Dowex 50. Under these conditions there was essentially no separation of yttrium and europium. The single peak in the citrate elution curve was shown to contain both yttrium and europium by comparison of an absorption curve with that obtained on the original tracer mixture. With slightly different conditions and longer columns, europium and yttrium have been separated using citrate.[7] These workers found yttrium between dysprosium and holmium in the order expected from crystal ionic radii. Others have reported[8] that, under conditions slightly different from those of Ketelle and Boyd and also different from those employed here, europium, gadolinium and yttrium are eluted at very nearly the same rate.

Discussion

The fact that successful separations by ion exchange using mixed solvents can be achieved suggests that many new complexing agents which are insoluble in water can be used if a suitable mixed solvent can be found which is sufficiently polar in nature to permit ion exchange to occur reversibly. The fact that the reaction by which the metal chelate is formed is not rapid does not rule out the use of the chelating agent, since HTTA is known to be slow in forming these complexes.

The method may be useful for more rapid and efficient separation of those rare earth elements which are commonly separated by citrate elution. It may also be applicable to the separation of certain transuranium elements.

LOS ANGELES, CALIFORNIA

(7) B. H. Ketelle and G. E. Boyd, THIS JOURNAL, **69**, 2800 (1947).

(8) Geoffrey Wilkinson and Harry G. Hicks, *Phys. Rev.*, **75**, 1370 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Studies on Ion Exchange Resins. IX. Capacity and Specific Volumes of Quaternary Base Anion Exchange Resins[1]

BY HARRY P. GREGOR, JACK BELLE[2] AND R. A. MARCUS

RECEIVED NOVEMBER 27, 1953

The exchange capacities, wet weights and volumes of a quaternary ammonium anion exchange resin in a number of univalent anionic states including the halide, strong mineral acid anion, hydroxide, chloro-substituted acetate and benzene and naphthalene sulfonate states, were measured. The exchange capacity was the same for all anions, and showed the absence of appreciable adsorption effects. The swelled volume of the resin phase was correlated with the partial molal volumes of the exchange anions. Swelling appears to be determined, to a considerable extent, by ion-pair formation.

This paper describes the exchange capacity of a quaternary base anion exchange resin for various univalent inorganic and organic anions. The specific wet weight and the specific volume of the resin phase when these ions occupy the exchange positions are also given. A subsequent paper in this series will present selectivity coefficient data on these same systems.

Experimental Methods

A series of Dowex 1 and Dowex 2 resins (Dow Chemical Co., Midland, Michigan) were used for these studies.[3] These resins are prepared from a polystyrene–divinylbenzene (DVB) copolymer having varying degrees of cross-linking. The designation DVB 8 refers to the 8% cross-linked material, which is the standard commercial product. DVB resins 1, 2, 4, 6 and 16 were also used. The exchange groups in the Dowex 1 resins are largely of the benzyltrimethylammonium type. In Dowex 2 resins they are of the benzylethanol–dimethylammonium type. Similar resins have been prepared by chloromethylation of the styrene–divinylbenzene copolymer, followed by treatment with the corresponding amine.[4,5] Since the chloromethylation step itself introduces a small amount of cross-linking, the actual degree of cross-linking is higher than that corresponding to the DVB content.

In this paper most of the data are for the Dowex 2 type of resin, which is referred to simply by its percentage cross-linking. Data for the Dowex 1 type of resin are so specified. Both types of resins were conditioned by treatment with 1 *m* (molal) sodium hydroxide and 1 *m* hydrochloric acid solutions alternately, using a twofold excess in terms of exchange capacity each time, at a flow rate of approximately 0.1 ml./min./ml. bed of resin. Three cycles of this treatment were followed by passing a 10-fold excess of 1 *m* sodium chloride through the bed at the same, slow flow rate. The resins were then rinsed with carbon dioxide free distilled water until the conductance of the effluent dropped to less than 2×10^{-5} mho. They were then air-dried to a free-flowing state and dry screened to $-18 + 30$ mesh and $-30 + 60$ mesh sizes for the DVB 8 and to $-60 + 100$ mesh for the DVB 1, 2, 4, 6 and 16 resins. This chloride state of the resins was taken as the "standard" state upon which all subsequent calculations of specific capacity, etc., were based.

