> The interpretation by Bascombe and Bell<sup>17</sup> of the acidity function of mineral acids in terms of ion-solvent interaction indicates the coordination of four water molecules to each proton, as do similar calculations by Wyatt.<sup>18</sup> One must note the work of Wicke, Eigen, and Ackermann on the specific heats of aqueous solutions, and their interpretation of a variety of data in terms of the  $\text{H}_3\text{O}(\text{H}_2\text{O})_3^+$  ion shown in Fig. 1(a).<sup>19</sup>

The study of the extraction of strong acids into organic solvents provides yet another and possibly more direct measurement of the primary hydration of the proton, especially if the anion is large enough to be unhydrated so that all the water carried into the organic phase is associated with the proton. The amount of water extracting into ethers with complex metal acids has been found to be four to five molecules per molecule of acid,<sup>20--23</sup> and electrolysis of ether extracts of  $\text{HFeCl}_4$  showed that this water is associated with the  $\text{H}^+$  ion only.<sup>24</sup> The present work arose out of studies of the extraction of the mineral acids into basic organic solvents and provides a further test of the degree of primary solvation of the proton. A preliminary account of these results has already been published.<sup>25</sup>



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Fig. 1. (a) The primary solvation of the hydronium ion. (b) Charge transfer in H<sub>9</sub>O<sub>4</sub><sup>+</sup>.



## EXPERIMENTAL

Reagents: Analytical grade perchloric, nitric, hydrochloric, hydrobromic, and trichloroacetic acids were suitably diluted some time before use. Commercial tri-*n*-butyl phosphate was purified by a procedure described previously,<sup>26</sup> and dibutyl cellosolve (ethylene glycol dibutyl ether) was shaken with 5% sodium carbonate solution, dried with anhydrous magnesium sulfate and stored over chromatographic alumina to prevent peroxide formation.<sup>27</sup>

In certain experiments, dilute solutions of solvent in analytical grade xylene were used.

Radioactive Tracers: Radioactive gold ( $\text{Au}^{198}$ ,  $t_{1/2} = 2.7$  d) and indium ( $\text{In}^{114}$ ,  $t_{1/2} = 50$  d) were obtained by neutron bombardment of the elements at the Atomic Energy Research Establishment, Harwell. Gold metal was dissolved in aqua regia, the solution taken to dryness on a steam-bath, and the residue dissolved in 2 *N* HCl. Indium metal was dissolved in concentrated HCl and stored in 6 *N* HCl to prevent hydrolysis. Suitable small aliquots of these solutions were added to the appropriate aqueous phase before equilibration.

Volume-Change Measurements: The procedure followed closely that described earlier by one of us.<sup>28</sup> Five ml of aqueous acid of known strength and an equal volume of solvent were pipetted carefully into a calibrated, stoppered measuring cylinder and gently shaken until equilibrium was reached. The increase in volume of the organic phase caused by the extraction of a measured quantity of acid gives, by a simple calculation, the composition of the extracted species. Acid concentrations were determined by titration with standard alkali; aliquots of the organic phase were dissolved in neutralized water-acetone mixture before titration.

The main supposition implicit in this method is that the total volume of the two-phase system shall remain constant throughout an experiment, and this has been confirmed in all our experiments unless otherwise noted in the text. One also needs to be sure that the solvent is effectively as insoluble in mineral-acid solution as it is in water; this has been checked by a technique described elsewhere.<sup>29</sup>

Volumetric Determination of Water: For the system perchloric acid - dibutyl cellosolve, the water content of the organic phase was determined volumetrically in a number of cases by the Karl Fischer method,<sup>30</sup> using a dead-stop end-point technique. One modification to the normal procedure was found to be necessary. In methyl alcohol (the titration medium), perchloric acid is strongly dissociated, so that the conductivity of the solution is high throughout the titration, making the end-point difficult to determine. This problem was overcome by the addition of 5 ml of A.R. grade pyridine, which complexes the perchloric acid by salt formation and thus reduces the initial conductivity. Under these conditions the end-point can be found accurately in the usual way.

Determination of Distribution Coefficients Using Tracer Methods: A number of distribution measurements were carried out with solutions of tri-*n*-butyl phosphate (TBP) in xylene and with both  $\text{HAuCl}_4$  and  $\text{HInCl}_4$  tracers to determine the number of solvent molecules associated with each extracted acid molecule in the organic phase. Varying (low) concentrations of TBP in xylene (5 ml) were allowed to come to equilibrium with 5 ml of a virtually constant aqueous phase, and the distribution coefficient,  $D$ , was determined by counting suitable aliquots of each phase, using a Philips NaI(Tl) crystal scintillator.

## RESULTS AND DISCUSSION

Perchloric Acid - Dibutyl Cellosolve: Dibutyl cellosolve (DBS) was chosen as a typical solvent of medium basicity and of relatively low solubility in and for water. Perchloric acid is extracted quite well by this solvent, as shown by the results in Table 1.

Table I

Extraction of $\text{HClO}_4$ into dibutyl cellosolve						
$\text{HClO}_4$ concn., aq. phase (M)	4.15	4.92	5.90	6.49	7.48	8.37
$\text{HClO}_4$ concn., org. phase (M)	0.15	1.10	1.91	2.33	3.02	3.79
$D_{\text{HClO}_4}$	0.036	0.22 <sub>2</sub>	0.32 <sub>4</sub>	0.35 <sub>9</sub>	0.40 <sub>4</sub>	0.44 <sub>1</sub>

