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ABSTRACT

Breakthrough histories of a few non-aqueous ion-exchange reactions involving hydrogen ion have been measured, in order to calculate the contributory diffusional rates by use of known design-calculation methods, and to attempt to interpret these rates. For this purpose, it has been necessary to review the available calculation methods.

Diffusivities so determined were found to be less than one-thousandth as large in dry benzene and dry acetone as in water, while the lower alcohols gave intermediate values. Comparison of the diffusion rates with known properties of these solvents suggests that their base strength may be a determining factor. The wide variation observed in the diffusivities indicates that empirical design procedures will be less effective than usual in arriving at practicable operating conditions and that theoretical design principles will be a useful supplement to available experimental measurements.

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An exploratory study has been made of a hydrogen-ion exchange reaction in non-aqueous solvents, using a typical sulfonated polystyrene resin (Dowex 50). The mass-transfer rates for this exchange, calculated from breakthrough measurements, are indicative of general column performance in the hydrogen cycle for given solvent-resin pairs. However, they must be combined with equilibrium data on a particular exchange before a complete prediction of the performance for that reaction can be made. This paper will review the principles of column design, and will then show how the data reported here can be interpreted for that purpose.

Outline of Column-Performance Theory

Two equally important factors determine column performance in any ion-exchange process. The first is the equilibrium constant for the exchange; this usually cannot be predicted without measurement, but often can be extrapolated from one solvent to another. In the available calculation methods, the equilibrium must be expressed as a mass-action function (K^{II}) calculated as if the exchanging ions have the same valence. For comparison with adsorption columns, an "equilibrium parameter", r, will be used, which for ion-exchange is simply $1/K^{II}$. (6, 16)

As was first indicated by Boyd, Adamson, and Myers (1), the rate of
exchange may be controlled by external, or film, diffusion (i.e., by
mass-transfer between the bulk fluid and the outer surfaces of the resin
particles), or by internal, or particle, diffusion within the "solid"
phase. In aqueous systems, at low concentrations of electrolytes in
solution, external diffusion is observed to be rate-determining. In
non-aqueous systems, due to smaller extent of ionization, internal
diffusion is more likely to be the slowest step, regardless of the
concentration level in the liquid phase. Hence the ensuing discussion
will be based upon this step as rate-controlling.

Column-performance studies, for fixed-bed columns, are concerned
with the concentration history of the column effluent; that is, with
the variation in concentration as a function of time or of volume of
effluent. The same principles are involved in two different types of
operation: saturation, in which one or more solute components are
separated from the solvent; and chromatography, in which two or more
solute components are separated from one another. In both these
operations, it is desirable to obtain a concentration-history curve
that is steep by comparison to the total volume of solution handled in
any one cycle. For saturation, a steep breakthrough curve makes it
possible to utilize a large fraction of the theoretical capacity of
the resin. For chromatography, steep-sided zones provide better
recoveries and purities of the individual components.

The relative steepness improves as the volume of the resin bed
increases, and also as the exchange rate increases. In order to use
generalized mathematical results, these two factors must be combined
into a dimensionless column-capacity parameter, Σ. In experimental

measurements of performance, a Σ value applies both to the column con-ditions and to the resulting breakthrough history. It is often evaluated from the latter, as will be shown, and then used to evaluate a rate coefficient. The rate coefficient, in turn, can be used with other proposed residence times (ratios of column volume to flowrate) to determine appropriate values of Σ.

$$\Sigma = k_p a_p D_G v f_E / R$$
$$= \frac{4 D_s \pi^2}{d_p^2} \circ D_G \circ \frac{v f_E}{R} \tag{1}$$

Here k_p is the mass-transfer coefficient for particle diffusion, a_p is the effective outer-surface area of the particles, D_G is a dimensionless ratio of concentrations in the resin and in solution, $v f_E$ is the void-volume of the column, R is the volumetric flowrate of solution through the column, D_s is the mean diffusivity of the exchanging components in the solid phase, and d_p is the average diameter of the resin particles. The column-capacity parameter, which has also been called the "thickness modulus" of the bed (9), is equal to the number of transfer units (NTU) for a fixed-bed column, or, roughly, to the somewhat inapplicable concept of a number of theoretical plates (NTP).

The volumetric throughput of the column must also be converted to dimensionless units in order to use generalized mathematical solutions for breakthrough behavior. Therefore we define a solution-capacity parameter ("solution-volume modulus") Θ:

$$\Theta = k_p a_p \circ \frac{V - v f_E}{R}$$
$$= \frac{4 D_s \pi^2}{d_p^2} \circ \frac{V - v f_E}{R} \tag{2}$$

Another useful parameter is the throughput ratio, Θ/Σ, which is actually a simple stiochiometric ratio. For each resin bed of a particular exchange capacity, there exists a volume V_{stoic} which would be just sufficient to utilize this capacity if the exchange were quantitative.

The throughput ratio at any value of cumulative effluent from the start of the run, $V - vf_E$, is given by

$$\frac{\Theta}{\Sigma} = \frac{V - vf_E}{V_{stoic}} \tag{3}$$

The experimental part of this paper has as its object the evaluation of $\underline{D}_s$, by way of Σ, in typical cases. When $\underline{D}_s$ is known or can be estimated, calculation of the parameters Σ and Θ under new conditions of column operation follows readily.

The concentration of a solute A in the effluent is used in dimensionless form as a ratio to the entering concentration, C_A/C_o. For a feed containing only a single solute, then, the breakthrough curve or concentration history depends upon the value of the equilibrium function K^{II} in accordance with the following outline. It must be emphasized that the general differential equations have never been solved exactly, and that the results are available only as a series of special cases which together cover all values of K^{II}, at all except relatively low values of Σ. The ranges of K^{II} behavior are as follows:

1. _Completely irreversible exchange_ ($K^{II} = \infty$, or $r = \Theta$). The effluent concentration is derived in the accompanying paper (15), as

$$\frac{c_A}{c_o} = 1 - \frac{1 - (q_A/q_\infty)^2}{1 + \dfrac{q_A}{q_\infty} + \dfrac{2}{\Sigma} \cdot \dfrac{q_A}{q_\infty} \cdot e^{-\Sigma}} \,, \tag{4}$$

where q_A and q_∞ are the concentration of A and the total concentration of exchanging ions, respectively, in the solid phase at the effluent end of the column; and

$$\frac{q_A}{q_\infty} \doteq \left[1 - \exp\left(-\Theta + \Sigma - \frac{2\Sigma}{2e^{-\Sigma} + \Sigma} + \frac{2\Sigma^2}{(2e^{-\Sigma} + E)^2} \ln \frac{2e^{-\Sigma} + 2\Sigma}{\Sigma} \right) \right]^{1/2} . \quad (5)$$

