

such cases, the theory described above predicts the degree of separation which may be expected. Its present limitations do, however, decrease its applicability to large scale industrial processes in which columns must be operated in such a way that the distribution coefficient may not remain constant throughout the bed and equilibrium conditions are not approached. To be generally useful for the development of such large scale, industrial separations processes, it will be necessary to extend this theory by a further study of the kinetics of column reactions and the rates of diffusion of the various substances entering into these reactions.

### Summary

A simple theoretical analysis of the ion exchange

column separations process has been developed for the case in which the distribution coefficient of the solute between the solid and liquid phases remains constant throughout the column. Application of this theory to the rare earth separations, reported earlier by one of the authors, and for the prediction of separation in another column separation, demonstrates its usefulness. The elution curves derived from the theory fit the observed data within the limits of experimental error when near-equilibrium conditions prevail in the column. The theory is also applied to determine the purities of the rare earths separated by this process. The general applicability of the theory to processes of this type is discussed.

P. O. BOX W, OAK RIDGE, TENN. RECEIVED JULY 14, 1947

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE RESINOUS PRODUCTS AND CHEMICAL CO.]

## The Anion Exchange Equilibria in an Anion Exchange Resin

BY ROBERT KUNIN AND ROBERT J. MYERS

The equilibria involved in ion exchange phenomena have received considerable attention since the early work of Thompson<sup>1</sup> and Way<sup>2</sup> in 1850. However, although considerable information has been obtained for the cation exchange phenomena, outside of the studies of Mattson and his students<sup>3,4</sup> and Jenny<sup>5</sup> in the field of soils, until recently, comparatively little information has been published for the anion exchange phenomena. The recent availability of durable and high capacity anion exchange resins has stimulated much work on this phenomenon during the past few years.

Mattson and his students<sup>3,4</sup> and Jenny<sup>5</sup> have shown that many silicates have the ability to exchange anions as well as cations. Jenny<sup>6</sup> and Sussman<sup>7</sup> have indicated that amine type exchange resins behave as true exchange substances. However, Schwartz, Edwards, and Boudreaux<sup>8</sup> have indicated that the amine type resins merely adsorb acids molecularly instead of exchanging anions. Bishop<sup>9</sup> considers the mechanism of the adsorption of acids by ion exchange resins to be one of covalent adsorption. Myers, Eastes and Urquhart<sup>10</sup> and Bhatnagar and his co-workers<sup>11</sup> have examined the adsorption isotherms for the

adsorption of acids by various amine type resins. Wiklander<sup>12</sup> recently has investigated briefly some of the anion exchange reactions for Wofatit M and has concluded that this amine resin behaves as a true exchange substance exchanging anions in a manner quite analogous to cation exchangers. Griessbach<sup>13</sup> also considers Wofatit M to be a true anion exchange resin. However, considerable data are lacking for the acid-base character of these resins and the nature and mechanism of the various exchange equilibria involved in many anion exchange systems. This work was undertaken in an attempt to study these factors in a typical anion exchanger resin.

### Experimental

**Preparation of Resins.**—The resin chosen for this study was Amberlite IR4B, an amine type resinous exchanger containing 14% nitrogen in the hydroxyl form of the exchanger. The hydroxyl form of the resin was prepared by repeated treatments with a normal solution of sodium hydroxide and subsequent rinsing of the resin with distilled water until a suspension of the resin remained neutral after twenty-four to forty-eight hours. Samples of the resins whose exchangeable ions were other than the hydroxyl ion were prepared by treating the hydroxyl form of the resin several times with an excess of the required acid (molar solutions) followed by several rinses with distilled water. Due to the hydrolysis of the salt forms of the resin, rinsing was discontinued when the pH of the suspension was about 3.5. The amount of excess acid remaining after the rinse was much below 10% of the total capacity. This value may be obtained from the data presented graphically in Figs. 5-9. Since the acid liberated upon equilibration with water was approximately 10%, the amount of uncombined anion must be below this value since this value includes hydrolytic acidity. The capacity of the hydroxyl form of the resin toward HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and CH<sub>3</sub>-