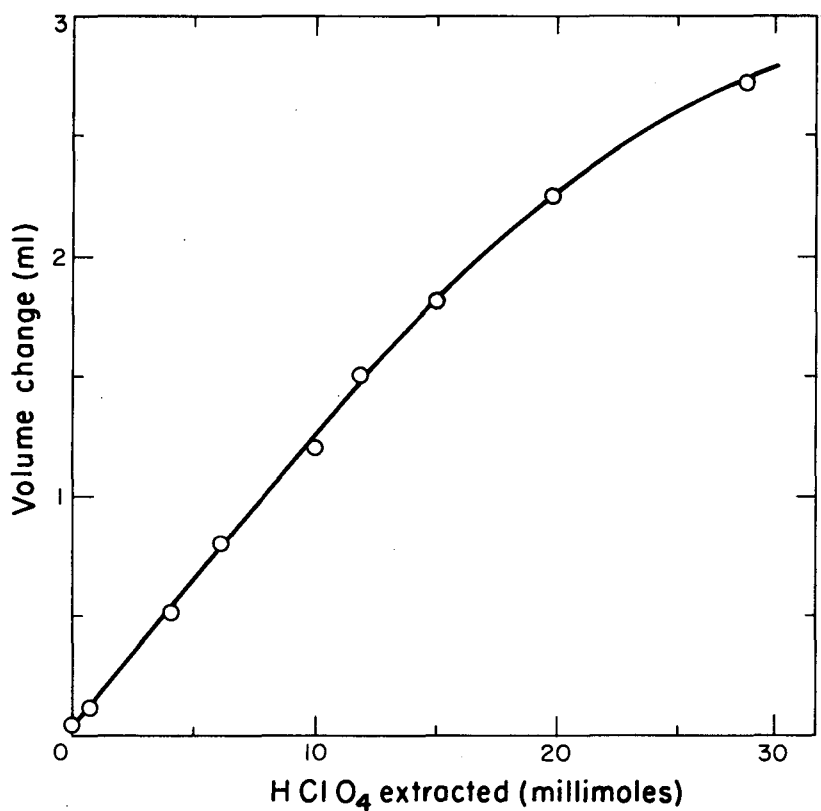
The experimental results for the increase in volume of the organic phase as a result of the extraction of perchloric acid are shown in Fig. 2. Up to approximately 2.2 M  $\text{HClO}_4$  in the organic phase, there is a linear dependence of  $\Delta V$  on total acid extracted, with a slope over this portion of the curve of 8.4 millimoles  $\text{HClO}_4$  extracted per 1 ml. increase in volume. This corresponds to the extraction of an aqueous solution of 845 g.  $\text{HClO}_4$  per liter, or 56.5%  $\text{HClO}_4$ , so that the  $\text{H}_2\text{O}:\text{HClO}_4$  ratio is 4.3. Similar experiments with perchloric acid and diisopropyl ketone gave a precisely analogous straight line of slope 8.65 millimoles/ml., corresponding to a  $\text{H}_2\text{O}:\text{HClO}_4$  ratio of 4.1. For this system the experiments were not carried to the point at which deviations from linearity in the plot became noticeable. (See Fig. 2.) The difference in the two ratios observed, 4.3 and 4.1, is probably not outside the experimental error.

The Karl Fischer determinations of water extracted into dibutyl cello-solve from perchloric acid solutions give the results in Table II, after correction for the solubility of water in the pure solvent.

Table II

Volumetric determination of water content of extract solutions of $\text{HClO}_4$ in DBS			
$\text{HClO}_4$ concn., org. phase (M)	$\text{HClO}_4$ concn., equil. aq. phase (M) (interpolated)	$\text{H}_2\text{O}$ concn., org. phase (M)	ratio $\text{H}_2\text{O}/\text{HClO}_4$
0.53	4.2	2.33	4.4
1.00	4.8	4.30	4.3
1.58	5.5	6.31	4.0
2.10	6.2	7.52	3.6

The mean of the first three results is  $4.2 \pm 0.3$  moles  $\text{H}_2\text{O}$  per mole  $\text{HClO}_4$ , which is in encouraging agreement with the volume-change results. With increasing acid concentration, however, there is a fall in the  $\text{H}_2\text{O}/\text{HClO}_4$  ratio which is especially noticeable at the highest acidity studied. The  $\text{HClO}_4$  concentrations are just within the range where the solvent volume-change method gives a linear plot (Fig. 2) indicating a constant water to acid ratio. The reason for this



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Fig. 2. Volume changes in the organic phase due to the extraction of perchloric acid into dibutyl cellosolve.

difference is possibly the following. The water concentration in the organic phase presumably can be represented by some expression such as

$$[\text{H}_2\text{O}] = \underline{h} [\text{HClO}_4] + f(\underline{a}_w, \underline{S})$$

where  $\underline{h}$  is the hydration number of the proton, and  $f(\underline{a}_w, \underline{S})$  represents the solubility of water in the solvent as a function of the activity of water in the equilibrium aqueous phase and of the activity of the solvent itself in the organic phase. Now in correcting the experimental titration results for water solubility, it has been assumed that this latter factor is constant over the range of acid concentrations studied and is equal to that of pure water. In fact, however, the increase in the aqueous phase acidity changes both  $\underline{a}_w$  and  $\underline{S}$ ; the former because more water is used up in hydration, and the latter because more solvent molecules are involved in secondary solvation of the proton in the organic phase. For these reasons, then,  $f(\underline{a}_w, \underline{S})$  probably decreases with increasing aqueous acid concentration, and we have increasingly over-corrected for water solubility in the organic phase. It seems possible that this explains part of the fall in the  $\text{H}_2\text{O}:\text{HClO}_4$  ratio shown in Table II.

The deviation from linearity shown in Fig. 2 becomes significant above ~ 15 millimoles  $\text{HClO}_4$  extracted; the equilibrium aqueous phase is approximately 6.3 M in perchloric acid, arising from an initial aqueous solution of 7 M  $\text{HClO}_4$ . Such an initial solution corresponds to 50%  $\text{HClO}_4$ , or a water to acid ratio of about 5.5. This suggests that the deviation may be the result of a total water deficiency, leading to incomplete hydration of the proton (see below). Such a deviation in the volume-change curve could also have arisen from an increase in the solubility of the organic solvent in the aqueous phase, but it was found that the solubility of DBS in 8 M  $\text{HClO}_4$  is essentially the same as the solubility in water.