The resins were also placed in the hydroxide state by treatment with base after the conditioning procedure. Rinsing with carbon dioxide free water was continued to an effluent conductance of 10^{-6} mho.

The moisture content of the chloride resin was determined by drying in a desiccator over phosphorus pentoxide; constant weight was attained in about 3 weeks. With oven drying at 100° the same, constant weight was attained within 24 hours. The hydroxide form was dried only in the desiccator, as it decomposed partially at the elevated temperature.

Quaternary base anion exchange resins which contain the ethanolic group are not stable in the hydroxide form, but decompose quite slowly to an amine.[3] Gilwood and Utermohlen[6] measured the stability of various resins in the hydroxide state at both room temperature and 100°, and observed that the ethanolic substituted quaternary ammonium resins are unstable relative to the purely aliphatic substituted ones. All types of resins are considerably more stable as salts of mineral acids than in the hydroxide state. However, even the decomposition of the ethanolic type resins is slow at room temperature, requiring several weeks to become measurable. In this investigation, all resins were stored in the salt (chloride) state, and were converted to the base state for use in that form.

---

(1) The authors wish to thank the Signal Corps, U. S. Army, and the Office of Naval Research for the support given this work.

(2) Taken in part from the dissertation of J. Belle, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, Polytechnic Institute of Brooklyn, October, 1951.

(3) R. M. Wheaton and W. C. Baumann, *Ind. Eng. Chem.*, **43**, 1088 (1951).

(4) Giffin D. Jones, *ibid.*, **44**, 2686 (1952).

(5) S. L. Thomas, paper given at the 120th Meeting of the American Chemical Society, New York, September, 1951.

(6) M. E. Gilwood and W. P. Utermohlen, paper presented at the 120th Meeting of the American Chemical Society, New York, Sept. 1951.

The Dowex 1 and Dowex 2 resins (both DVB 8 and −18 + 30 mesh) were titrated as described by Gregor and Bregman.[7] The exchange capacity toward anions which could readily be analyzed directly, such as chloride, bromide, iodide, thiocyanate and hydroxide, was determined by equilibration with 0.01 *m* solutions of the sodium or potassium salt, followed by displacement elution.[8] In some cases the corresponding acids also were used. The exchange capacity toward the fluoride, perchlorate, benzenesulfonate, toluenesulfonate, trichloroacetate, trifluoroacetate and β-naphthalene sulfonate anions was determined by converting the resin into the hydroxide state, adding a measured excess of the corresponding acid and back-titrating after equilibrium was reached.

The specific volume of the resin particles was determined using the centrifugation technique.[9] All data reported herein refer to one gram of dry resin originally in the chloride state: W^r_e is the specific wet weight; V^r_e the specific wet volume; the mole fraction of the exchange capacity in the chloride state is designated X^r_{Cl}; m^r is the molality of a species in the resin phase; and W^r_w the specific water content (in grams).

Suitable rate experiments were performed to determine the time required to reach equilibrium. When the DVB 8 resin in the chloride or hydroxide state was treated with 0.1 *m* solutions of the various salts, bases or acids, equilibrium was reached within one-half hour, with a half-time of about 1 minute. With 0.01 *m* solutions, the half-time was about 15 minutes. The process follows the familiar % equilibrium-$\sqrt{t}$ law, in conformity with the diffusion equation. Routinely, all exchange reactions were allowed to proceed for at least 24 hours, and all data reported herein are equilibrium values.

All experiments were carried out in the temperature range 24–26°. The solution phase was always dilute (< 0.1 *m*) unless otherwise specified.