- (1) H. S. Thompson, *J. Roy. Agr. Soc. (London)*, **11**, 68 (1850).
- (2) T. T. Way, *ibid.*, **25**, 313 (1850).
- (3) S. Mattson and L. Wiklander, *Soil Science*, **49**, 109 (1940).
- (4) S. Mattson and K. G. Larson, *ibid.*, **61**, 313 (1946).
- (5) H. Jenny, *Kolloid Chem., Beiheft*, **23**, 428 (1927).
- (6) H. J. Jenny, *Colloid Sci.*, **1**, 33 (1946).
- (7) S. Sussman, F. C. Nachod and W. Wood, *Ind. Eng. Chem.*, **37**, 618 (1945).
- (8) M. C. Schwartz, W. R. Edwards, Jr., and G. Boudreaux, *ibid.*, **32**, 1462 (1940).
- (9) J. A. Bishop, *J. Phys. Chem.*, **50**, 6 (1946).
- (10) R. J. Myers, J. W. Eastes and D. Urquhart, *Ind. Eng. Chem.*, **33**, 1270 (1941).
- (11) Bhatnagar, et al., *J. Indian Chem. Soc.*, **18**, 447 (1941).

- (12) L. Wiklander, *Annals of the Roy. Agric. Coll. Sweden*, **14**, 1 (1946).
- (13) R. Griessbach, *Z. Ver. deutsch. Chemiker., Beih.*, **31**, 1 (1939).

COOH has already been discussed in a previous paper.<sup>14</sup> The maximum capacity of the resin toward HCl and  $\text{CH}_3\text{-COOH}$  leveled off at approximately 10 milliequivalents per gram, which corresponds to one chloride ion for every nitrogen in the resin. The capacities toward sulfuric acid and phosphoric acid were 11.6 and 27.7 milliequivalents per gram, respectively. This would indicate that some of the capacity toward  $\text{H}_2\text{SO}_4$  was satisfied with  $\text{HSO}_4^-$  as well as  $\text{SO}_4^{2-}$  ions and toward  $\text{H}_3\text{PO}_4$ , the capacity was satisfied with  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  ions. The resins were filtered on a Büchner funnel and stored in a moist form in stoppered bottles. Moisture contents of the hydroxyl, chloride, sulfate, phosphate, and acetate forms of the resin were 39.9, 71.3, 40.5, 33.9, and 60.8%, respectively.

**Method of Study.**—The study of the various exchange reactions was conducted by equilibrating the resin with the appropriate solution for forty-eight hours, a time found to be quite sufficient for equilibration according to results previously reported.<sup>14</sup> The ratio of solid to liquid phase was held constant at 1 g. of resin for each 50 ml. of solution. The extent of reaction was varied through a variation in concentration of the solution added. The concentration of the initial solutions was varied from 0.004 to 0.100 normal. The exchange reactions were followed by an analysis of the liquid phase for the anions involved. The titration curves were determined in a similar manner,  $\text{pH}$ 's being measured with a glass electrode. Although it is doubtful whether an acid such as phosphoric behaves as a tribasic acid toward exchange, all results for polybasic acids were calculated on a true equivalent basis rather than on apparent basis.

**Systems Studied.**—In this investigation, systems involving the three operations commercially designated as *acid adsorption*, *regeneration*, and *anion interchange* were studied. For the acid adsorption cycle, the titration curves for the neutralization of several mono-, di- and tri-basic inorganic and organic acids by the hydroxyl form of Amberlite IR4B in water and in neutral salt solutions were determined. For the "regeneration cycle," the titration curves were obtained for the reaction between the chloride and sulfate forms of the resin and solutions of NaOH,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$  and  $\text{NH}_4\text{OH}$ . The "anion interchange" cycle was studied for the reactions between the chloride and sulfate forms of the resin and solutions of NaOH,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ , and  $\text{NH}_4\text{OH}$ . The "anion interchange" cycle was studied for the reactions between the chloride, sulfate, acetate and phosphate forms of the resin and solutions of various organic and inorganic salts.

