nitrogen analyses; and to Miss Elizabeth Gebert for assistance with the spectrophotometric studies.

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Anion-exchange Studies. XII.[1,2] Adsorption of Acids by Strong Base Anion-exchange Resins in Polyvalent Forms. Separation of Weak and Strong Acids

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RECEIVED APRIL 24, 1954

In previous communications,[3,4] it was demonstrated that a strong base anion-exchange resin in the sulfate form can adsorb strong acids and that this property can be utilized to separate strong acids from salts. In these earlier communications it was implied that this adsorption of acids should not be restricted to the sulfate form of the resin but should also occur with resins containing other polyvalent ions, *e.g.*, phosphates, citrates, etc. Additional experiments have now been carried out which confirm this hypothesis.

Since adsorption of strong acids by the polyvalent forms of anion-exchange resins probably involves an acid–base reaction, it appeared probable that weak acids such as acetic acid, boric acid, as well as non-electrolytes, should show considerably less absorption and hence should be separable from strong acids. However, ion-exchange resins appear to have unusual solvent properties for some organic materials such as indicated, for example, by the widely varying selectivities of ion exchange resins for various organic acids.[5] Hence, successful separation of weak acids and non-electrolytes from strong acids probably depends on absence of significant acid–base reactions as well as on absence of unusual solvent properties of the resin.

1. Adsorption of Acids by Polyvalent Forms of Strong Base Anion-exchange Resins.—As an extension of the work on the adsorption of sulfuric acid by the sulfate form of a strong base anion-exchange resin, the adsorption of phosphoric acid by the phosphate form of the resin was investigated, as well as adsorption of hydrochloric acid and citric acid by the citrate form of the resin. The resin (200–230 mesh) was from the same batch of the quaternary amine polystyrene divinylbenzene resin (Dowex-1) used in the earlier work.[3,6] Adsorption was demonstrated by a column method. Acids were passed into *ca.* 7.5-ml. columns of cross-sectional area 0.5 cm.^{2} at a flow rate of *ca.* 0.5 cm./min. and the break-through volume determined by acid–base titrations of the effluent. The phosphate and citrate forms of the resin[7] were prepared in a manner analogous to the method used for the preparation of the sulfate forms,[4] *i.e.*, by passing concentrated solutions of ammonium citrate (*p*H 8) or sodium phosphate (*p*H 11) through the chloride form of the resin until there was a negative chloride test in the effluent and then washing the resin extensively with water.

The results of some typical experiments are illustrated in Fig. 1, which is divided into four parts. Part A illustrates the adsorption of 0.08 *M* H_2SO_4 by the sulfate form of the resin, part B, the adsorption of 0.25 *M* H_3PO_4 by the phosphate form, part C, the adsorption of 0.24 *M* citric acid by the citrate form, and part D, the adsorption of 0.5 *M* HCl by the citrate form. The apparent interstitial volume of the columns was taken to be 42%[8] of the total column volume and is shown by a dashed line in the figures. As seen from Fig. 1, several column volumes of the acids can be passed through the columns before significant break-through of acid occurs and thus it appears that adsorption of acids by the polyvalent forms of the anion exchangers is general. In addition, as shown in part C, for the citrate form of the resin regeneration by water elution is at least partially successful, as it also was for the sulfate form, since *ca.* 60% of the adsorbed citric acid was removed in four volumes of water wash.

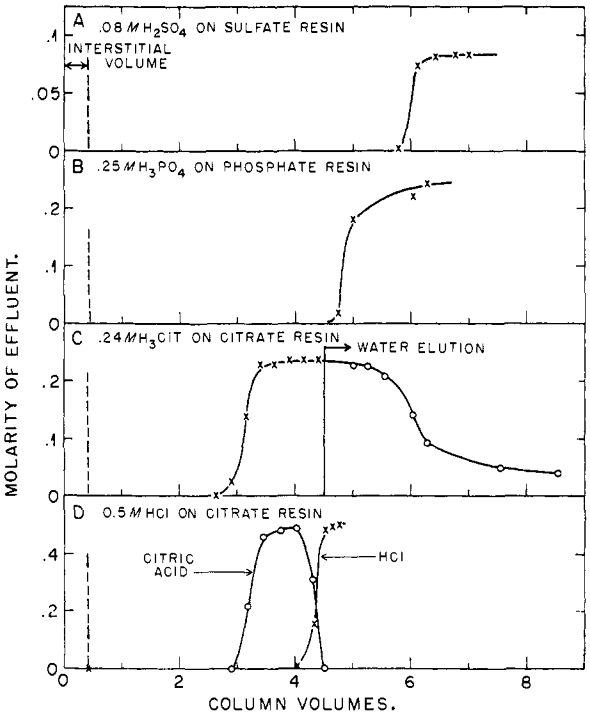

Fig. 1.—Adsorption of acids by polyvalent forms of anion-exchange resins.

