The Rate of Acid Removal by Liquid Ion Exchangers

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The recent advent of liquid ion exchangers has opened up many possibilities for continuous operation of ion-exchange equipment. As always, a rational design of such equipment depends on the knowledge of basic system behavior, which includes the pertinent rate processes. The present preliminary study was initiated to elucidate the possible rate-controlling process in liquid ion-exchange processes.

The material studied in this work was the liquid anion exchanger Amberlite LA-II, a secondary liquid amine with long chain, aliphatic groups which may be used for acid removal, by contact of free amine in an organic phase with mineral or organic acids in an aqueous phase

$$[R\,R'\,N\,H]_{org} + H^+ + A^- \rightarrow [R\,R'\,N\,H_2\,A]_{org} \quad (1)$$

and for anion exchange by contact with an amine salt formed as in Equation (1) with a different anion in aqueous solution

$$[R\,R'\,N\,H_2\,A]_{org} + B^- \rightleftarrows [R\,R'\,N\,H_2\,B]_{org} + A^- \quad (2)$$

Regeneration of the original free amine or amine salt is brought about by contact with a base or the appropriate ionic constituent, respectively.

The assumption of irreversibility should be satisfactory as long as complete utilization of the free amine is not approached too closely. In the experiments to be described below a maximum of 44% utilization (or reaction) was achieved, thus making this assumption reasonable.

Since ionic reactions of the types described above are usually considered to be rapid, it is likely that some kind of diffusional process will control the overall rate in any particular case. Clearly the exact nature of this process will undoubtedly vary with equipment type and chemical nature of the overall system. However, it was felt that an investigation in a suitably simplified system might give some indication of the most appropriate models for subsequent detailed study. As a result, it was decided to study the removal of hydrochloric acid from dilute aqueous solutions in a simple countercurrent spray column.

A series of experiments was made in which Amberlite LA-II, dissolved in a suitable organic solvent, was passed upward as the dispersed phase through a dilute hydrochloric acid solution. The flow rate of the continuous aqueous phase and the height of the column were varied and the extent of acid removal was measured. The resultant data were then interpreted in the light of an appropriate mathematical model for the rate process.

EXPERIMENTAL

The column used in this work was made of glass and had an I.D. of 2.84 cm. It was sealed at both ends with rubber stoppers through which glass input and outlet tubes were passed. The continuous acid phase, ranging in concentration from 0.033N to 0.074N, was fed in at the top of the column through a glass distributor with six symmetrical ports. The dispersed organic phase entered the bottom of the column through a glass distributor with three equally spaced nozzles. The organic phase consisted of a 10 volume % solution of Amberlite LA-II in Soltrol-170 a commercial solvent consisting of isoparaffinic hydrocarbons. The resulting mixture had a measured acid-binding capacity of 0.2218 meq./ml. The dispersed phase coalesced above the acid inlet distributor and was removed from the column. The stripped aqueous phase flowed out of the column through a glass exit tube located below the organic inlet nozzles. The feed streams were delivered to the column by gravity flow from overhead feed tanks. Rotameters were used to regulate and control the flow rates. The effective column height was varied by interchanging glass columns and/or by adjusting the positions of the various glass tubes in the rubber stoppers.

Runs were made with this equipment by adjusting inlet and outlet rates until steady state operation was achieved. The two outlet streams were then sampled over a 15 to 20 min. period. In all cases the aqueous phase samples were analyzed directly for acid content by titration with standard sodium hydroxide solution. In several experiments the acid content of the organic phase was also similarly measured to check the material balance. The results of these experiments indicated that about 99% of measured acid lost from the aqueous phase could be recovered from the organic phase. This was considered to be a satisfactory material balance for present purposes.

No effort was made to control temperature in this system. Experiments were made at ambient temperature which ranged from 75° to 86°F.

Further details of equipment and experimental procedures are reported elsewhere (2).

RESULTS

The equipment described above was used to make four series of runs in each of which column length was varied while acid and organic phase flow rate and composition were unchanged. Acid flow rate was varied from one series of runs to another. The range of variables studied is indicated in Table 1. Typical data are shown in Figure 1 where the fractional exhaustion, E, of the organic phase is plotted as a function of column length for series 1.