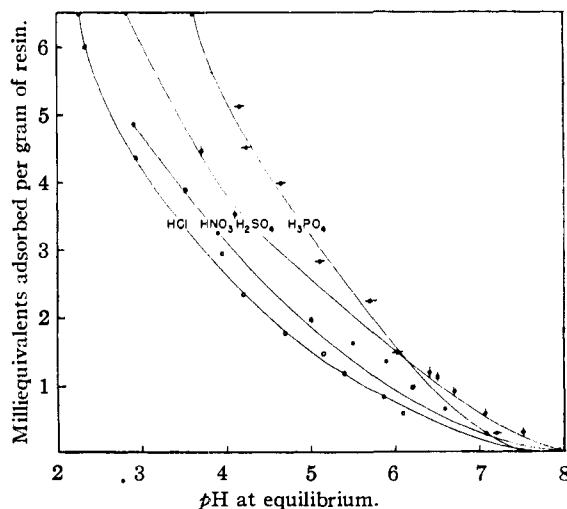


Fig. 1.—Adsorption of HCl,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{H}_3\text{PO}_4$  by Amberlite IR4B.

(14) R. K. Kunin and R. J. Myers. *J. Phys. Chem.*, **51**, 1111 (1947).

## Results

**The Acid Adsorption Titration Curves.**—The titration curves for the adsorption of ten different acids by the hydroxyl form of Amberlite IR4B are shown in Figs. 1, 2 and 3. The curves obtained are quite similar to what may be expected of a very weak base. In this series of curves, signs of an inflection point are not evident at all. However, complete neutralization of the hydroxyl form of the resin was not attained. This was anticipated since acid adsorption or exchange of anions with anion exchange resins follows an adsorption isotherm that indicates continued adsorption for concentrations in excess of those used in the titration study.<sup>10</sup> For the inorganic acids studied, the order of increasing adsorption as measured by the adsorption or exchange at any fixed  $\text{pH}$  was  $\text{HCl} < \text{HNO}_3 <$

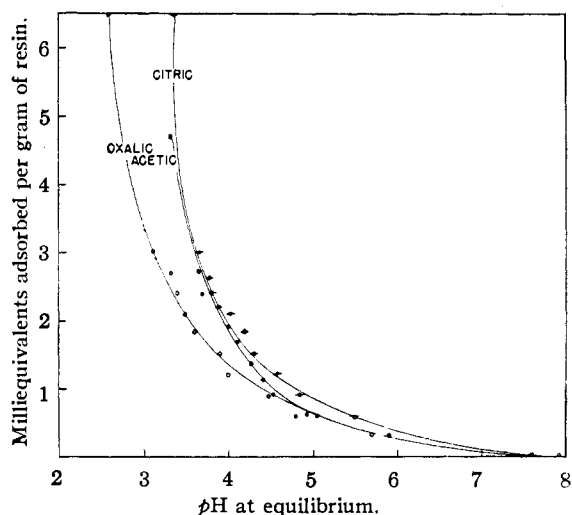


Fig. 2.—Adsorption of acetic, oxalic and citric acids by Amberlite IR4B.

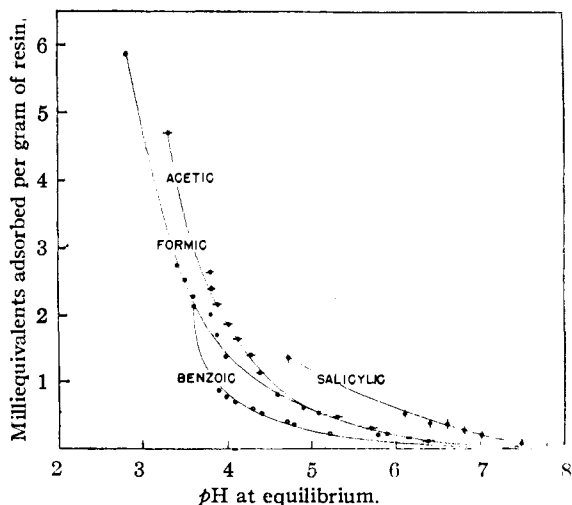


Fig. 3.—Adsorption of formic, acetic, benzoic and salicylic acids by Amberlite IR4B

$H_2SO_4 < H_2PO_4$ . With respect to organic acids, the order of adsorption was, in general, benzoic < oxalic < formic < acetic = citric < salicylic. However, this series was not constant over the pH range investigated. Some deviations were apparent at lower pH's.