In dilute aqueous solution, the trihydrated hydronium ion (Fig. 1(a)) must itself be considerably further solvated. At least one water molecule (possibly two) can be hydrogen-bonded to each of the three primary-shell water molecules, forming a less tightly bound secondary solvation shell. Beyond this secondary solvation shell, other water molecules will be oriented towards the

proton by successively weaker interactions. Now as the water to acid mole ratio approaches a value of four with increasing acid concentration, a greater proportion of the water molecules must be involved in the strong primary hydration, and there will be a decreasing amount of secondary-shell solvation. Even in moderately dilute aqueous solution, there may be insufficient water to provide secondary solvation for all the hydronium ions present. If basic organic solvent molecules are also present, as in the two-phase systems under discussion, they can also hydrogen bond to the primary-shell water molecules. Thus, the inability of the aqueous acid phase to provide secondary solvation for the hydronium ion forces the latter across into the basic solvent to solvate there. Ample evidence is available that coordination with the solvent is involved, since acids show no significant extraction into nonbasic organic solvents and show lowered extraction if the coordinating group in the molecule is blocked.<sup>11,12,31</sup> The results of the present paper show that when the strong acids, such as  $\text{HClO}_4$  and the metal complex acids (e.g.,  $\text{HFeCl}_4$ ,  $\text{HAuCl}_4$ ,  $\text{HInCl}_4$ ), extract from aqueous solutions of less than about 7 to 8 M concentration, the hydronium ion extracts retaining its primary hydration shell. The coordination of solvent molecules of medium basicity (i.e., ethers, ketones, esters, etc.) is therefore to this shell of water molecules, and does not involve direct coordination to the proton, that is, displacement of the primary hydration shell. Organic molecules do not, in general, replace the primary-shell water molecules because the  $\text{H}_2\text{O}$  molecule is small and possesses a relatively high dipole moment. The ion-water interactions are stronger than the corresponding ion-solvent interactions, and the water molecules can pack around the ion in a primary solvation shell much more easily than can the bulkier organic molecules. These considerations do not apply, however, to the very basic amine extractant systems, nor to any but the very strong acids (see below).

The order of extraction of the strong acids is usually  $\text{HCl} < \text{HBr} < \text{HI} < \text{HClO}_4$ , and this illustrates a second major influence on extraction behavior. Anions cannot receive primary (coordinate) solvation in the organic phase (if we eliminate alcohols and amines from consideration in this paper) and so they certainly will extract with difficulty if they are small enough to be strongly

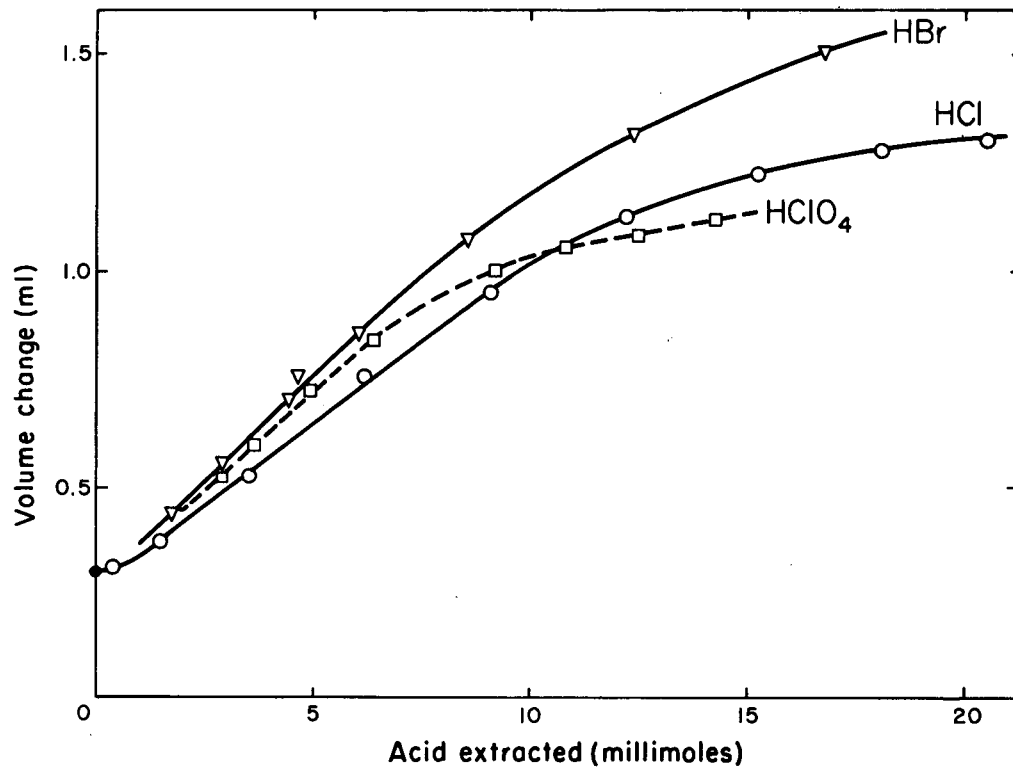
hydrated in aqueous solution. But the larger the anion, the smaller its primary hydration energy and so the smaller the loss in energy in transferring to the organic phase. With large ions the disruption of the hydrogen-bonded water structure by the bulk of the ion actually helps eject the ion into the nonstructured organic solvent.<sup>11</sup> That is, the loss in ion-solvation energy is compensated for by the increased number of water-water hydrogen bonds formed. Thus, the hydronium ion goes into the organic phase to achieve better solvation, and the large anions go across in order of increasing size to maximize the water-water interactions.

The Extraction of Strong Acids into Tri-n-butyl Phosphate: The extractions of the hydrogen halides into solvents such as ethers and ketones is too poor to permit one to carry out volume-change experiments on such systems. With strongly basic solvents such as the phosphate esters, however, there is significant extraction of these acids, as well as of  $\text{HClO}_4$ . The solvent volume changes found in the extraction of  $\text{HCl}$ ,  $\text{HBr}$ , and  $\text{HClO}_4$  into tri-n-butyl phosphate (TBP) are shown in Fig. 3. The results obtained from these experiments are summarized in Table III.