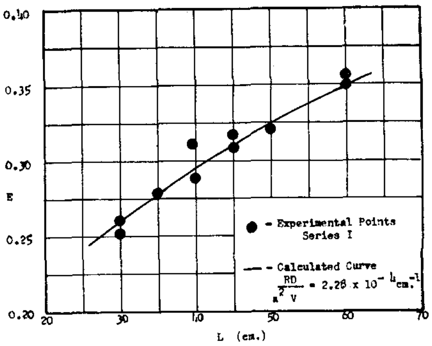

Fig. 1. Experimental and calculated data—series 1.

The size of the bubbles of dispersed phase present in the spray column was estimated under actual operating conditions by photographing a column

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TABLE 1. EXPERIMENTAL CONDITIONS

Series	Q_o (ml./min.)	Q_A (ml./min.)	L (cm.)	C_L (meq./ml.)	q^* (meq./ml.)	No. of runs
1	12	80	30-60	0.033	0.2218	10
2	12	60	33-50	0.044	0.2218	5
3	12	48	30-60	0.056	0.2218	8
4	12	36	30-60	0.074	0.2218	8

section and measuring a number of bubbles on the resultant photograph. Although only limited data were thus obtained, it was determined that the average bubble radius was approximately 0.41 mm and did not change significantly with continuous-phase flow rate.

A model was next formulated to account for the observed data in terms of a physical rate process. Since tests showed no significant solubility for free acid in the organic solvent Soltrol-170 or for free amine in the aqueous phase, models involving the existence of such species in these phases were discarded. Because of the usual rapidity of ionic reactions such as Equation (1), it was felt that a diffusional process would be the rate-controlling phenomenon. The model selected was one in which free amine within the dispersed-phase bubbles moved to the bubble surface where it reacted instantaneously and irreversibly with free acid also present at the bubble-aqueous interface. The rapid reaction at this point resulted in a free amine concentration equal to zero at the interface. Although Equation (1) may be reversed, the equilibrium is generally strongly in favor of the combined product (*1*). It was assumed for present purposes that the reaction may be safely taken as irreversible. The experimental results discussed below were in accord with this assumption.

If the dispersed-phase bubbles are now assumed to behave as rigid spheres, this model may be described in terms of the usual diffusion equation:

$$\frac{\partial q}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial q}{\partial r} \right] \tag{3}$$

Here t represents the time during which bubble and aqueous phase are in contact, that is, the contact time in the spray column.

Appropriate auxiliary conditions to complete the problem description are as follows:

$$\text{At } r = a, \quad q = 0, \quad \text{for all } t > 0 \tag{4}$$

$$\text{At } r = 0, \quad q \text{ is finite for all } t > 0 \tag{5}$$

$$\text{At } t = 0, \quad q = q^*, \quad \text{for all } r \leq a \tag{6}$$

The solution to this set is well known (*3, 4*) and when combined with a simple overall material balance for a column of length (L) it yields

$$E = \frac{(C_L - C_O)Q_A}{q^* Q_O} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(- n^2\pi^2 DL/(a^2V)\right) \tag{7}$$

Here E represents the fractional exhaustion of the free amine in the dispersed phase, and contact time has been replaced by column length (L) divided by bubble-rise velocity (V).

If the above analysis is modified to allow for streamline circulation within the bubbles, it may be shown that the result can be given by Equation (7) again, but with D replaced by an effective diffusivity several times larger (*5*).
Thus

$$D_{\text{eff}} = RD \tag{8}$$

defines R as the factor accounting for circulation. Its value has been shown to vary from 1 for noncirculating bubbles to about 3 for bubbles with laminar circulation and to higher values for turbulent circulation (*5, 6, 7, 8*).

It was decided to test the validity of this result by fitting the experimental data to Equation (7) by a selection of the value of the group $\frac{RDL}{a^2V}$ Such values were found for every datum point in each series of runs. The best value of $\frac{RD}{a^2V}$ was then found for that series by the method of least squares. The results are shown in Table 2. These mean values were used to find calculated E values. The latter were compared to experimental E values, and average absolute differences were calculated. As can be seen from Table 2, the agreement is quite satisfactory. In addition, Figure 1 shows the fit graphically for the data of series 1. Note that error in experimental E values might be expected to be as high as 10% owing to analytical errors (*2*).