In Fig. 4 is shown the effect of performing the titrations with HCl in 0.01 *N* and 1.0 *N* solutions of KCl. The results are quite striking and indicate an increase in adsorption at any fixed pH with increasing salt concentration. The same results were obtained for the titrations with  $HNO_3$  and  $H_2SO_4$  in solutions of  $KNO_3$  and  $K_2SO_4$ .

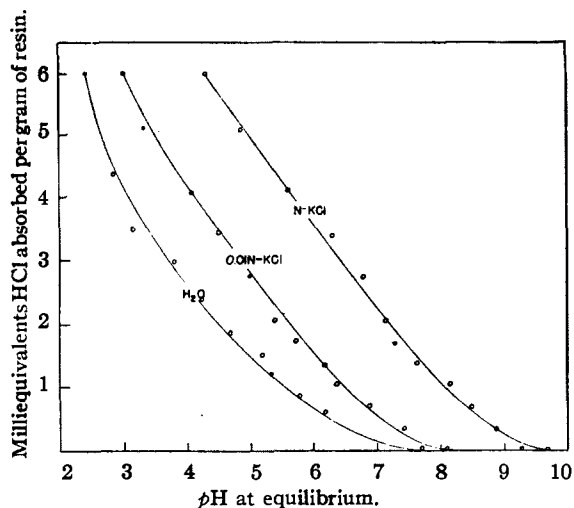


Fig. 4.—Adsorption of HCl in KCl solutions by Amberlite IR4B.

**The "Regeneration" Titration Curves.**—The "regeneration" titration curves for the "regeneration" of the chloride and sulfate forms of Amberlite IR4B are shown in Fig. 5. The data quite clearly indicate that the order of "regeneration" power was  $NaOH > Na_2CO_3 > NH_4OH$ . The results also indicated that the regeneration of the sulfate salt of the resin was more difficult to

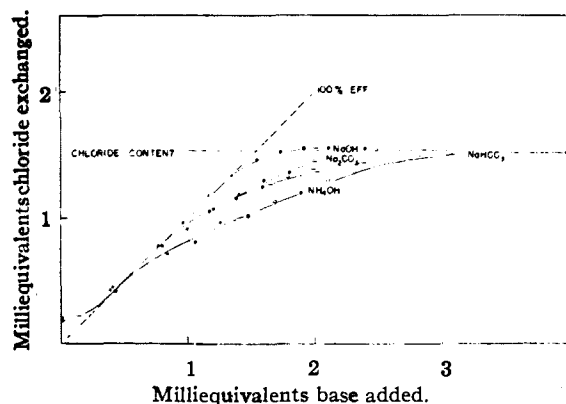


Fig. 5.—Regeneration of Amberlite IR4B-chloride with various bases.

achieve than the regeneration of the chloride salt. It is quite interesting to note that the extent of regeneration depends more upon the nature of the anion of the regenerant than upon the pH.

**Anion Exchange for Ions Other than Hydroxyl.**—The exchange reactions for the systems involving the sulfate, chromate, citrate, tartrate, nitrate, arsenate, phosphate, molybdate, acetate, iodide, bromide, chloride and fluoride anions are shown graphically in Figs. 6–10. The data for

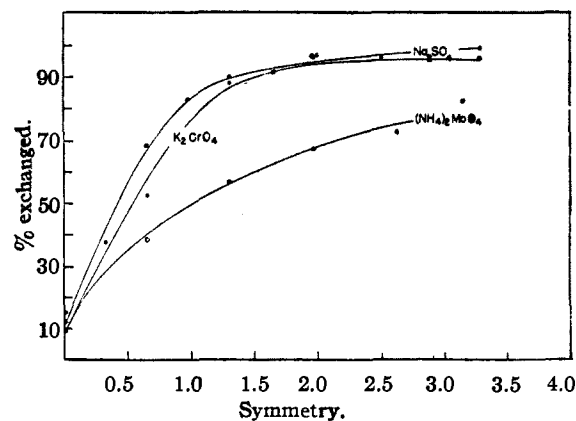


Fig. 6.—Anion exchange with Amberlite IR4B-chloride.