This result is only approximate, but it conforms to the boundary conditions and fairly well to the experimental curves. The values obtained from these equations of c_A/c_o are plotted in Figure 1 against the throughput ratio Θ/Σ, for various constant values of Σ. A probability scale is used for expanding the regions of concentration ratio near zero and near unity, and a logarithmic scale is used on the solution-capacity parameter for convenient curve-matching against volume or time scales. At moderate to large values of Σ $(E \geqslant 4)$, Equations 4 and 5 reduce to

$$\frac{c_A}{c_o} \doteq \frac{q_A}{q_\infty} \doteq \left[1 - \exp\left(-\Theta + \Sigma - 2 + 2\ln 2 \right) \right]^{1/2} \quad (6)$$

or,
$$-\ln\left\{ 1 - \left(\frac{c_A}{c_o}\right)^2 \right\} \doteq \Theta - \Sigma + 0.614 \quad (6a)$$

so that the breakthrough curve of c_A/c_o plotted on a linear scale for Θ will then have a shape independent of Σ, i.e., a constant pattern as shown in Figure 2.

2. __Partially irreversible exchange.__ Constant pattern, with Σ large and K^{II} large (for instance, $\Sigma > 20$; $K^{II} > 2$, or $r < 0.5$.) Here $c_A c_o$ ($\equiv x_A$) is given by the implicit relation:

$$-\frac{(K^{II})^2 - K^{II}}{(K^{II})^2 - 1} \ln \left[(1 + \frac{1}{K^{II}}) + (1 - \frac{1}{K^{II}})x \right]$$

$$+ \frac{(K^{II})^2 + K^{II}}{(K^{II})^2 - 1} \cdot \ln \frac{1}{1 - x} + \frac{2}{(K^{II})^2 - 1} \cdot \ln \frac{1}{x} = \Theta - \Theta_c \quad . \quad (7)$$

The constant of integration must be determined by graphical integration of the relation

$$\Sigma = \int_0^\infty (1 - x_A)d\theta \ ,$$

but appears generally to have a value near 0.6. Graphs are available (6) which simplify the evaluation of x as a function of K^{II}, Σ, and θ.

3. <u>Reversible exchange</u>. (a) Linear equilibrium ($K^{II}=1$ or $r=1$). The solution reduces to a well-known and tabulated form (2, 4, 9, 10)

$$c_A/c_O = J'(\Sigma, \theta) = 1 - \int_0^\Sigma e^{-\theta - \varkappa} I_O (2\sqrt{\varkappa\theta})d\varkappa \qquad (8)$$

where I_O is a Bessel function of the first kind of zero order, with imaginary argument; or, at $\Sigma \geqslant 40$,

$$c_A/c_O \approx 1/2 \left\{ 1 + \text{erf}(\sqrt{\theta} - \sqrt{\Sigma}) \right\}. \qquad (8a)$$

(b) Non-linear equilibrium (either $K^{II} > 1$, $r < 1$; or $K^{II} < 1$, $r > 1$).

$$\frac{c_A}{c_O} = \frac{J (rs, t)}{J (rs, t) + e^{(r-1)(t-s)} \left[1 - J (s, rt) \right]} \qquad (9)$$

as given by Thomas (14) in different notation, where s and t are the column-capacity and solution-capacity parameters, respectively, for a hypothetical reaction-rate-controlled case, and

$$\frac{s}{\Sigma} = \frac{t}{\theta} = \frac{1}{(1-r)(c_A/c_O) + r} \ . \qquad (9a)$$

For this pair of simultaneous equations, with internal-diffusion parameters Σ and θ as independent variables, solutions for c_A/c_O also are available in graphical form.

4. **Equilibrium exchange.** At small values of K^{II} (< 0.1) or large values of r, back reaction becomes the controlling factor, and a limiting shape is obtained except at very low values of Σ. Under these conditions the relative steepness of the breakthrough curve is not improved by increasing the resin volume or by decreasing the flowrate, and the concentration becomes a function of the throughput ratio Θ/Σ :

$$\frac{c_A}{c_o} = \frac{1}{1 - K^{II}} \left[1 - \sqrt{\frac{K^{II}}{\Theta/\Sigma}} \right]$$

$$= \frac{r}{r - 1} \left[1 - \sqrt{\frac{s}{rt}} \right. \left. \cdot \right]$$

(10)

This is similar to a relation for q_A/q_∞ given by Walter (17).

For resin beds operated at equal residence times (V/R) and with equal concentrations of feed solution (equal D_G) Figure 1 indicates how the relative sharpness of breakthrough increases with the resin-phase diffusivity $\underline{D}_s$ or with the mass-transfer coefficient k_p, corresponding to an increase in Σ at constant r. The effect of back reaction, or of a decreasing equilibrium constant, on breakthrough from a bed of constant volume and constant diffusivity under constant flowrate conditions (increasing r at constant Σ) is shown in Figure 3.

Chromatographic zones. Elution is the reverse of saturation; when the bed is completely saturated, the elution curve has the shape of a saturation curve, with its K^{II} the reciprocal of K^{II} in the saturation step. If elution is begun before saturation of the column is complete, a rounded-top chromatographic curve is generated which may be regarded qualitatively as an elution curve subtracted from a saturation curve (7, 16). In a typical chromatographic separation, each component is

present only to a small extent, and its concentrations may be calculated
by considering the feed as a binary mixture of that particular component
with the gross eluting component. When the concentration of solutes
undergoing separation is less than 10% of that of the gross component
both on the resin and in solution, then a linear equilibrium is
approached ($r = 1$) and the distribution of each chromatogram (e.g., for
a solute A) is given by

$$c_A/(c_A)_o = \underset{\sim}{J}\,(\Sigma_A, \Theta_A) - \underset{\sim}{J}\,(\Sigma_A, \Theta_A - \Theta_{sat}) \tag{11}$$