Table III  
Volume changes in the extraction of  $\text{HCl}$ ,  $\text{HClO}_4$ , and  $\text{HBr}$  in TBP

Acid	Slope of straight line portion (millimoles/ml)	$\text{H}_2\text{O}$ :acid ratio	Approximate beginning of deviations from linearity			
			Millimoles extracted	Organic phase molarity	Aqueous phase molarity	Original aqueous phase molarity
$\text{HCl}$	13.1	$3.0 \pm 0.2$	9.5	1.58	5.4	6.2
$\text{HClO}_4$	11.1	$3.1 \pm 0.3$	7	1.20	3.1	5.6
$\text{HBr}$	10.5	$3.4 \pm 0.2$	9.5	1.55	4.9	5.8

The errors quoted for the water to acid ratio are estimated from the uncertainties in deducing the slope of the experimental curve. The value of approximately three found for this ratio is in agreement with the hydration number of four deduced above, as the following discussion indicates. It has been shown that the solubility of water in TBP at  $\sim 25^\circ\text{C}$  is equivalent to 1 mole

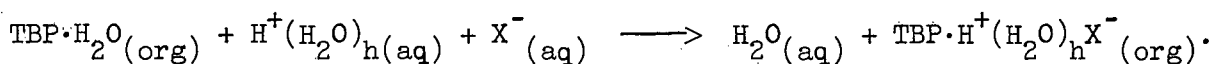


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Fig. 3. Volume changes in the organic phase due to the extraction of HCl, HBr, and HClO<sub>4</sub> into tributyl phosphate.

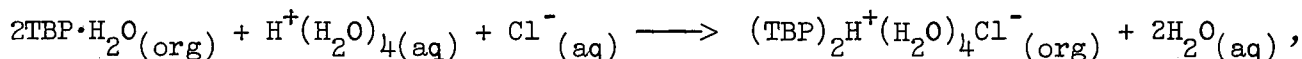


of water per mole of TBP.<sup>26,32,33</sup> There is evidence that this solubility is the result of the formation of a weakly hydrogen-bonded complex  $\text{TBP}\cdot\text{H}_2\text{O}$ .<sup>32</sup> The solvent volume change at any given acidity represents the effect of extracting both  $\text{H}_2\text{O}$  and  $\text{HX}(\text{H}_2\text{O})_{\underline{n}}$  in a proportion that depends on their respective activities in the aqueous phase and on the formation constants of the species  $\text{TBP}\cdot\text{H}_2\text{O}$  and  $\text{TBP}\cdot\text{HX}(\text{H}_2\text{O})_{\underline{n}}$ . As the aqueous acid concentration is increased, the over-all effect in the organic phase is the increasing replacement of  $\text{H}_2\text{O}$  by  $\text{HX}(\text{H}_2\text{O})_{\underline{n}}$ . The result can be written as



The slope of the linear part of the curves in Fig. 3 [ $\delta(\Delta V)/\delta[\text{HX}]_{\text{org}}$ ] is therefore the volume change associated with this process and gives a concentration equivalent to  $\text{HX}(\text{H}_2\text{O})_{\underline{n}-1}$ . Thus the experimental results again indicate that the proton is tetra hydrated in the solvent, and the discussion is also in agreement with the suggestion that under these conditions the extraction process can be regarded as a competition between water and the organic solvent for the secondary solvation positions of  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ .

It is noticeable that at very low acid concentrations in the organic phase (see HCl-TBP curve, Fig. 3), the slope of the plot of  $\Delta V$  vs.  $[\text{HX}]_{\text{org}}$  decreases. It seems possible that this is the result of the over-all reaction



which is only likely to occur when the concentration of TBP is much greater than that of acid in the organic phase (see below).

The reasons for the marked deviations from linearity (Fig. 3) at high acidities are not completely clear but must certainly involve the fact that at high acidities there is no longer sufficient water to solvate all the ions completely. Similar effects appear in the work of Baldwin, Higgins, and Soldano,<sup>34</sup> who determined the amount of water in TBP extracts of aqueous hydrogen halide solutions by direct titration.

At high  $\text{HClO}_4$  concentrations there is an increase in the total volume of the two-phase system after equilibration amounting to about 2% of the original volume. Under these conditions it is not possible to interpret the volume-change results. No reason for this effect is immediately forthcoming.

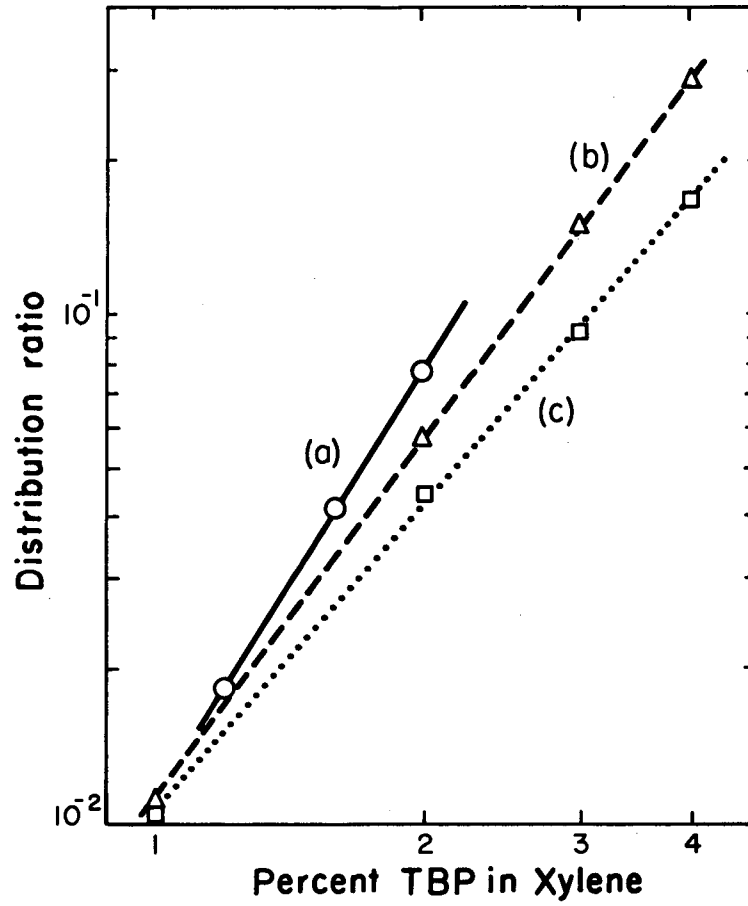
The Extraction of  $\text{HAuCl}_4$  and  $\text{HInCl}_4$  into Solutions of TBP in Xylene:

The technique of measuring the variation of  $\underline{D}$  with TBP concentration, using dilute solutions of TBP in some inert solvent, has been employed in order to determine the number,  $\underline{n}$ , of TBP molecules attached to each extracted acid molecule:

$$\underline{n} = \delta \log \underline{D} / \delta \log [\text{TBP}] .$$

This method is applicable only at low concentrations of TBP and at very low concentrations of the extracted species. A discussion of the limits of this technique has been given by Hesford and McKay.<sup>35</sup> The correction necessary when the inert solvent itself extracts a significant amount of the species in question is discussed elsewhere.<sup>36</sup>

The acids studied in the solvent volume-change experiments are unsuited for this type of experiment because of their comparatively low distribution coefficients. We have therefore used aqueous tracer solutions of the complex chlorides of Au(III) and In(III) tracers in dilute HCl. These compounds are known to extract into basic solvents as  $\text{HAuCl}_4$  and  $\text{HInCl}_4$ , and are strong acids, similar to  $\text{HClO}_4$ . The extraction of these acids is much greater than that of HCl, so that the results are believed to be unaffected by the slight coextraction of HCl. The results for  $\text{HAuCl}_4$  are shown in Fig. 4. For the lowest concentration of Au(III) used, the slope of curve (a) gives  $\underline{n} = 2.9$ . This value is in agreement with the arguments advanced earlier for the existence of a  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$  species, which under these experimental conditions can coordinate a TBP molecule in the organic phase at each of the  $\text{H}_2\text{O}$  molecules in the primary hydration shell of  $\text{H}_3\text{O}^+$ . As the concentration of extracted acid molecules in the organic phase increases,  $\underline{n}$  begins to fall; curves (b) and (c) have slopes of 2.4 and 1.95 respectively. The absolute values of the latter slopes have little significance, but serve to show the effect of the increasing competition between the hydronium



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Fig. 4. Extraction of gold(III) chloride into solutions of tributyl phosphate in xylene. Aqueous phase is 2 M in HCl: (a)  $3 \times 10^{-3}$  M in  $\text{AuCl}_4^-$ , (b) 0.1 M in  $\text{AuCl}_4^-$ , (c) 0.2 M in  $\text{AuCl}_4^-$ .

ions for the available TBP molecules. The lower limit of this competition is reached when macro amounts of acid are extracted, as is the case in the volume-change experiments. Here the results given earlier are in agreement with  $\underline{n} = 1$ . There is a further reason for believing that a value of  $\underline{n} = 3$  is only possible when the concentration of free TBP in the organic phase is greatly in excess of the concentration of extracted acid. It has been suggested earlier that the  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$  species is especially favorable for the coordination of one molecule of a basic solvent, since it can undergo transfer of charge to give the species shown in Fig. 1(b), clearly one of three such forms. This should result in a strong 1:1 solvent-acid complex; the 2:1 and 3:1 complexes should have smaller formation constants.

For  $\text{HInCl}_4$ -TBP, reasonable extraction into dilute solutions of TBP in xylene could only be achieved in the presence of salting-out agents. For a solution approximately  $14 \text{ M}$  in  $\text{LiCl}$  a value of  $\underline{n} = 2.7$  was found. Under such conditions, where there is not enough "free" water in the aqueous phase to allow the coordination of three  $\text{H}_2\text{O}$  molecules per  $\text{H}_3\text{O}^+$ , TBP molecules can probably be hydrogen-bonded into the primary hydration shell of the  $\text{H}_3\text{O}^+$  ion.

Nitric and Trichloroacetic Acids: Nitric acid extracts well into dibutyl cellosolve, as it does into other similar solvents (see reference 12). The extraction data are given in Table IV.

The solvent volume-change results from this system (Fig. 5) show a linear dependence of  $\Delta V$  on total  $\text{HNO}_3$  extracted over the whole range studied. The slope of 20.6 millimoles per ml. of solvent volume increase is to be compared with a value of 18.1 millimoles/ml found for the higher analogue dibutyl carbitol;<sup>28</sup> this latter value corresponds to extraction of the species  $\text{HNO}_3 \cdot \text{H}_2\text{O}$ . It is possible that the present (larger) value arises as a result of the two processes:



and

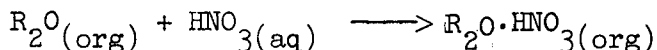
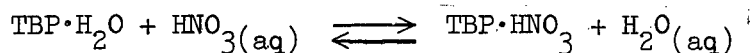


