ions of the same charge. In the case of gold a plot of log $(D(m_{\mathrm{Cl}^-}/m^r_{\mathrm{Cl}^-}))$ *vs.* m_{HCl} (Fig. 1) yields a straight line, *i.e.*

$$\log (D(m_{\mathrm{Cl}^-}/m^r_{\mathrm{Cl}^-})) = \log 1/\Gamma = a + bm_{\mathrm{HCl}} \quad (14)$$

with $a = 6.0$ and $d \log \Gamma / d\, m_{\mathrm{HCl}} = -b = 0.13$.

Although this treatment is general, since it involves only stoichiometric quantities, the assumption might be made that $HAuCl_4$ and HCl are essentially completely dissociated to H^+, Cl^- and $AuCl_4^-$ in both phases and that dissociation of $AuCl_4^-$ does not occur. If the same standard states are retained, equation 2 can then be written as $K = D((Cl^-)/(Cl^-)_r) = 1/G$. Since G contains the ratio of activity coefficients ($G = G^2_{\mathrm{HAuCl_4}}/G^2_{\mathrm{HCl}}$) of 1–1 electrolytes, the difficulties mentioned earlier regarding extrapolation to $m_{\mathrm{HCl}} = 0$ may not occur and the Debye–Hückel term of the quotient should vanish at low m_{HCl}. Hence, as a good approximation

$$a = \log \frac{1}{G^0} = \log \left(\frac{g_{\mathrm{AuCl_4^-}}\, g^r_{\mathrm{Cl}^-}}{g_{\mathrm{Cl}^-}\, g^r_{\mathrm{AuCl_4^-}}}\right)_{m_{\mathrm{HCl}} = 0} = \log \left(\frac{g^r_{\mathrm{Cl}^-}}{g^r_{\mathrm{AuCl_4^-}}}\right)_{m_{\mathrm{HCl}} = 0} = 6.0 \quad (15)$$

where G^0 is the activity coefficient quotient for the distribution equilibrium at $m_{\mathrm{HCl}} = 0$.

OAK RIDGE, TENN.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Anion-Exchange Studies. I. Bromide Complexes of Co(II), Cu(II), Zn(II) and Ga(III)[*]

BY ROLFE H. HERBER AND JOHN W. IRVINE, JR.

RECEIVED SEPTEMBER 18, 1953

The anion-exchange behavior of Zn(II), Cu(II), Ga(III), Co(II) and Ni(II) was studied in hydrobromic acid solutions. On the basis of widely differing adsorbabilities, several separations of these ions from each other in HBr solutions are feasible. With the exception of Ga(III), the anion-exchange behavior of these divalent transition elements in HBr closely parallels their behavior in HCl solutions.

A recent study by Kraus and Moore[1] has demonstrated the feasibility of separating several divalent transition elements from each other by means of an ion-exchange technique. By use of the strongly basic resin Dowex-1, a quaternary amine polystyrene–divinylbenzene resin, they were able to separate Ni(II), Mn(II), Co(II), Cu(II), Fe(III) and Zn(II) by gradually decreasing the hydrochloric acid concentration from 12 to 0.005 *M* in the eluting solution. Kraus and Moore concluded from their study that one species primarily involved in the retention by the resin was the monovalent anion, and that the order of elution from the column with increasingly dilute solutions of HCl could be correlated to the association constant of this complex. The formation of the anion complex can then be expressed as

$$M^{+\nu} + (\nu + 1)X^- = MX^-_{\nu+1} \quad (1)$$

for which

$$K_1 = \frac{(MX^-_{\nu+1})}{(M^{+\nu})(X^-)^{\nu+1}} \quad (2)$$

where M^+ represents the ν-positively charged transition element ion. The adsorption of the anion complex is given by

$$RX + MX^-_{\nu+1} = RMX_{\nu+1} + X^- \quad (3)$$

with

$$K_2 = \frac{(RMX_{\nu+1})(X^-)}{(RX)(MX^-_{\nu+1})} \quad (4)$$

where R represents the organic portion of the polymer, and which is assumed to be inert with respect to the ionic equilibria established in the system.