where $\Theta_{sat} = k_p a_p V_{sat}/R$, and V_{sat} is the charge-volume of mixed feed
containing solute A at concentration $(c_A)_o$ in admixture with eluting
component at concentration c_o (with $c_o \gg (c_A)_o$). At $\Theta_{sat} \ll \sqrt{\pi \Sigma_A}$,

$$\frac{c_A}{(c_A)_o} \triangleq \frac{\Theta_{sat}}{2\sqrt{\pi \Sigma_A}} \exp\left\{ - \frac{(\Theta_A - 0.5\,\Theta_{sat} - \Sigma_A)^2}{4\,\Sigma_A} \right\} \tag{12}$$

a result similar to that given by Mayer and Tompkins (13) and Matheson
(12). In calculations of chromatographic separations, with particle
diffusion controlling, Θ remains as defined by Equation 2, but Σ_A is
now given by

$$\Sigma_A = \frac{4\,(D_s)_A\,\pi^2}{d_p^2} \circ D_A \circ \frac{vf_E}{R} \tag{13}$$

where D_A is the distribution ratio for solute A between the resin and
the solution:

$$D_A = \frac{q_A^* \rho_b}{C_A f_E} = (K^{II})_A\,\frac{q_\infty \rho_b}{c_o f_E} \tag{14}$$

and $q_\infty \rho_b$ is the moral resin capacity per unit bulk volume; i.e., ρ_b is

the bulk density of dry resin as packed in the column. The more the D values for the trace solutes differ from one another, the more easily these components can be separated.

A separate set of definitions of Σ and θ would be required if film diffusion controlled, and Equations 4-7 and 9 would have to be modified. However, Equations 8-12 would still apply in conjunction with the correct Σ and θ.

Experimental Program

The largest difference between breakthrough curves arising from particle-diffusion and from film-diffusion mechanisms is to be found in the completely irreversible case. Experiments under such conditions provide an excellent test of the equations derived for the respective mechanisms. Also, interpretation of the experiments is simplified, because the equilibrium constant for the exchange does not need to be evaluated. Originally it was thought that the rates of exchange for a neutralization reaction would be comparable to those of other non-aqueous exchanges. The rate values obtained suggest that this may not be correct, and show that data also will be needed on exchanges not involving hydrogen ion. These values are of interest both as entirely new data and as simple examples of the use of column-performance theory.

Apparatus. A simple column was assembled from standard laboratory apparatus and materials. The column proper was a Pyrex glass tube 11.3 mm. in inside diameter (1.00 sq. cm. cross-section) and 20 cm. long, constricted at the lower end and fitted with a flattened plug of glass wool. Gravity feed of the exchanging solution was used, from a 500 ml. separatory funnel about four feet above the column, connected by polyethylene tubing into which was inserted a 1/2-inch Hoke stain-less-steel needle valve for controlling the flowrate manually at a constant value of 0.5 ml./min. Flow was measured by timing the dropping rate with a stopwatch. The effluent was divided into 7.5-minute portions by a fraction collector and timer of standard design. Runs were usually of about five hours duration. Selected fractions were analyzed by titration with 0.010 $\underline{N}$ hydrochloric acid, using methyl orange as indicator.

A commercial grade of Dowex 50 was used, which was converted entirely to the hydrogen with 1 N hydrochloric acid, rinsed thoroughly with distilled water, and dried in air at room temperature for several days. For runs with anhydrous solvents, the resin was further dried in a vacuum desiccator over Drierite for 48 hours. Two size ranges were selected for this treatment, a wet-screened 20-35 mesh fraction derived from a sample contributed by the Dow Chemical Company, and a 250-500 mesh fraction as received from Microchemical Specialties Company. The column was charged with 4.80 gm. of vacuum-dried resin of 4.95 gm. or air-dried resin, or, in a few runs, with twice this quantity. Before each exchange run, the resin was equilibrated with pure solvent by flowing the latter through the column.

Materials. Most of the runs used ethanolamine as the solute, of Eastman White-Label grade. Cyclohexylamine, Eastman White-Label grade, and n-butylamine, student preparation, were also used. These were each used as solutions of approximately 0.10 N concentration. The solvents were either reagent or U.S.P. grade, and included absolute methanol, absolute ethanol, n-propanol, n-butanol, ethylene glycol, acetone, and benzene. In addition to these dry solvents, distilled water and two water-acetone mixtures were run.

Results and Discussion

Interpretation of Data. The effluent concentration values, deter-
mined by titration, were divided by the feed concentration to obtain
c/c_o ratios, and were then plotted (on a probability scale) against
the logarithm of effluent volume for matching against the curves of
Figure 1. The matching of curve shape in each run led to a value of
the column-capacity parameter Σ, and a value of the stoichiometric-
equivalent volume of effluent that matched $\Theta/\Sigma = 1$ on the abscissa.
The volume, multiplied by the solute concentration in the feed, and
divided by the weight of vacuum-dried resin, gave the gram-equivalent
capacity per gram of resin. The breakthrough data were replotted on
coordinates of c/c_o against Θ/Σ.

In each run with a steep breakthrough near $\Theta/\Sigma = 1$, which indi-
cated a Σ value greater than 4, Equation 6 was used to evaluate the
Θ difference between two selected effluent volumes, V_1 and V_2,
corresponding to concentrations c_1 and c_2:

$$\ln \left\{ 1 - \frac{c_1^2}{c_o^2} \right\} - \ln \left\{ 1 - \frac{c_2^2}{c_o^2} \right\} = \Theta_2 - \Theta_1 \quad (15)$$

From Equations 1 and 2,

$$\Sigma = v \, f_E \, D_G \frac{\Theta_2 - \Theta_1}{V_2 - V_1} = \frac{q_{\infty} \rho_b^V}{c_o} \cdot \frac{\Theta_2 - \Theta_1}{V_2 - V_1} \quad (16)$$

and by this relation the Σ value for the run was calculated.

The resin beds had volumes of 5 to 8 ml., depending upon the extent
of swelling. The apparent contact times were thus 10 to 16 minutes,
and the actual contact times (assuming 40% void-volume, external to the

particles) were 4 to 6.4 minutes. In some cases, the breakthrough occurred so rapidly that the test conditions would have no direct practicle interest. However, the constants evaluated from such runs can be used to predict the operating conditions needed to give any desired breakthrough behavior.