Experimental Results

The experimental results of the titration of the Dowex 1 and Dowex 2 resins (DVB 8) are shown in Fig. 1. In each case 1 meq. of chloride resin converted to the hydroxide state was added to 100 ml. of 1 *m* potassium chloride solution, and then titrated with acid. The data are plotted in terms of the percentage titrated; 100% titration corresponds to 1 meq. of acid added.

It should be emphasized that resins bearing the same trade mark but prepared in different batches may show fairly wide variations in their properties. Only materials not only from the same batch but also of the same particle size can be compared properly. Also, the exchange capacity of these resins decreases as the degree of cross-linking increases, for particles of the same size. With −60 + 100 particles of Dowex 2 resin, capacities were as follows: DVB 1, 4.03; DVB 2, 3.86; DVB 4, 3.51; DVB 6, 3.26; DVB 8, 2.52; DVB 16, 2.14. Also, resins with the same DVB content showed increased capacity with decreasing particle size. The theoretical capacity, calculated from the formula $-CH_2CH(C_7H_6)N(CH_3)_2(CH_2CH_2OH)Cl^-$, is 4.15 millimoles per gram. The mode of preparation of the resins, which involves reactions which are in large part diffusion controlled, is responsible for this variability in the exchange capacity.

In Table I exchange capacities, wet weights W^r_e, wet volumes V^r_e and molalities m^r of the exchange anion in the resin phase are given for a number of univalent anions with resin DVB 8. The halide, thiocyanate and hydroxide capacities are for salt-equilibrated (0.01 *m*) resins, the others are for acid-equilibrated (0.02–0.05 *m*) resins. Also included in Table I are values for the partial molal anionic volumes at infinite dilution, $\bar{V}_i$, calculated from density data. These values are based on the assumption that $\bar{V}_{K^+} = \bar{V}_{Cl^-} = 18.0$ ml. mole^{-1}. Most of these values are taken from a recent summary by Fajans and Johnston,[10] the value for the trichloroacetate ion from the "International Critical Tables," for chloroacetate from Drucker,[11] for dichloroacetate by interpolation of $\bar{V}_i$ values of unsubstituted and substituted ions, and for benzenesulfonate from the "International Critical Tables." The value for the *p*-toluenesulfonate ion was calculated from the difference in $\bar{V}_i$ values of the acetate and formate ions, added to the value for the benzenesulfonate ion.

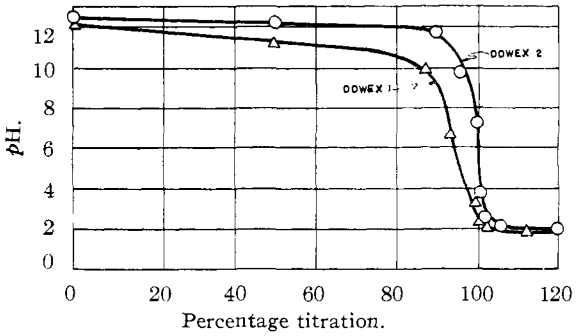

Fig. 1.—Titration of Dowex 2 (O) and Dowex 1 (Δ) resins (DVB 8) in 1 *m* potassium chloride, under equilibrium conditions.

TABLE I

SPECIFIC CAPACITY WET WEIGHTS, VOLUMES AND MOLALITIES OF DVB 8 RESIN IN VARIOUS STATES

Equilibrating solution (0.01 *m*)	Capacity mmoles/ g.	W^r_e; g.	V^r_e ml.	m^r	$\bar{V}_i$ ml.
NaF	2.30	1.715	1.571	3.01	−1.8
HCl	2.25	1.519	1.373	4.35	18.0
KCl	2.26	1.525	1.384	4.30	18.0
KBr	2.25	1.515	1.288	5.45	25.1
KI	2.25	1.516	1.216	7.31	36.7
KCNS	2.28	1.353	1.214	7.48	40.6
$HClO_4$	2.21	1.392	1.163	9.15	44.5
KIO_3		1.917	1.505	3.66	25.1
KNO_3		1.447	1.283	5.84	29.4
NaOH	2.25	1.624	1.500	3.39	−4.8
CH_3COOH		1.707	1.561	3.46	40.5
$CClH_2COOH$		1.657	1.472	4.30	51.7
CCl_2HCOOH		1.647	1.401	5.16	67
CCl_3COOH	2.22	1.664	1.382	5.99	81.3
CF_3COOH	2.23	1.606	1.366	5.24	...
$C_6H_5SO_3H$		1.695	1.533	5.38	106
p-$C_6H_4CH_3SO_3H$	2.22	1.707	1.493	5.65	120
$C_{10}H_7SO_3H$	2.25	1.765	1.512	5.99	...