TABLE 2. CALCULATED RESULTS

Series	$\frac{RD}{a^2V} \times 10^4$ (cm.)$^{-1}$	$\frac{E_{\text{exp}} - E_{\text{calc}}}{E_{\text{exp}}} \times 100$
1	2.28	1.98
2	2.41	2.78
3	2.86	3.36
4	3.73	2.42

Three additional runs were made at the condition of series 3, except that q^* was both lower than shown in Table 1 and varied in these runs. Based on the same value for $\frac{RD}{a^2V}$ as shown in Table 2, the E calc. values differed by only 6 to 8% from measured values

DISCUSSION

Consideration of these results seems to indicate that the basic model is capable of fitting the data in a very satisfactory manner. Yet, some explanation is certainly required for the order of magnitude and the variability from series to series of the group $\frac{RD}{a^2V}$.

A check on the magnitude of this group was made after estimation of the various terms. The value of D, the molecular diffusivity of Amberlite LA-II in Soltrol-170, was estimated from the properties of both materials and the generalized correlation of Wilke and Chang (*9*). With manufacturer's property data, D was estimated to be 1.20×10^{-6} sq.cm./sec. Bubble radius was estimated, as indicated earlier, to be 0.41 mm. As a first approximation it might be assumed that the bubbles rise through the aqueous phase at their single-bubble terminal velocities. Using the correlation of Klee and Treybal (*10*), V was thus estimated to be 5.26 cm./sec. Subsequent calculation according to the method of Weaver, Lapidus, and Elgin (*11*), indicated that true rise velocity would be only slightly lower than the terminal velocity under the conditions of these experiments.

These values were combined to give $\frac{D}{a^2V} = 1.35 \times 10^{-4}$ cm.$^{-1}$. When compared with the values shown in Table 2, this result indicates that the experimental values of $\frac{RD}{a^2V}$ are of reasonable magnitude and the value of R ranges from 1.69 to 2.76 in these experiments. The latter conclusion is based on the correction necessary to make calculated values of $\frac{D}{a^2V}$ and experimental values of $\frac{D_{\text{eff}}}{a^2V}$ equal. This magnitude of R is as expected, although the rather wide range is perhaps surprising. Qualitatively, it might be expected that R should increase as Q_A decreases, since smaller values of Q_A lead to less holdup of dispersed phase and thus to higher slip velocity (*11*). Further, as slip velocity increases, one might expect increased agitation of bubble surfaces, increased bubble circulation, and hence, higher R values. One other possible explanation for the changing values may be found in entrance and exit effects associated with bubble formation and coalescence. Thus, the value of R might have been 1.0 in all these runs, but end effects may have changed

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INFORMATION RETRIEVAL

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Forces in a moving bed of particulate solids with interstitial fluid flow, Brandt, Herman L., and Benjamin M. Johnson, **A.I.Ch.E. Journal, 9,** No. 6, p. 771 (November, 1963).

Key Words: Granular Solids-9, Moving Bed-9, Flowing Fluid-5, Solid Stress-8, Radial Stress-8, Vertical Stress-8, Wall Friction-7, Stress Ratio-7, Pressure Transducer-10, Resin-9, Glass Beads-9, Internal Friction-7, Concurrent-6, Countercurrent-6, Ion Exchange-9, Oscillograph-10, Pressure Drop-6.

Abstract: The radial stress at the wall and the average vertical stress have been measured in a moving bed of particulate solids through which a fluid is flowing. Three sizes of ion exchange resin and 20 to 50-mesh glass beads were used.

In countercurrent flow the coefficient of friction at the wall and the radial-to-vertical stress ratio were constant. In concurrent flow this was true only for one size of resin; in all the solids studied these parameters reached asymptotic values in deep beds.

Quenching the plasma reaction by means of the fluidized bed, Goldberger, W. M., and J. H. Oxley, **A.I.Ch.E. Journal, 9,** No. 6, p. 778 (November, 1963).

Key Words: Quenching-7, High Temperature-6, Ultrahigh Temperature-6, Fluidized Bed-10, Fluidization-10, Plasma-1, Plasma-Jet-1, Plasma Generator-10, Argon-10, Alumina-10, Reactions-9, Heat Transfer-8, Cooling-8, Temperature Decay-8, Decay Time-7, Heat Rejection-8, Jet-10, Plasma Injection-10.

Abstract: Quenching ultrahigh-temperature reactions to give a desired selectivity without wasting energy is a major obstacle in the development of high-temperature chemical processes. Use of a fluidized bed as a plasma quench device was found to give high quench rates. An argon plasma was injected into a bed of fluidized alumina under various conditions, and temperatures were measured at different locations within the bed. Estimated quench rates as high as 50×10^6°K./sec. were obtained. Possible applications of the fluidized bed for quenching plasma reactions are discussed.