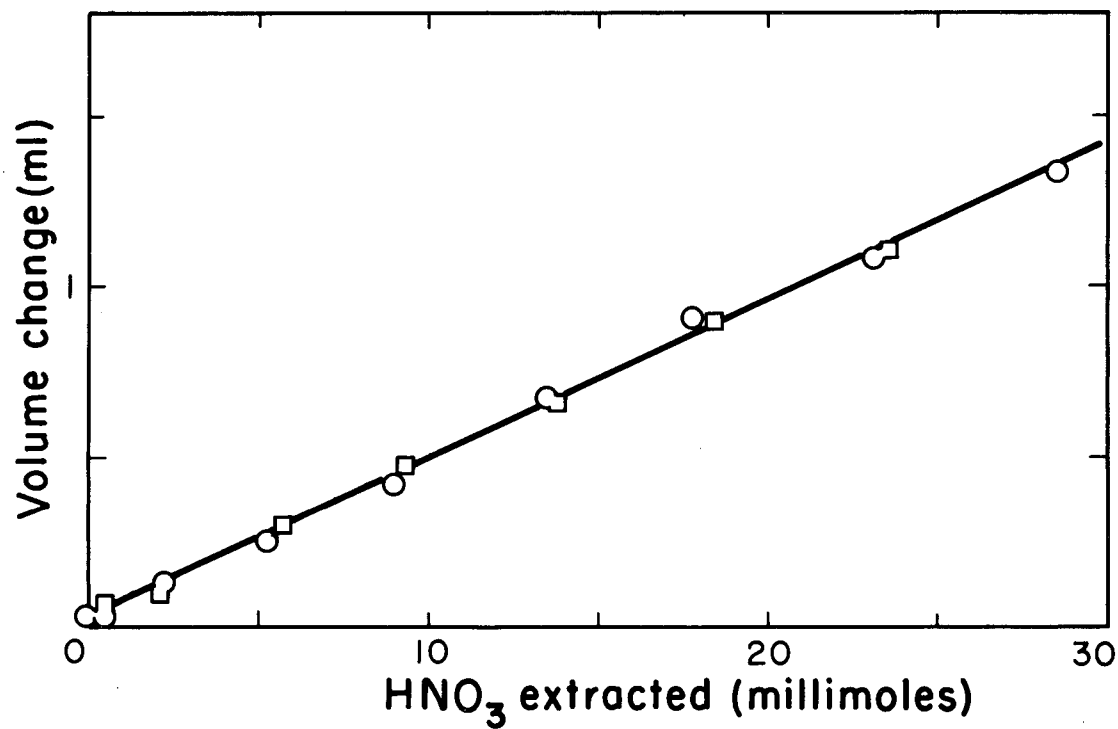
Table IV

Extraction of HNO <sub>3</sub> into dibutyl cellosolve		
HNO <sub>3</sub> concn., aq. phase (M)	HNO <sub>3</sub> concn., org. phase (M)	D <sub>HNO<sub>3</sub></sub>
1.60	0.09	0.055
3.02	0.41	0.13 <sub>6</sub>
4.30	1.09	0.25 <sub>3</sub>
5.34	1.74	0.32 <sub>6</sub>
6.58	2.51	0.38 <sub>2</sub>
7.65	3.22	0.42 <sub>1</sub>
8.82	3.96	0.45 <sub>0</sub>
9.92	4.68	0.47 <sub>2</sub>
11.04	5.33	0.48 <sub>3</sub>
12.23	6.14	0.50 <sub>2</sub>

The solvent volume-change arising from the latter process yields a value of 42.5 millimoles/ml,<sup>26</sup> so that the first process must predominate. In general, it seems that the hydration number of nitric acid extracted into organic solvents is seldom above unity, and in only one case does a value near four appear. (For pentaether,<sup>37</sup> the hydration number found by direct titration is 6.6, but the solubility of water in this solvent is high, and the possibility of inter- and intra-molecular interactions of the basic groups rather confuses the issue.) In HNO<sub>3</sub> extraction into strongly basic solvents, however, the anhydrous acid may be present. For example, in extraction into TBP, involving the strongly basic phosphoryl group, the acid is present as HNO<sub>3</sub>·TBP,<sup>26,32</sup> and the process can be represented as



Thus, in extract solutions of HNO<sub>3</sub> in a basic solvent, the proton is essentially different in its chemical bonding and environment from its state in similar extract solutions of strong acids such as HClO<sub>4</sub>, HI, HBr, and HCl.



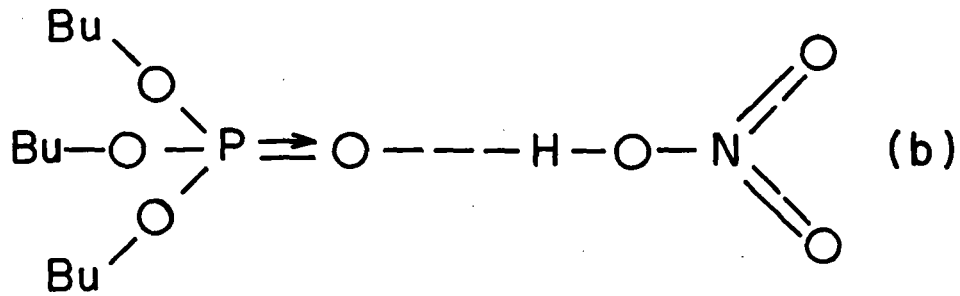
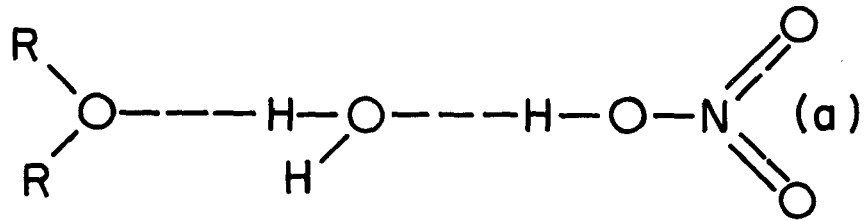
MU-18324

Fig. 5. Volume changes in the organic phase due to the extraction of HNO<sub>3</sub> into dibutyl cellosolve.

We believe that the reason lies in the comparatively low ionization constant of nitric acid ( $K_i = 23$ )<sup>38</sup> relative to those of HCl, HBr, and HClO<sub>4</sub>, for which values of  $p_K = -7$  and higher have been estimated.<sup>39,40</sup> (The value of  $K_i = 40$  found for HClO<sub>4</sub> by N.M.R. measurements<sup>41</sup> seems to be unreasonably low for this acid.)