The exchange capacity of the resins was independent of ionic strength in dilute solutions (< 0.1 *m*), and was found to be the same in both the salt and acid equilibrated systems. Also, the resin as prepared in the standard chloride state had the same specific exchange capacity as that prepared in the hydroxide state (referred to the same standard state) within experimental error.

When any two different univalent anions of the ones studied were present in the resin phase, the total exchange capacity was found to be the same within 1%. Figure 2 shows a plot of the specific volumes and specific water content for DVB 8 resin in mixed ionic states as a function of the chloride mole fraction.

Discussion

The titration curves of Fig. 1 show that the resin presumably containing the benzyldimethylethanolammonium group (Dowex 2) is not only stronger base, but also is more monofunctional than the one having the benzyltrimethylammonium group (Dowex 1). The Dowex 2 curve shows the presence of a small amount of exchange groups which are somewhat weaker than the majority

---

(7) H. P. Gregor and J. I. Bregman, THIS JOURNAL, **70**, 2370 (1948).

(8) H. P. Gregor, J. I. Bregman, F. Gutoff, R. D. Broadley, D. E. Baldwin and C. G. Overberger, *J. Colloid Sci.*, **6**, 20 (1951).

(9) H. P. Gregor, F. Gutoff and J. I. Bregman, *ibid.*, **6**, 245 (1951).

(10) K. Fajans and O. Johnston, THIS JOURNAL, **64**, 668 (1942).

(11) C. Drucker, *Arkiv. Kemi. Mineral Geol.*, **14A**, No. 15 (1941).

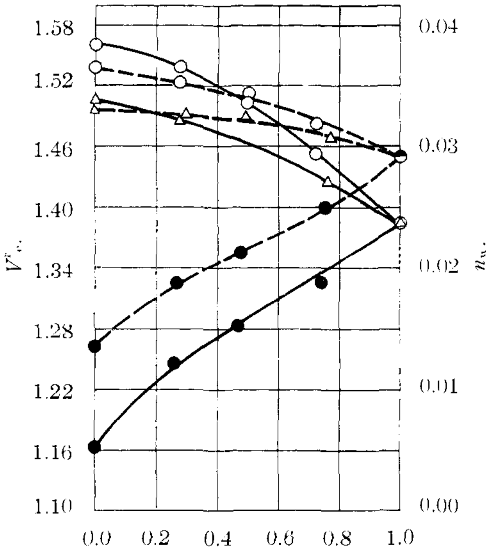

Fig. 2.—Specific volume V^r_e (solid lines) and specific water content in moles n^r_w (dotted lines) for DVB 8 resin in various mixed anionic states: chloride–acetate (O); chloride–iodate (Δ); and chloride–perchlorate (●).

present, but still of sufficient base strength to give the same exchange capacity for neutral salts as for acids, as will be shown later. The Dowex 1 resin appears to possess groups having a variety of base strengths, most of which must be weaker than the predominant group of Dowex 2 resin. Dowex 1 resin shows an increased capacity in acid media as compared with neutral solutions, as predicted from its titration curve.

These titration curves are quite different from those reported for the same resins by Wheaton and Bauman[3]; however, the titration techniques employed were quite different. Wheaton and Bauman suspended finely divided hydroxide form resin (−200 + 400 mesh) in water in the absence of added salt, and titrated directly with acid. The system was stirred continually to allow the resin particles to impinge upon the glass electrode; when the particles were allowed to settle, the *p*H dropped. This titration procedure is not one which can give results as to the true base strength of the resin, but rather measures the hydroxide ions present in the double layer surrounding the particles. The direct titration with an excess of salt added to swamp the Donnan effects gives results comparable to those that would be obtained if the polyelectrolyte were soluble, as was shown by Gregor and Bregman[6]; the other procedure measures a suspension effect.