Resin Capacity. The equivalents of solute combining with one gram of vacuum-dried resin could be determined more accurately in the runs showing a steep breakthrough. Published values of the capacity of Dowex 50 are in the vicinity of 4.0 - 4.25 milli-equivalents per gram, and such values were confirmed on the present 20-35 mesh sample during saturation and elution runs involving hydrogen ion and sodium ion. A lower capacity was observed with amines as solutes, which appeared to depend more upon solute than upon solvent. Four runs with ethanolamine as solute, but with different solvents, showed the following capacities in milli-equivalents per gram:

Water	2.50
Methanol	2.60
Ethanol	2.63
Water (10 vol.-%)-Acetone (90%)	2.41

The 250-500 mesh sample of Dowex 50, run only with dry acetone as solvent, showed a capacity of 2.94 milli-equivalents per gram.

A run with n-butylamine on 20-35 mesh resin showed 2.03, and another with cyclohexylamine gave 2.09 milli-equivalents per gram. The reasons for the variation in capacity are not known to the writers.

Effect of Water Content of Solvent. The concentration level of solute was sufficiently high so that, even with water as solvent, the

rate was controlled almost entirely by particle diffusion. All of the
solvents studied showed markedly lower diffusion rates for the neut-
ralization reaction, and hence for hydrogen-ion exchange in general,
than water.

Dry acetone, in particular, gave a rate only 1/2500 that of water.
The acetone was used as received, without additional treatment; though
its water content was not known precisely, the rate results indicate
that it was extremely low. It was of interest to determine the
behavior of acetone solutions containing small known amounts of water,
and mixtures containing 2% and 10% by volume of water were prepared and
run. The results are shown in Figure 4. The Σ values determined for
these curves were as follows: dry acetone, 0.007; 2% water, 2;
10% water, 5; pure water, 19.

It is likely that the equilibrium water content of the resin,
after equilibration with a mixed solvent, is substantially higher than
the water content of the solvent. Better breakthrough performance is
seen to be obtained if the solvent is not entirely non-aqueous. An
anhydrous solvent could of course be used with a water-saturated resin.
However, any solvent in which water is appreciably soluble would
desiccate the resin, progressively reduce its exchange rate, and acquire
a finite but variable water content. Thus, if water can be tolerated
in such a solvent, more consistent results will be obtained by adding
it to the solvent, rather than to the resin.

Use of Water-Wet Resin. When a solvent is used in which water is
entirely immiscible, striking advantages are found for a water-wet
resin. Such operation may be considered as a type of partition
chromatography. In runs with benzene as a solvent, n-butylamine and

cyclohexylamine were used as solutes, because of the low solubility of
ethanolamine. Figure 5 shows the results from use of both a benzene-
wet resin bed (of twice the standard weight) and a water-wet bed. The
diffusion rate for n-butylamine in water is very close to that for
ethanolamine, and at least four times as great as that for cyclohexyl-
amine. Again the ratio of rates in aqueous and non-aqueous solvents
is of the order of 1000:1. The variation in n-butylamine concentrations
in the effluent appears to have been caused by fluctuations in flowrate;
the concentrations of cyclohexylamine did not differ significantly from
those in the feed. Other authors in this symposium have reported
similar conclusions (3).

Effect of Particle Size. Boyd and his coworkers (1) established
that the exchange rate would be inversely proportional to the square of
particle diameter if internal diffusion controlled, or more nearly to
the first power in an external-diffusion case. A quadratic dependence
is reflected in Equations 1 and 2. An acetone solution of ethanolamine
was fed to a bed of 250-500 mesh Dowex 50, with excellent results in
terms of the steepness of breakthrough as is shown in Figure 6.
Comparison with the 20-35 mesh resin result gave a qualitative confirm-
ation that particle diffusion was the controlling mechanism. The rates
differed by a ratio of 700, while the square of the ratio of average
particle diameters was 200. The discrepancy in these two values might
be accounted for by a high proportion of smaller particles in the fine
material, or by a lower extend of cross-linking in it, and partially
also by its higher measured exchange capacity since Σ is proportional
to D_G and hence to q_{∞}. Clearly, particle size is an important design
variable in cases of unusually low solid-phase diffusivity.

Effect of Solvent. Figure 7 shows the concentration histories for ethanolamine solutions in a series of alcohols of commercial absolute or anhydrous grade. These are all intermediate between water and acetone and show a very wide range of rates.

The Σ values from these runs and those of Figures 4 and 5 were used with Equation 1 to calculate the solid-phase diffusivity, D_s, which are listed in Table 1. The value for water as solvent, $1.2 \times 10^{-6} cm^2$/ sec., can be compared with values of 1.2 to 3.5×10^{-6} reported by Boyd, Adamson, and Myers (1) for exchange of alkali metals in Amberlite IR-1. As diffusivities are generally inversely proportional to viscosity, the product of these two variables has been calculated and is given in the third column of Table 1; the solvents are arranged in the order of diminishing values of this product.

TABLE 1. DIFFUSIVITIES OF ETHANOLAMINE vs. SOLVENT PROPERTIES

Solvent	$D_s \times 10^6$ cm^2/sec.	$D_s \mu \times 10^8$	Swelling of resin, vol.-%	$\left(\dfrac{\Delta E_v}{V_m}\right)^{1/2}$	Dielectric constant
Water	1.2	1.2	47-60	23.2	78
Methanol	.28	.15	47	14.4	33
Glycol	.0075	.13	63	14.6	41
Ethanol	.025	.027	39-44	12.6	25
Propanol	.0025	.0055	38	11.5	21
Butanol	.0025	.0063	27	10.6	18
Benzene*	.00063	.00039	0	9.1	2.3
Acetone	.00044	.00014	15-35	9.9	21

* With this solvent, n-butylamine was used as solute.

Several other properties of the solvents are shown for comparison. The swelling of Dowex 50 was measured, both in the column and in separate experiments using calibrated centrifuge tubes. Equilibrium values of swelling are given. In most cases these were reached quickly; but, for acetone and butanol, swelling may only have been about 50% complete at the close of the column runs. Hildebrand's solubility parameter or square root of internal pressure (8), $(\Delta E_v/V_m)^{1/2}$, and the dielectric constant are also tabulated.

The general trend of each of these parameters is in the same direction as the corrected diffusivities. However, in each case, the properties of benzene and acetone are reversed, and the other values do not plot smoothly.