In experiment D, acid–base titrations were supplemented by chloride titrations ($AgNO_3$). The results show that hydrochloric acid can be adsorbed by the citrate form of the resin and that on extensive treatment with hydrochloric acid, citric acid is essentially completely removed before

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[1] This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] Previous paper, K. A. Kraus and F. Nelson, THIS JOURNAL, **76**, 5916 (1954).

[3] K. A. Kraus, F. Nelson and J. F. Baxter, *ibid.*, **75**, 2768 (1953).

[4] K. A. Kraus and F. Nelson, *ibid.*, **75**, 3273 (1953).

[5] See, *e.g.*, S. Peterson, *Ann. N. Y. Acad. Sci.*, **57**, 144 (1953).

[6] K. A. Kraus and G. E. Moore, THIS JOURNAL, **75**, 1457 (1953).

[7] These terms will be used although the resins contain, in addition to phosphate and citrate ions, certain amounts of hydrogen phosphates and hydrogen citrates.

[8] K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, **58**, 11 (1954).

large break-through of hydrochloric acid occurs. Analogous results were obtained earlier with hydrochloric acid and the sulfate form of the resin.[3]

2. **Adsorption of Weak Acids and Non-electrolytes.**—The adsorption of some typical weak acids or non-electrolytes, namely, acetic acid (HAc), boric acid and phenol, by the sulfate form of the resin was investigated. Approximately 0.5 *M* solutions of these materials were passed into 7.5 cm. × 0.5 cm.[2] columns and the volume measured at which significant break-through occurred.[9] The results of the experiments are summarized in Fig. 2A. The effluent concentration became 50% of the initial concentration ("50% break-through") at 1.3, 1.8 and 6.5 column volumes for HAc, boric acid and phenol, respectively, indicating slight retention of acetic and boric acids and relatively strong retention of phenol. Since the phenol from approximately 6 column volumes was adsorbed, the phenol concentration of the resin was apparently greater than 3 moles per liter of bed, which may be compared with its anion-exchange capacity of *ca.* 1.6 equivalents per liter of bed.[6] Similar experiments were carried out with the chloride form of the resin (see Fig. 2B). In this case "50% break-through" occurred after 0.9 column volumes for acetic and boric acids and after 5.5 column volumes for phenol. The slight retention of acetic and boric acids in this case is probably largely due to the fact that these acids distribute more or less evenly through the aqueous and resin phases in a manner analogous to that described by Wheaton and Bauman.[10,11] The differences in retention of these acids for the chloride and sulfate forms are analogous to similar differences in adsorption of organic materials for different ionic forms found by Gregor, Collins and Pope[12] and Wheaton and Bauman[11] and may be only little affected by possible acid–base reactions with the sulfate form of the resin. The strong adsorption of phenol which was previously reported for the chloride form of the resin,[11] on the other hand, is probably typical of the specific solvent effects which one might anticipate, considering that a large fraction of the resin is organic material.

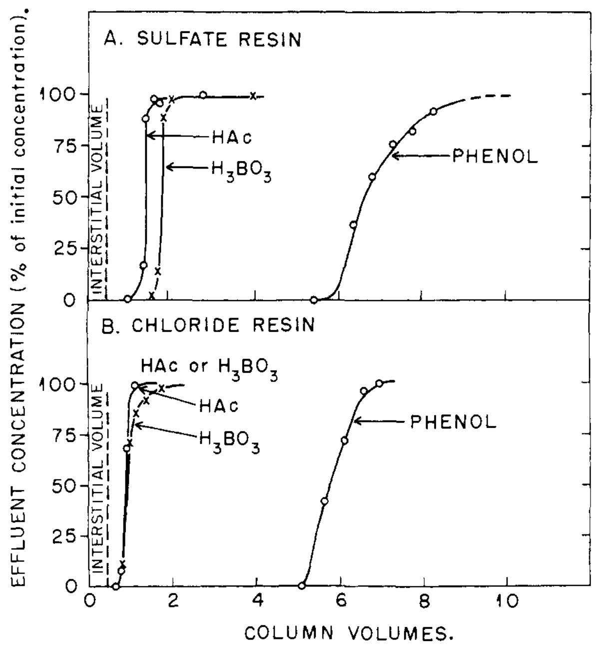

Fig. 2.—Adsorption of acetic acid, boric acid and phenol by a quaternary amine resin.