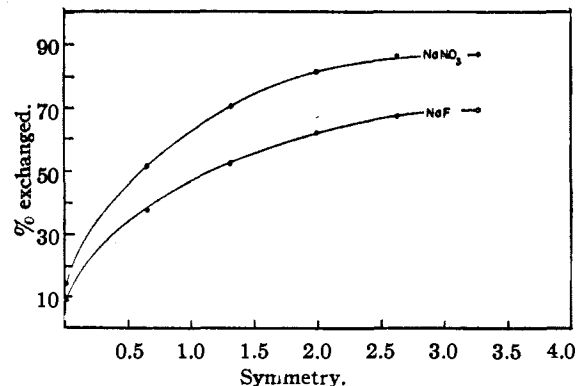


Fig. 7.—Anion exchange with Amberlite IR4B-chloride.

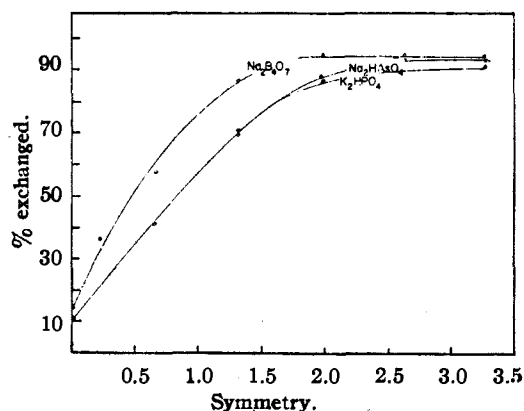


Fig. 8.—Anion exchange with Amberlite IR4B-chloride.

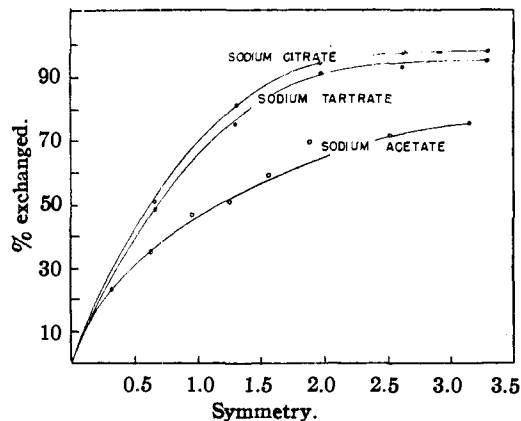


Fig. 9.—Anion exchange with Amberlite IR4B-chloride.

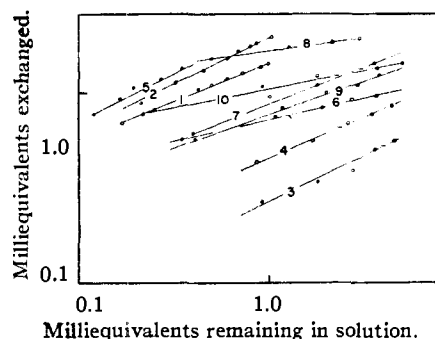


Fig. 10.—Freundlich plots for anion exchange with Amberlite IR4B: (1) Amberlite IR4B-chloride vs.  $\text{NH}_4\text{OH}$ ; (2) Amberlite IR4B-sulfate vs.  $\text{NaOH}$ ; (3) Amberlite IR4B-sulfate vs.  $\text{NaCl}$  (0.5 g.); (4) Amberlite IR4B-sulfate vs.  $\text{NaCl}$  (1 g.); (5) Amberlite IR4B-chloride vs.  $\text{Na}_2\text{CO}_3$ ; (6) Amberlite IR4B-acetate vs.  $\text{KBr}$ ; (7) Amberlite IR4B-acetate vs.  $\text{NaCl}$ ; (8) Amberlite IR4B-acetate vs.  $\text{Na}_2\text{SO}_4$ ; (9) Amberlite IR4B-chloride vs.  $(\text{NH}_4)_2\text{MoO}_4$ ; (10) Amberlite IR4B-chloride vs.  $\text{NaNO}_3$ .