Thus it seems possible that none of these variables provides a correct explanation. Neutralization occurs at the outer surface of a resin particle, and the solid-phase diffusion is a matter of redistribution of hydrogen and amine groups without net change in internal energy. The mobility of hydrogen ions within the particle may well depend upon the base strength of the solvent, as defined by Hammett (5). Kunin and Barry (11) have reported that metal-metal exchange is 5000 times as rapid as hydrogen-metal exchange in Amberlite IRC-50, an aqueous carboxylic-acid exchanger. If this interpretation should be borne out by further investigation, the measurement of hydrogen-cycle exchange rates might provide a new method of estimating base strengths of non-aqueous solvents.

The result of Kunin and Barry also suggests strongly that, in the non-aqueous systems involving sulfonic-acid resins, the solid-diffusion

rates for exchange of ions other than hydrogen will be higher than those found in the present work, i. e., nearer to those found when water is the solvent.

Sizing of Equipment

A wide latitude exists in the specification of operating conditions for a column to carry out a desired exchange. Usually the feed concentration and flowrate are determined by the supply, and the limiting concentration at breakthrough is fixed by purity requirements. The choice of resin is apt to depend upon cost, availability, and general suitability for the exchange. When it is once chosen, its particle size, capacity, diffusivity, and equilibrium for the exchange become fixed. Table 2 shows a series of sample calculations based upon an arbitrary combination of solution and resin, where the latter has a diffusivity representative of anhydrous glycol or ethanol.

Three possible design cases are considered. First, economic factors (including the chemicals consumption in regeneration) may fix a lower limit for the resin utilization and the shortest process period which will give such a utilization must be calculated, as in Case 1. Here Θ/Σ is specified. Then Σ is determined from Figure 1, v/R is calculated by Equation 1, and $vq_{\infty}\rho_b$ follows by way of v from the known values of R and of $q_{\infty}\rho_b$. Combination of Equations 1 and 2 with the relation $D_G - q_{\infty}\rho_b/c_o f_E$ gives

$$c_o(V - vf_E) = \frac{\Theta}{\Sigma} \cdot vq_{\infty}\rho_b \, . \qquad (17)$$

Division by c_o and then by R yields $\tau - (vf_E/R)$, the "useful time" per cycle of operation, during which effluent of the requisite purity is being produced by the column.

In case 2, the "useful time" of the operating cycle is specified, and the order of calculations (as shown by the numbers in parenthesis)

is completely reversed. In order to apply Equation 17, a trial value of

θ/Σ must be assumed. A better value is obtained from Figure 1 at the end

of the sequence, and, if it is appreciably different, it must then be used

in a repetition of steps 5 through 9 to arrive at a still more reliable

value.

It often happens that a column of known volume is available, or is

specified as a matter of particular convenience. A still different order

of calculation is indicated here (Case 3), with the "useful time" as the

end result.

TABLE 2. STEPS IN COLUMN DESIGN

Specifications:

Breakthrough c/c_o, 1%	Particle diameter, 0.011 cm.
Flowrate R, 10 l./hr.	Diffusivity $\underline{D}_s$, 1×10^{-8} cm.^{2}/sec.
Feed Concentration c_o, 0.10 N	Resin capacity $q_{oo}\rho_b$, 1.0 meq./ml.

Equilibrium constant $K = \infty$ ($r = 0$)

θ/Σ	Σ	hr. v/R	liters v	gm.-equivs. $vq_{oo}\rho_b$	gm.-equivs. $c_o(V - vf_E)$	liters $V - vf_E$	hr. $\tau - (vf_E/R)$

Case 1. Utilize 80% of Resin Capacity

(1)*	(2)	(3)	(4)	(5)	(6)	(7)	(8)
0.80	3.1	0.026	0.26	0.26	0.21	2.1	0.21

Case 2. Operate on 16-hr. Schedule

(4,9)	(8)	(7)	(6)	(5)	(3)	(2)	(1)
1.00** } .997	192	1.6	16	16	16	160	16

Case 3. Given the Column Volume, 2 l.

(4)	(3)	(2)	(1)	(5)	(6)	(7)	(8)
0.974	24	0.2	2	2	1.95	19.5	1.95

* Numbers in parenthesis indicate step in calculation.

** Trial estimate, step 4.

Nomenclature

Dimensions of the variables are indicated in terms of a typical self-consistent set of units.

a_P = effective area for mass transfer inside adsorbent particles, sq. ft./cu. ft.

ad = superscript indicating a variable pertaining to a case of physical adsorption.

c_A, c_B, etc. = concentration of solute in a fluid phase at a specified point in the column, lb.-moles (or lb.-equivalents)/cu. ft.

c_o = concentration of total solute in the fluid phase entering the column.

D_A = distribution ratio or partition coefficient, $(q_A)\rho b/(c_A)f_E$, for trace component A.

D_G = ratio of concentrations on solid and in fluid phase at saturation, $q_{\infty}\rho_b/c_o f_E$, dimensionless.

d_P = mean diameter of adsorbent particles, ft.

$(\underline{D}_s)_{AB}$ = effective ionic diffusivity, square cm. per second, for trace component A diffusing against component B.

$\Delta E_v/V_m$ = internal pressure, lb./sq. in. or B.t.u./cu. ft.

f_E = ratio of void space outside particles of adsorbent to total volume of packed column, dimensionless.

erf = the error function.

$$(2/\sqrt{\pi}) \int_0^z e^{-\zeta^2} d\zeta$$

I_0 = Bessel function of zero order, and first kind, with imaginary argument,

$$I_0(2\sqrt{xy}) =$$

$$\sum_{m=0}^{\infty} (xy)^m/(m!)^2$$

dimensionless.

J = solution function giving c/c_0 at $r = 1$, dimensionless.

k_P = mass-transfer coefficient for case of transfer inside solid particles controlling, ft./min.

K = chemical equilibrium constant for ion exchange.

K^{II} = apparent second-order equilibrium constant as approximated for exchanging ions of unequal valence, dimensionless.

q_A, q_B, etc. = concentration of solute in the solid phase at a specified point in the column, lb.-moles (or lb.-equivalent.)/lb. dry absorbent.

q_A^*, etc. = concentration of solute on the solid phase, in equilibrium with the coexisting liquid phase at concentration c_A, etc.

q_∞ = total concentration of solute in the solid phase when complete saturation is reached.