Because of its relatively low ionization constant, nitric acid exists to a large extent as  $\text{HNO}_3$  molecules in concentrated aqueous solution. This association will be greatly enhanced in solutions in organic solvents of low dielectric constant. In aqueous solution,  $\text{NO}_3^-$  does not compete too well with  $\text{H}_2\text{O}$  for coordination with the proton until moderately concentrated solutions are reached where the  $\text{NO}_3^-$  concentration is becoming high and that of water is becoming low. In the low-dielectric-constant organic phase, the ion-ion interaction is much stronger, and the  $\text{NO}_3^-$  can and does take the proton away from its primary hydration shell. If the solvent is not too basic, a water molecule will hydrogen-bond to the  $\text{HNO}_3$  molecule and will in turn be similarly bonded to by an organic molecule (Fig. 6(a)). This behavior has been observed with extraction into ethers, polyethers, and ketones.<sup>28,42,43</sup> However, a more basic solvent such as TBP can compete favorably with water for coordination to the  $\text{HNO}_3$  molecule, and so leads to the species represented in Fig. 6 (b).

Thus the small primary hydration numbers of  $\text{HNO}_3$  in organic solvents ( $0 \rightarrow 1$ ) are due to the ability of  $\text{NO}_3^-$  to compete with  $\text{H}_2\text{O}$  for the proton in a low-dielectric-constant medium. Whether the value is 0 or 1 or something between, indicating a mixture, depends upon the basic strength of the solvent molecule, that is, upon its ability to compete with  $\text{H}_2\text{O}$  for hydrogen-bonded coordination to the  $\text{HNO}_3$  molecule. In a basic solvent of high dielectric constant, it is possible that  $\text{HNO}_3$  would be more dissociated and would behave more like the other strong acids, showing a primary hydration number approaching four. In either of the cases represented by Figs. 6(a) and 6(b), the chemical bonding of the  $\text{NO}_3^-$  ion and the solvent molecule to the proton compensates for the latter's loss of aqueous solvation energy on its transfer from the aqueous to the organic phase. Consequently, the nitric acid molecule is extracted readily from aqueous solution, even better than perchloric acid (see Tables I and IV). The difference between the chemical state of these two acids



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Fig. 6. Coordinated nitric acid species in (a) ethers and (b) tributyl phosphate.



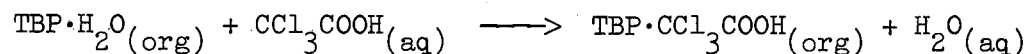
in organic-extract solutions is also reflected in the electrical conductivity of the solutions. Ether-extract solutions of  $\text{HNO}_3$  are much poorer conductors than are the corresponding solutions of  $\text{HClO}_4$ .

Evidence that the different (low) hydration numbers of  $\text{HNO}_3$  are really due to its weakness as an acid, that is, evidence for the importance of acid strength (or base strength of the anion) in determining the extent of proton hydration in the solvent phase, is clearly shown by the extractive behavior of trichloroacetic acid ( $p_K = 0.7$ ).<sup>44</sup> This acid extracts well into dibutyl cellosolve, as shown by the results given in Table V.

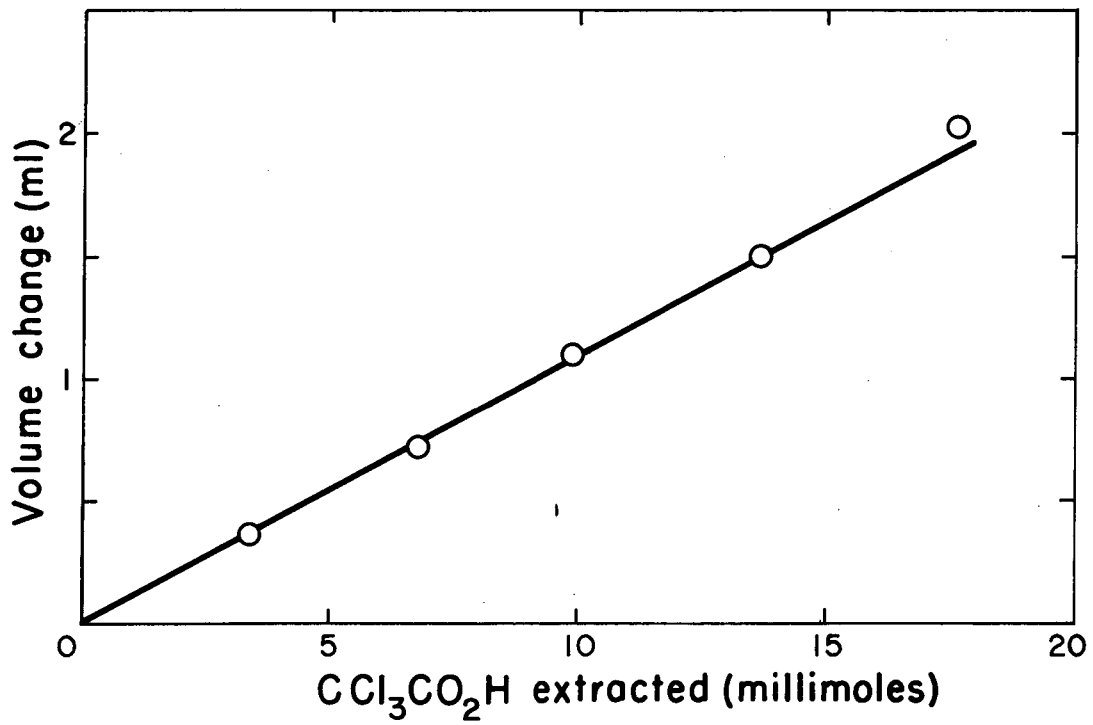
Table V

Extraction of $\text{CCl}_3\text{COOH}$ into dibutyl cellosolve					
$\text{CCl}_3\text{COOH}$ concn., aq. phase (M)	0.10	0.20	0.28	0.37	0.52
$\text{CCl}_3\text{COOH}$ concn., org. phase (M)	0.63	1.18	1.63	2.10	2.51
$D\text{-CCl}_3\text{COOH}$	6.3	5.9	5.8	5.6	4.8