3. **Separation of Acetic Acid and Sulfuric Acid.**—The separation of weak acids from strong acids with the polyvalent forms of anion-exchange resins is illustrated by the separation of acetic acid from sulfuric acid using the sulfate form of the resin (see Fig. 3). For this experiment a 2-ml. sample of a mixture of 0.5 *M* HAc and 0.5 *M* H_2SO_4 was placed on a 15.7 cm. × 0.48 cm.[2] column of Dowex-1 in the sulfate form and elution was carried out with water at a flow rate of 0.3 cm./min. Excellent separation of acetic acid from sulfuric acid was obtained. Regeneration of the column, *i.e.*, removal of the adsorbed sulfuric acid, was relatively slow due to the excessive tailing which appears to occur with this resin.[3] The acetic acid fraction of the effluent was essentially free of sulfate ($M\ SO_4^= < 10^{-4}$) as determined by barium sulfate precipitation (turbidity) tests.

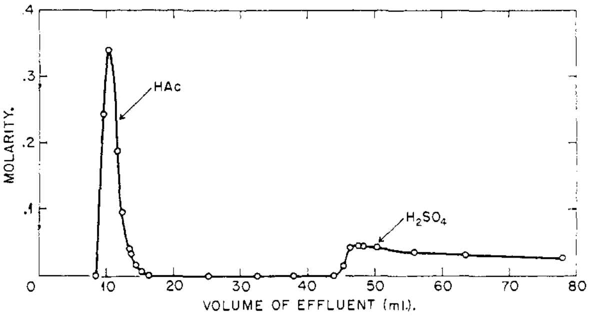

FIGURE 3.

Fig. 3.—Separation of acetic and sulfuric acids; 15.7 cm. × 0.488 cm.[2] Dowex-1 column; 2.0 ml. 0.5 *M* HAc–0.5 *M* H_2SO_4; eluent, water; flow rate 0.3 cm./min.

The result of this experiment is concordant with the analogous experiment of Fig. 2A, since the acetic acid was slightly retained by the resin, but not sufficiently strongly to impair the success of the separation. One might, therefore, also expect that separation of sulfuric acid from boric acid would be satisfactory. On the other hand, separation from phenol could probably not be achieved satisfactorily in view of its inherent strong adsorbability.

Thus, the technique of adsorbing strong acids on the polyvalent forms of strong base anion-exchange resins, which was earlier shown to permit their separation from certain electrolytes, can also be used for their separation from certain non-electrolytes and weak acids. However, before the technique is applied to a specific separation, it will be necessary to determine whether the materials in

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[9] Boric acid and phenol concentrations in the effluent were determined by standard analytical techniques: see Scott's "Standard Methods of Chemical Analysis," Vols. 1 and 2, 5th Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1939.

[10] R. M. Wheaton and W. C. Bauman, *Ind. Eng. Chem.*, **45**, 228 (1953).

[11] R. M. Wheaton and W. C. Bauman, *Ann. N. Y. Acad. Sci.*, **57**, 159 (1953).

[12] H. P. Gregor, F. C. Collins and M. Pope, *J. Colloid Sci.*, **6**, 304 (1951).

question show unusual adsorptive properties, *i.e.*, the electrolytes form strongly adsorbable complexes or the resin shows unusual solvent properties for the non-electrolytes or weak acids.

Acknowledgment.—The authors are indebted to Mrs. L. W. Magnusson, Jr., and Miss Zella Bonner for valuable technical assistance.

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The Reaction of Lithium Amide with Diborane

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RECEIVED JULY 29, 1954

Diborane reacts with an ether slurry of lithium amide to give lithium borohydride and polymeric aminoborine.

$$B_2H_6 + LiNH_2 = LiBH_4 + BH_2NH_2 \qquad (1)$$

When there is an excess of diborane, the reaction proceeds rapidly and completely, the excess diborane is recovered unchanged, all of the lithium is found as the ether-soluble borohydride, and all of the nitrogen remains as an ether-insoluble material possessing the empirical formula NH_2BH_2.

No appreciable reaction takes place between solid lithium amide and diborane gas but if diethyl ether[2] is added, the reaction proceeds smoothly and rapidly, even at −64°. The need of an ether medium is similar to its necessity in the reaction between diborane and lithium hydride to give lithium borohydride. Using finely ground lithium amide the reaction was usually complete in less than one-half hour; for somewhat coarser material, the time of reaction was considerably longer. If care is not taken to moderate the reaction, significant amounts of hydrogen are produced or if lithium amide is taken in considerable excess, all of the diborane reacts and a large amount of hydrogen is produced. It appears from the observed pressure changes that the initial reaction between the amide and diborane is unchanged and that the hydrogen probably arises from further reaction between the products of the initial reaction and the excess amide. These hydrogen-producing reactions have not been investigated.