R = volumetric flow rate of fluid through fixed solid, cu. ft./min.

r   = equilibrium parameter, dimensionless; for ion

            exchange, $r = 1/K$.

s   = column-capacity parameter for the kinetic case,

            dimensionless.

t   = solution-capacity parameter for the kinetic

            case, dimensionless.

v   = bulk-packed volume of column, cu. ft.;

            vf_E is the void volume of the column.

$v\rho_b$ = weight of dry adsorbent charged to column, lb.

V   = volume of saturating fluid fed to column, cu. ft.;

            $V - vf_E$ is the volume of saturating fluid that

            has reached adsorbent at a volume v downstream

            from the column inlet.

x_A = c_A/c_o, dimensionless.

ζ = a variable.

ρ_b = density of dry adsorbent, lb./cu. ft. bulk volume

            (as packed in the column and saturated with carrier

            fluid.)

μ = viscosity, lb./hr./ft.^{2}

θ = solution-capacity parameter for diffusional cases,

            dimensionless; see Equation 2.

θ/Σ = throughput parameter.

Σ = column-capacity parameter for diffusional cases,

            dimensionless; see Equation 1.

τ = time elapsed from start of run.

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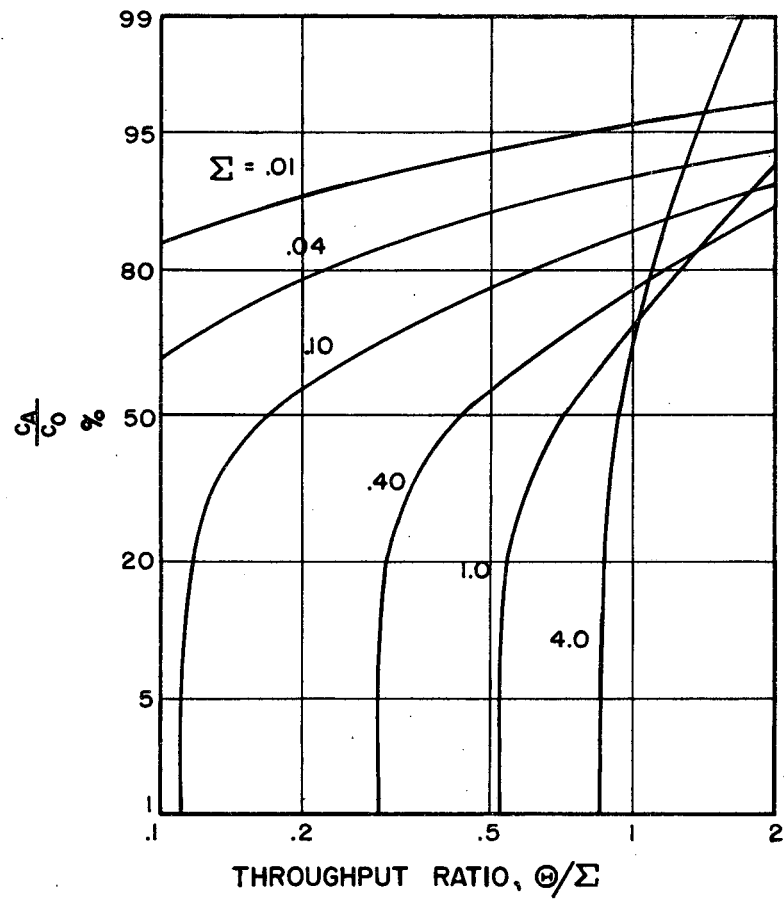
(17) Walter, J. E., J. Chem. Phys., 13, 229 (1945).

FIG. I DEPENDENCE OF CONCENTRATION HISTORY
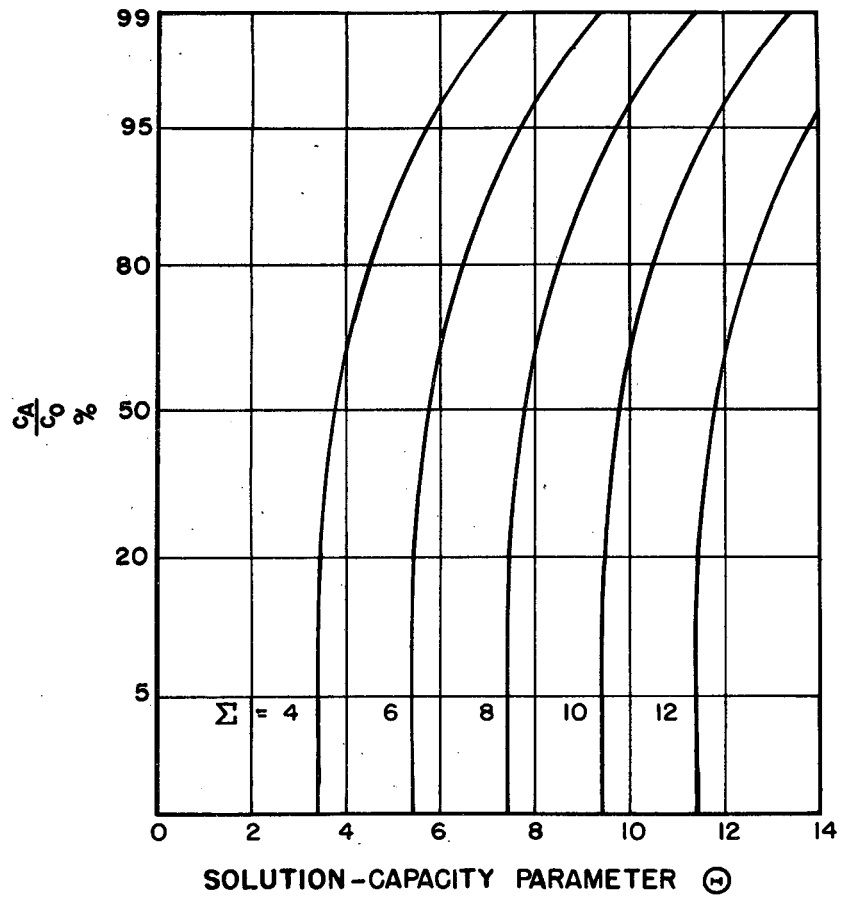UPON COLUMN - CAPACITY PARAMETER (r = 0)