The exchange capacity of the DVB 8 resin was the same, 2.25 ± 0.02 mmoles per gram, for all of the ions studied, for both acids and salts. Thus it appears that neither molecular nor hydrolytic adsorption occurs to an appreciable extent. Similarly, complex ion formation also appears to be absent. The same conclusions can be drawn when mixtures of different anions are present.

The fluoride ion is absorbed in its univalent state, consistent with its properties in the salt rather than acid form. It is somewhat surprising that anions as large as β-naphthalene sulfonate are able to occupy all of the exchange sites in the resin. However, the resin swells with the uptake of large exchange cations, and is in this manner able to accommodate them.[8]

The specific wet weights, volumes and molalities for the DVB 8 resin, given in Table I, show wide variations. Gregor[12] has pointed up the relationship between the activity of exchange ions and the pressure–volume changes involved in swelling the resin matrix. These considerations suggest that the resin volume be related to the solvent activity in the resin, such that large volumes correspond to low solvent activity.

Factors affecting the solvent activity in these systems include: (a) size of the unhydrated anion; (b) extent of interaction between solvent and ion (as reflected in the degree of ionic hydration); (c) extent of ion-pair formation. The data on cation exchange systems are adequately interpreted on the basis of the first two factors. For example, in cationic resins containing large, unhydrated ions, (the quaternary ammonium ions), factor a is of major importance and the resin volume increases with increasing ionic size.[9] In resins containing ions of negligible volume, (the smaller alkali and alkaline earth metals), factor b is largely operative and the resin volume increases with increasing extent of hydration.

However, these two factors do not provide a basis for interpreting the volumes of anion exchange resins. For example, the volume of the resin containing the trichloroacetate ion is considerably smaller than one containing the acetate ion. Both ions are relatively large and it is expected that factor b would be relatively unimportant. Factor a, however, predicts the reverse behavior.

Other examples are found from an examination of the resin volumes of the larger halide ions. It will be noted that these ions show a decrease of resin volume with increasing (unhydrated) ionic size. Even if the effects of hydration on the water activity are approximately allowed for by computing the mole fraction of the "unbound" water molecules[13] and setting the solvent activity proportional to this, the resin volume still increases with increasing water activity, as calculated on this basis. However, the assumption that ion-pairing exists and increases with increasing size of the halide ion provides a simple correlation of the data.

Much of the data in Table I can be readily explained if one assumes factor c, the occurrence of ion-pair formation, predominates. The solvent activity then is related to the number of *mobile* ions in the resin and not so much to the total number of ions present there. With increasing atomic weight in the halide series, it is expected that increased ion-pair formation will occur, with the result of increased solvent activity and decreased resin vol-

---

(12) H. P. Gregor, THIS JOURNAL, **73**, 642 (1951).

(13) The mole fraction of the unbound solvent is $(n_w - nn_i)/(n_w + (1 - n)n_i)$, where n is the number of molecules bound by one anion; n_w and n_i are the number of moles of water and of ions in solution. The values of n employed (H. Ulrich, *Z. Elektrochem.*, **36**, 497 (1930); *Z. physik. Chem.*, **168**, 141 (1934)) were on the large side so that the calculated effect was probably a maximum one.

ume. Another example is found in the substituted acetate ions, where increasing size might be expected to result in increasing ion-pair formation and, correspondingly, in decreasing resin volume, as is observed. In fact, the resin volumes of the majority of ions in Table I reflect the order of ions in the Hofmeister series, which in turn is perhaps related to ease of ion-pair formation.