Experimental

Materials.—Commercial lithium amide of 98% purity, as determined by the ammonia produced on hydrolysis, was used. Diborane was prepared from lithium hydride and diethyl ether–boron fluoride.[3]

Reaction of Lithium Amide and Diborane.—A weighed sample of lithium amide was introduced through a side-arm into a reaction tube attached to the usual vacuum apparatus for the handling of condensable gases,[4] after which the side-arm was sealed and the reaction tube evacuated. Anhydrous ether and a measured volume of diborane were condensed onto the lithium amide. The reaction tube was so arranged that it could be sealed from the vacuum apparatus or could be made to connect to a manometer by means of which pressure changes could be followed.

After completion of the reaction, the hydrogen was measured and all other volatile products were transferred to the vacuum apparatus and carefully examined. The results of several experiments are given in Table I. The excess diborane in the amount recorded and pure diethyl ether were the only volatile substances detected. No nitrogen was found in the ether-soluble material. If the diborane was in excess (experiments 1 to 5), one mole reacted for each mole of lithium amide taken within the time needed (about one-half hour) to bring the reactor to room temperature. Extending the time of contact resulted in no further change (compare experiments 1 and 5). When the reaction mixture was brought to room temperature rapidly (experiments 6 and 7), considerable hydrogen was produced, probably because of localized heating which, under these conditions, would always occur during the initial phase of the reaction.

TABLE I

THE REACTION OF LITHIUM AMIDE WITH DIBORANE

Expt.	$LiNH_2$, mmoles	B_2H_6, mmoles	B_2H_6 consumed, mmoles	Time	H_2, cc.	B_2H_6/ $LiNH_2$
1	9.7	17.7	8.5	1 hr.	Trace	0.88
2	4.77	8.17	4.33	1 da.	Trace	.91
3	3.57	6.52	3.53	1 da.	Trace	.99
4	6.30	13.4	6.21	1 da.	7	.99
5	9.68	14.3	9.60	7 da.	7	.99
6	8.03	12.2	7.36	1 da.	61	.92
7	9.15	13.4	8.08	3 hr.	67	.88
8	16.4	13.7	13.7	14 da.	188	
9	10.7	2.90	2.90	1 da.	34	
10	13.4	4.91	4.91	1 da.	43	

When the amide was in excess, all the diborane taken was consumed (experiments 8, 9 and 10), but considerable hydrogen was produced. By observation of the pressure changes during the reaction it was evident that hydrogen continued to evolve by a slower, but nevertheless rapid, reaction after the absorption of diborane was complete.

Identification of the Products.—In two experiments (1 and 2) under conditions which presumably resulted in a simple process, the non-volatile reaction products were extracted with diethyl ether, the product being divided into ether-soluble and ether-insoluble portions. The technique which was employed permitted complete recovery of the ether soluble material but only partial recovery of the ether-insoluble material. Analyses of the total ether-soluble material for boron and hydrolyzable hydrogen and of a portion of the insoluble material for boron and nitrogen are recorded in Table II. From these data it is evident that the ether-soluble material is lithium borohydride (boron to hydrogen ratio 1.0 to 3.8, theory 1.0 to 4.0) and that one mole of the borohydride is found for each mole of lithium amide taken (boron to lithium amide ratio 1.00 to 1.01). By difference, the ether-insoluble material should be BH_2NH_2 and this is confirmed by the boron to nitrogen ratio of 1.00 to 0.95 (theory 1.00 to 1.00) obtained by direct analysis.

TABLE II

ANALYSIS OF THE REACTION PRODUCTS

$LiNH_2$ taken, mmoles	H_2, meq.	Ether-soluble portion			Ether-insoluble portion		
		HBO_2, meq.	B/H	Li/B	HBO_2	NH_2	B/N
	15.1	4.07	1:3.70		2.96	3.05	1:1.02
4.65	18.3	4.78	1:3.82	1:0.97	1.83	1.69	1:0.93
3.47	12.82	3.38	1:3.80	1:1.02	1.31	1.22	1:0.93

The identity of the ether-soluble product is confirmed by a further observation on the reaction product derived from 5.23 mmoles of lithium amide. Diethyl ether was added in portions, the equilibrium pressure being recorded after each addition. The plot of pressure against mole ratio of ether to the lithium amide originally taken was identical with that expected for 5.23 mmoles of lithium borohydride. The observed dissociation pressure between mole ratio of 0.54 and 0.92 was 9 to 12 mm. compared with 11.4 mm. for lithium

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[1] Taken from a thesis submitted to the Graduate School of St. Louis University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. Rapp, THIS JOURNAL, **75**, 199 (1953).

[3] H. I. Schlesinger, H. C. Brown, J. K. Gilbreath and J. S. Katz, *ibid.*, **75**, 195 (1953).

[4] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.