MU-4330

FIG. 2 DEPENDENCE OF CONCENTRATION HISTORY
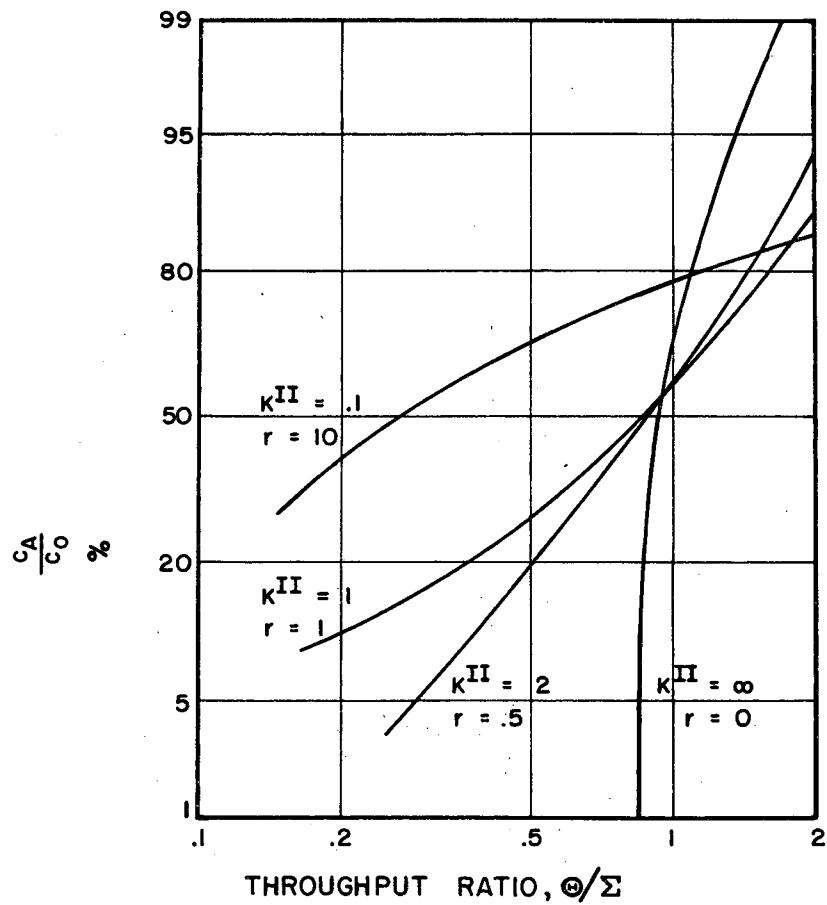UPON COLUMN-CAPACITY PARAMETER (r = O)

MU-4331

FIG. 3 DEPENDENCE OF CONCENTRATION HISTORY
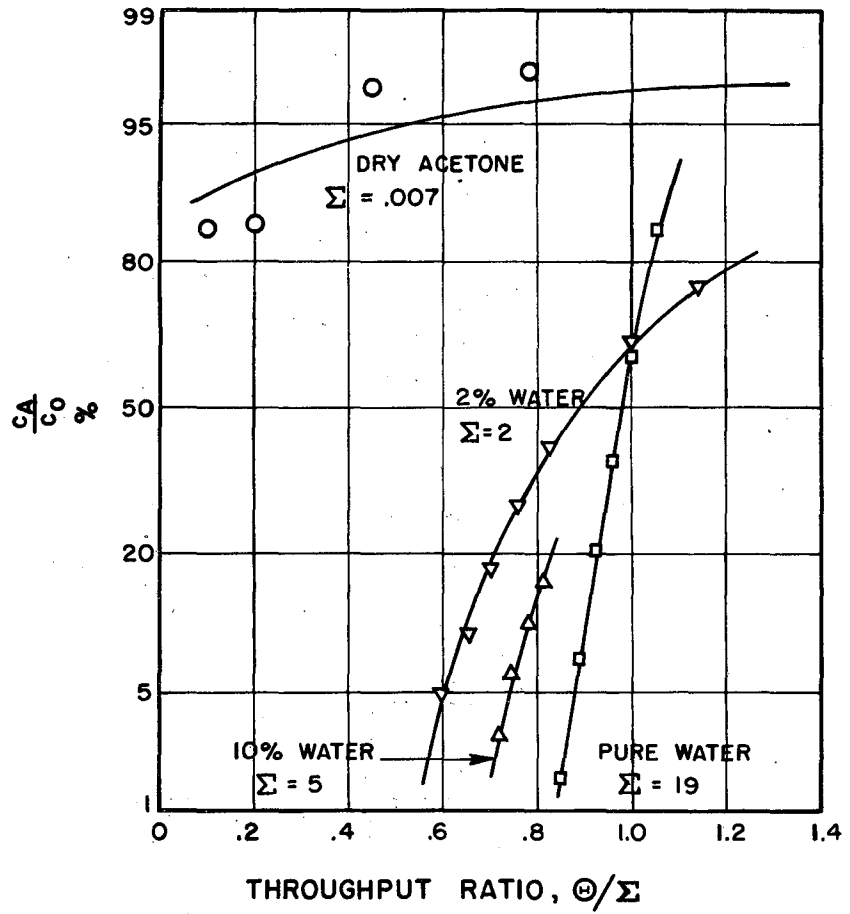UPON EQUILIBRIUM CONSTANT ($\Sigma = 4$)