We have measured the ~~changes~~ in volume of the organic phase resulting from the extraction of this acid into DBS (Fig. 7) and TBP (Fig. 8). The results are remarkably similar to those for nitric acid. For DBS the slope of 9.95 millimoles/ml corresponds to a solution in which the  $\text{CCl}_3\text{COOH}:\text{H}_2\text{O}$  ratio is 1:0.9. For TBP, the analogy with  $\text{HNO}_3$  is even closer. Up to a TBP: $\text{CCl}_3\text{COOH}$  ratio of approximately one (18.1 millimoles  $\text{CCl}_3\text{COOH}$  extracted), the reciprocal of the volume change is 12.5 millimoles/ml. Taking the extrapolated density of  $\text{CCl}_3\text{CO}_2\text{H}$  as 1.62,<sup>45</sup> one finds that the volume change for the process

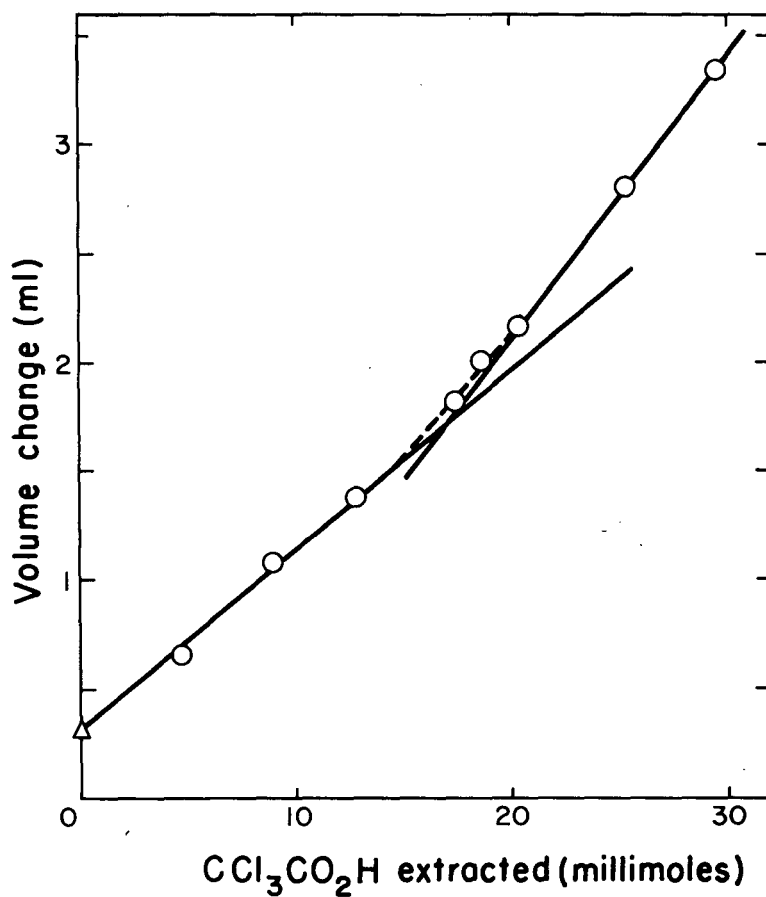


is (101 - 18) ml/mole, corresponding to 12.1 millimoles/ml. The excellence of the agreement with the experimental result is perhaps rather fortuitous, because



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Fig. 7. Volume changes in the organic phase due to the extraction of CCl<sub>3</sub>COOH into dibutyl cellosolve.



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Fig. 8. Volume changes in the organic phase due to the extraction of CCl<sub>3</sub>COOH into tributyl phosphate;  $\Delta V$  at zero acid is taken from previous work.<sup>26</sup>

the density of liquid  $\text{CCl}_3\text{COOH}$  is an extrapolated value. However, there seems to be little doubt possible about the conclusion. Above a  $\text{CCl}_3\text{CO}_2\text{H}:\text{TBP}$  ratio of 1.0 in the organic phase, the phosphoryl group is completely saturated, and the volume-change slope changes to approximately 7.9 millimoles/ml. Here again then, there is rather less than one molecule of  $\text{H}_2\text{O}$  per acid in the region in which extraction is due to the basic oxygen of the P-O-C bond; nitric acid behaves in precisely the same way.<sup>26</sup> It seems, then, that as far as hydration in the organic phase of solvent extraction systems, nitric and trichloroacetic acids have very similar behavior. This is also borne out by results on the extraction of these acids into diisopropyl ketone.<sup>43</sup>

Comparison with Previous Results: As noted in the introduction, there are results in the literature on the water carried into organic solvents with the complex halo-acids of the transition elements. These results were usually obtained by direct titrimetric estimation of the water content of the organic phase, which, as mentioned earlier, involves certain corrections. Laurene *et al.*<sup>22</sup> found 5 molecules of water per molecule of  $\text{HFeCl}_4$  in isopropyl ether, but their method makes no correction for the water merely dissolved in the solvent. Other work on the water associated with  $\text{HFeCl}_4$  in organic solvents<sup>20-23</sup> also gives results slightly higher than found in this work,<sup>20,21,22,23</sup> namely, four to five molecules.

The value of four for the primary hydration number of the proton has been previously suggested by a number of authors, and the present work appears to be in complete agreement with this value. It may also be noted that the work of Baldwin, Higgins, and Soldano<sup>34</sup> can be interpreted in the light of the present work as giving a value of  $\underline{h} = 4$ . They find that the total concentration of water in acid (extract) solutions of  $\text{HCl}$ ,  $\text{HBr}$ , and  $\text{HI}$  in TBP increases as approximately 3.3 times the concentration of acid. This type of experiment gives the same result as the solvent-volume-change experiments on the same systems (Fig. 4), and by a similar argument as that used above leads to a value of  $\underline{h} \approx 4.3$ .

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