these studies are presented graphically according to the method of Jenny<sup>5,6</sup> in which the per cent. exchanged is plotted against the symmetry ratio, the symmetry ratio being defined as the ratio of the equivalents of anion added as soluble electrolyte and the equivalents added as exchangeable anion. This method of presentation permits one to compare the relative exchange potentials of the various anions. An examination of the data presented in Figs. 6–10 indicates the relative exchange abilities of the various anions studied to be sulfate > chromate > citrate > tartrate > nitrate > arsenate > phosphate > molybdate > acetate = iodide = bromide > chloride > fluoride. In the reaction between the chloride form of the resin and sodium borate, it was found that although the chloride was easily replaced, no borate was adsorbed. Apparently, the borate salt of the resin is too easily hydrolyzed because of the extremely weak acidity of boric acid.

**Equivalence of Exchange.**—The equivalence of the exchange for several systems involving

the exchange of the chloride and sulfate salts of the anion exchange resin is indicated in Fig. 11. After accounting for the small degree of hydrolysis, it is quite evident that the exchange of anions is equivalent. The equivalence for the regeneration of the chloride and sulfate forms of the resin with  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{NH}_4\text{OH}$  was similar to the case of the chloride-sulfate exchange.

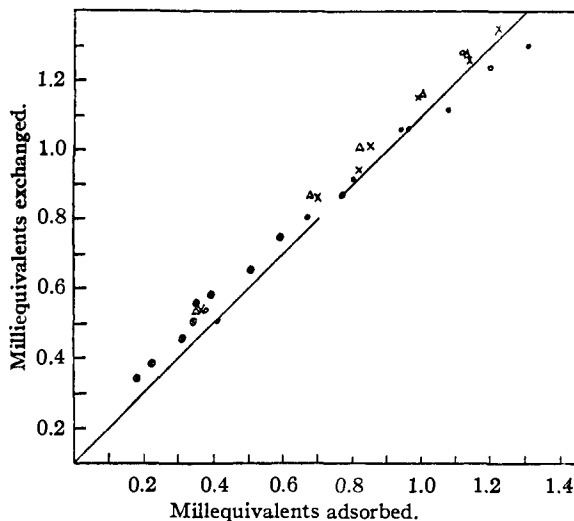


Fig. 11.—Equivalence of anion exchange with Amberlite IR4B: O, Amberlite IR4B-chloride vs.  $\text{NaOH}$ ; ●, Amberlite IR4B-chloride vs.  $\text{NH}_4\text{OH}$ ; Δ, Amberlite IR4B-chloride vs.  $\text{Na}_2\text{CO}_3$ ; ×, Amberlite IR4B-chloride vs.  $\text{NaHCO}_3$ ; ⊗, Amberlite IR4B-chloride vs.  $\text{Na}_2\text{SO}_4$ . Straight line shows theoretical slope for equivalence.

**Exchange Equation.**—Various plots were made of the data utilizing the Freundlich, Langmuir, mass action, and the Rothmund and Kornfeld<sup>15</sup> relationships. Although a fair agreement was obtained with the Freundlich equation (Fig. 10) and not with the others, this may not be cited as evidence for a simple adsorption mechanism. In fact, it should be stated that agreement with the Freundlich equation is not obtained at concentrations higher than those investigated in this study. The results at higher concentrations were reported previously.<sup>14</sup> Inability in applying the mass action relationship may merely be due to the inability in obtaining the true activities in the solid phase.