MU-4332

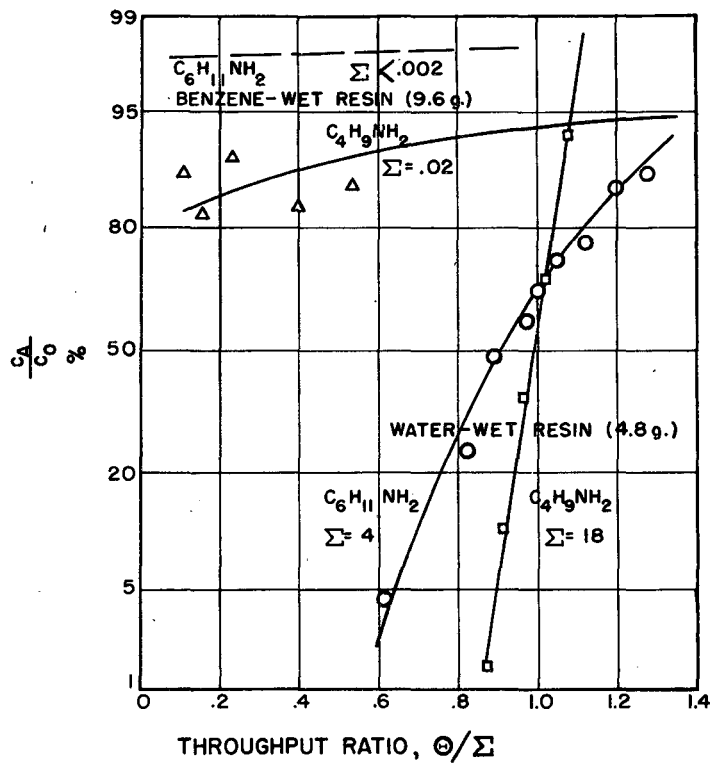FIG. 4 EFFECT OF SOLVENT WATER-CONTENT
ON BREAKTHROUGH

MU-4333

FIG. 5 COMPARISON OF WATER—WET AND BENZENE—WET
RESINS FOR REMOVAL OF AMINES FROM BENZENE SOLUTION

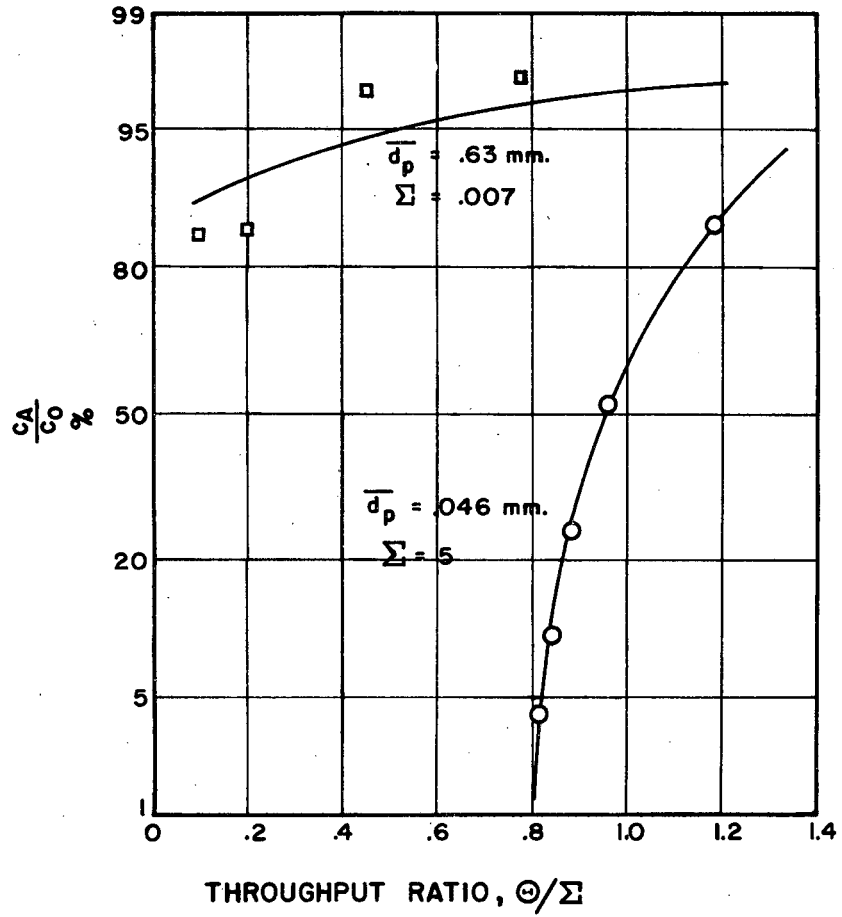MU—4334

THROUGHPUT RATIO, Θ/Σ

FIG. 6 EFFECT OF PARTICLE SIZE UPON REMOVAL
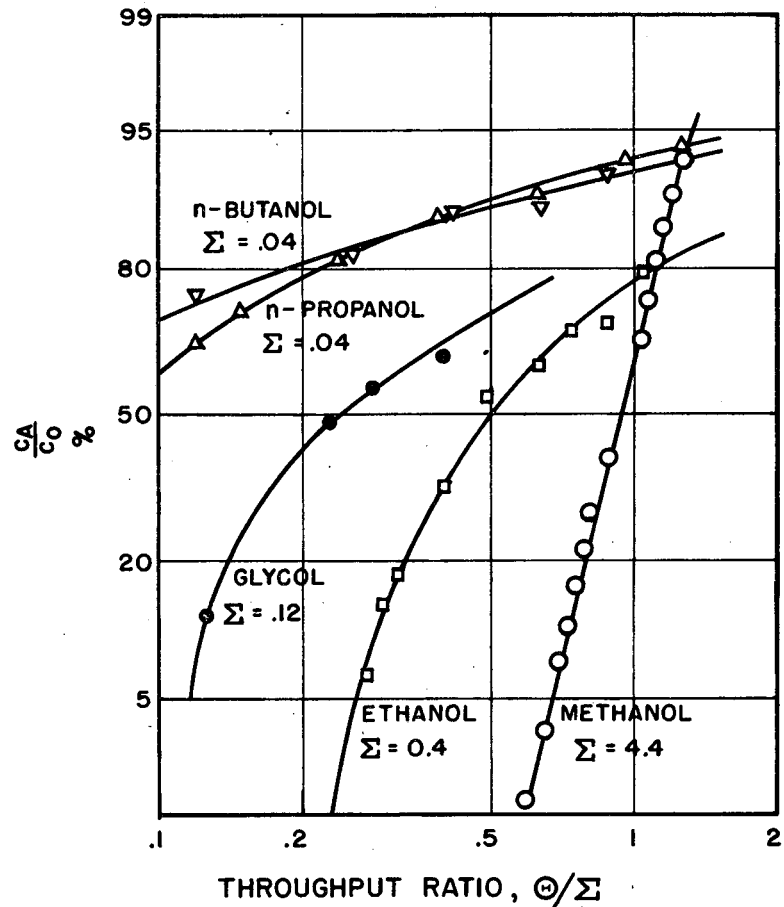OF ETHANOLAMINE FROM ACETONE SOLUTION

MU-4335

FIG. 7 EFFECT OF SOLVENT ON BREAKTHROUGH

MU-4336