The *p*-toluenesulfonate and *β*-naphthalenesulfonate ions show surprisingly low values of V_e, considering their large volumes. However, it is known, that large organic ions, particularly aromatic ones, are strongly adsorbed by the hydrocarbon portion of the resin matrix. Here adsorption effects tend to compensate for large volumes of the ions themselves,[14] by reducing the number of mobile ions.

Measurements of selectivity coefficients, which support these arguments for ion-pairing, will be presented in a later paper. In fact, much of the data in Table I will be correlated there on this basis.

Quantitative calculations for these resin systems are simplified if the volumes of the components are additive in the sense that $V^r_e = V^r_m + n^r_w \bar{V}_w + n^r_i \bar{V}_i$, where V^r_m, the volume of the resin matrix, $\bar{V}_w$, the partial molar volume of the solvent, and $\bar{V}_i$ are all sensibly constant. Values for $\bar{V}_i$ were given earlier in Table I. In Fig. 3 $V^r_e - n^r_i \bar{V}_i = V^r_m + n^r_w \bar{V}_w$ is plotted against the weight of the water in the various resins, all data being taken from Table I. A good straight line relationship is observed. The slope of the line gives the average partial molal volume of water in the resin phase, calculated to be 17.7 ml. mole^{-1}. This value is less than the value for pure water at 25° (17.95), and somewhat higher than values calculated from water sorption data by polystyrenesulfonic acid resins by Gregor, Sundheim, Held and Waxman.[15] In view of the weaker hydration forces present in these systems, as evidenced by their water sorption curves,[15] the value of 17.7 ml. mole^{-1} appears very reasonable. The value of V^r_m, the specific resin matrix volume, was determined for the dry resin in the chloride state, and found to be 0.820 ml. This value compares favorably with the value 0.828 ml., calculated from the data of Table I for the chloride resin.

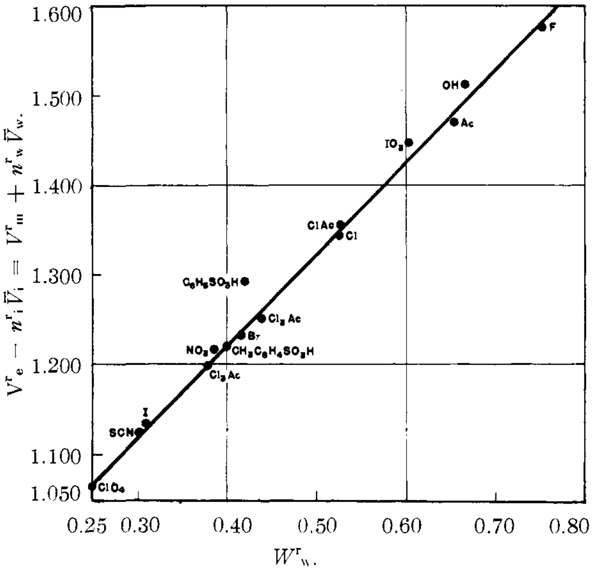

Fig. 3.—Plot of the sum of the specific volume of the resin matrix and the volume of sorbed water, which is equal to the sum of the specific resin phase volume minus the anionic volume, *vs.* the specific weight of water in the resin phase for resin DVB 8.

The deviations from the linear plot of Fig. 3 represent either deviations from volume additivity, experimental errors in V^r_e, or errors in the assumptions employed in calculating the values of $\bar{V}_i$. These are seen to be at most about 0.02 ml. (disregarding the point for the benzenesulfonate ion). It is interesting to note that the fraction of the total solution volume taken up by the exchange anion $(n_i \bar{V}_i / n_i \bar{V}_i + n_w \bar{V}_w)^r$ is 0.5% for the smallest ion (fluoride) and is 70% for the largest (*p*-toluenesulfonate).

BROOKLYN, NEW YORK

---

[14] H. P. Gregor and J. I. Bregman, *J. Colloid Sci.*, **6**, 323 (1951).

[15] H. P. Gregor, B. R. Sundheim, K. M. Held and M. H. Waxman, *ibid.*, **5**, 511 (1952).