#### Discussion of Results

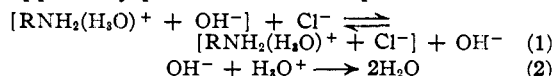
This investigation has revealed evidence to support the theory that the mechanism for the adsorption of electrolytes by the amine type "anion exchange" resins is essentially an exchange of anions rather than an adsorption of the whole acid molecule. Although the resin may contain primary, secondary, and tertiary amine groups, for simplicity of presentation, one may simply consider one of these groups, the  $\text{RNH}_2$  group for example. In aqueous media, the  $\text{RNH}_2$  groups may

(15) Rothmund and Kornfeld, *Z. anorg. Chem.*, **108**, 129 (1918).

combine with a hydronium ion in a manner analogous to ammonia or a soluble amine according to the equilibrium

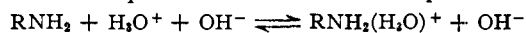


A reaction between this resin and acid (HCl) apparently proceeds in two steps



In other words, the neutralization of the acid depends just upon the exchange of a hydroxyl ion.

These conclusions are in agreement with those of Wiklander,<sup>16</sup> Griessbach,<sup>17</sup> and Jenny<sup>6</sup> but are in disagreement with those of Schwartz, *et al.*<sup>8</sup> These conclusions are also in disagreement with those of Bishop,<sup>9</sup> who considers the adsorption as involving the formation of covalent bonds between the nitrogen of the resin and the hydrated proton of the acid, the anion being retained by electrostatic attraction. However, the conclusion of Schwartz, *et al.*, and Bishop that the adsorption of acid was essentially an adsorption of whole molecules was based upon the fact that in neutral and basic solutions no adsorption of anions was evident. Such a situation does not exclude the exchange mechanism since one is dealing with a weak base whose dissociation is low and therefore is incapable of exchanging anions to any extent in neutral and basic solutions. However, in acid solutions the hydroxyl ion activity is so small that dissociation of the base is appreciable enough for anion exchange to take place to a great extent. Since the resin is weakly basic, it is quite difficult to prove the existence of hydroxyl groups in the "exchange" complex of the resin. However, the fact that the *pH* of the equilibrium solution formed on the addition of a neutral salt to the "hydroxyl" form of the resin is alkaline and increases in alkalinity with increasing concentration is strong evidence for the existence of hydroxyl groups. Since soluble amines set up an equilibrium in aqueous media which corresponds to



one should therefore expect the amine groups of the insoluble resinous polyamine to behave similarly. In other words, one may picture the resinous exchanger as containing amine groups which function in aqueous media as soluble amines. Since the basic strength of the resin is low, the

hydroxyl ion activity is low and therefore anion exchange with neutral electrolytes is extremely slight, but detectable. However, in acid solutions, the exchange becomes appreciable due to the continuous removal of the exchangeable hydroxyl ions by neutralization. It is quite interesting to note that results similar to those reported here have also been reported for alumina<sup>16</sup> and have been quite frequently reported for charcoal.<sup>17</sup>

As has been observed by many investigators, for cation exchangers, it is quite apparent that the anion exchange abilities of the various anions depend upon the structure, size, valence of the anion, and upon the type of salt formed. A comparison of the results obtained for HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>, and the differences observed between acetic and benzoic acids would indicate that the ionization is not an important factor. However, for such acids as weak as boric and silicic acids, the extent of exchange is nil due to the ease in which the resin salts of these acids are hydrolyzed.

**Acknowledgment.**—The authors are indebted to Mr. Edward Keyser for his extensive laboratory assistance during the course of the study.

### Summary

1. A study has been made of various anion exchange equilibria associated with the anion exchange resin, Amberlite IR4B, a polyamine type resin. This study has included reactions usually designated as *acid adsorption, regeneration, and anion interchange*.

2. Evidence has been obtained which indicates that all three processes are true anion exchange reactions in which the equilibria for the various anions involved are dependent upon the structure and valence of the anion as well as the ionization constant of the corresponding acid. The order of the exchange "potentials" of the various anions studied was found to be: hydroxide > sulfate > chromate > citrate > tartrate > nitrate > arsenate > phosphate > molybdate > acetate = iodide = bromide > chloride > fluoride.

PHILADELPHIA, PA.

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(16) R. P. Graham and A. E. Horning, *THIS JOURNAL*, **69**, 1214 (1947).

(17) T. Svedberg, "Colloid Chemistry," Chem. Cat. Co., Inc., Reinhold Publ. Corp., New York, N. Y., 1928, p. 243.