Multicomponent diffusion in semi-infinite systems, Cussler, E. L., Jr., and E. N. Lightfoot, **A.I.Ch.E. Journal, 9,** No. 6, p. 783 (November, 1963).

Key Words: Diffusivities (Multicomponent)-1, Flux Equations-1, Fick's Law (Generalized)-1, Volume-Average Velocity-1, Concentration Profiles-2, Mass Fluxes-2, Variation of Diffusivities (Neglected)-3, Time-6, Distance-6, Concentration-7, Diffusion (Semi-Infinite)-8, Mass Transfer, Understanding of (Multicomponent)-9, Penetration Theory, Extension of-9, Diffusivities (Multicomponent), Calculation of, from Experimental Data-9, Combination of Variables-10, Matrix Algebra-10.

Abstract: The Arnold problem of semi-infinite diffusion is extended to one-dimensional systems of two to five components with arbitrary flux ratios at the system boundary. The approach used follows that of Fujita and Gosting. Exact solutions for the concentration profiles are given for the assumptions of constant diffusivities and of constant partial specific volumes. This development facilitates experimental determination of multicomponent diffusion coefficients and also should permit extension of the penetration theory to multicomponent systems.

Thermal diffusion of salt solutions in single-stage cells and in continuous horizontal columns: the system copper sulfate-cobalt sulfate-water, Fisher, G. T., John W. Prados, and L. P. Bosanquet, **A.I.Ch.E. Journal, 9,** No. 6, p. 786 (November, 1963).

Key Words: Thermal Diffusion-8, Diffusion-8, Soret Coefficient-9, Water-2, Copper Sulfate-2, Salts-2, Cobalt Sulfate-2, Membrane-10, Thermal Diffusion Column-10, Clusius Column-10, Cellophane-10.

Abstract: The thermal diffusion of the copper sulfate-cobalt sulfate-water system was investigated in a new Soret cell design and in a new horizontal continuous column utilizing diffusion through a cellophane membrane. Design equations were developed for the operation, and experimental results are compared with theory.

the flow rate of the aqueous phase changed. However, such end effects were neglected in this analysis in the absence of complete data.

Further quantitative arguments were not considered in view of the limited experimental and physical property data available.

In view of the results obtained in this study it may be concluded that the diffusional model described above is satisfactory for correlating, spray-column data and is in good agreement with basic physical data for the system under consideration. Although additional data are required to extend the range of application of this model, it shows promise of being useful in analysis of liquid ion-exchange processes.

NOTATION

a = radius of dispersed phase bubbles, cm.
C_L = concentrations of fresh acid streams, meq./ml.
C_O = concentration of stripped acid stream, meq./ml.
D = molecular diffusivity sq.cm./sec.
E = fractional exhaustion of organic phase
L = effective length of column, cm.
q = concentration of amine in organic phase, meq./ml.
q^* = entrance concentration of amine in organic phase, meq./ml.
Q_A = aqueous-phase flow rate, ml./min.
Q_O = organic-phase flow rate, ml./min.
t = contact time of bubble and continuous phases, sec.
r = radial variable, cm.
R = circulation correction factor
V = bubble rise velocity, cm./sec.

LITERATURE CITED

1. Amberlite LA-1 Tech. Notes, Rohm and Haas Co., Philadelphia, Pa. (1958)).
2. Wert, J. L., M.S. thesis, Northwestern University, Evanston, Ill. (June, 1963).
3. Newman, A. B., *Trans. Am. Inst. Chem. Engrs.*, **27**, 203 (1931).
4. Crank, J., "The Mathematics of Diffusion," Oxford Univ. Press, New York (1956).
5. Calderbank, P. H., and I. J. O. Korchinski, *Chem. Eng. Sci.*, 65 (1956).
6. Johnson, A. I., and A. E. Hamielec, *A.I.Ch.E. Journal*, **6**, 145 (1960).
7. Kronig, R., and J. C. Brink, *Appl. Sci. Res.*, **A-2**, 142 (1950).
8. Handlos, A. E., and T. Baron, *A.I.Ch.E. Journal*, 3, 127 (1957).
9. Wilke, C. R., and Pin Chang, *ibid.*, **1**, 264 (1955).
10. Klee, A. J., and R. E. Treybal, *ibid.*, **2**, 444 (1956).
11. Weaver, R. E. C., Leon Lapidus, and J. C. Elgin, *ibid.*, **5**, 533 (1959).