Ion-exchange techniques, by virtue of their ability to handle carrier-free amounts of material, are ideally suited to separation problems where concentrations of less than 10^{-8} are involved. As part of an extensive study of the separation of carrier-free amounts of cyclotron produced radioactivities, it seemed of interest, on the basis of the work of Kraus and Moore,[1] to determine the behavior of the bromide anion complexes, to see whether significant differences in elution behavior between the bromide and chloride complexes existed, and in particular to check the order of complexing of the transition elements Zn(II), Cu(II), Co(II) and Ni(II), when the complexing anion was the bromide rather than the chloride.

Due to the similarity in the anion-exchange behavior of Ga(III) and Cu(II) in HCl solutions in the presence of Dowex-1, it was also deemed of interest to study the behavior of gallium in hydrobromic acid systems, to see whether or not a separation from copper was more feasible in the latter system than in the former.

Experimental

The anion exchanger used in this study was the strongly basic resin, Dowex-1.[2] This resin, received in the chloride form, was converted to the bromide form, dried at 105° for 4–6 hours, ground in a mortar, and screened through standard (Tyler Mesh) screens. The fraction −150 +200 was slurried with distilled water, and transferred to 7–8 mm. i.d. Pyrex glass columns to make a deep bed 20–30 cm. long. The bottoms of these columns were plugged with a small amount of glass wool, fitted with a stopcock, and connected to a plastic spiral flow cell,[3] housed in a lead shield by means of a standard ball-and-socket joint. The outflow of the

---

[*] This work was supported in part by the U.S. Atomic Energy Commission.

(1) K. A. Kraus and G. E. Moore, THIS JOURNAL, **75**, 1460 (1953).

(2) Marketed by the National Aluminate Corporation under the trade name Nalcite SBR, and generously supplied to us by Dr. J. I. Bregman.

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

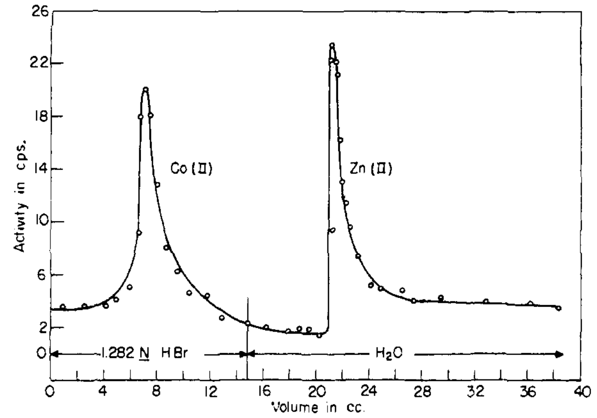

Fig. 1.—The anion separation of Co(II) and Zn(II) by bromide complexing.

spiral cell was a capillary tube drawn to a tip, and directed into (a) graduated centrifuge tubes mounted on a rotary sample changer, (b) a tared glass stoppered bottle, or (c) a small volumetric flask, depending on the collection method (see below).

The spiral flow cell inside the lead housing was faced by an end-window β,γ-sensitive G.M. tube. The output signal of this counter was divided between a pulse counter and a counting rate meter. The response of the latter was plotted on an Esterline–Angus strip chart recorder driven at about 2 cm. min.$^{-1}$. The pulse counter was used to determine periodic plateaus of the counter tube, to allow accurate activity and background determinations to be made, and to give a rapid visual indication of the counting rate, given by the scaling lights.

The radiotracers employed in this study were made by bombarding appropriate targets with 16 Mev. deuterons in the M.I.T. cyclotron. The radionuclides used were 38m Zn^{63}, 250d Zn^{65}, 12.8h Cu^{64}, 2.6h Ni^{65}, 9h Ga^{66} and 5.3y Co^{60}. The latter was obtained from the Atomic Energy Commission.

In cases where the behavior of a single activity was to be studied, the undesirable activities co-produced in the target were either allowed to decay (if short-lived) or separated by standard radiochemical techniques.[4] The radiochemical purity of the activities was determined by half-life and β-ray absorption measurements.

Aqueous hydrobromic acid was prepared by bubbling gaseous HBr through a fritted glass disc into ice-cooled distilled water, and subsequently standardized against Na_2CO_3. Analytical grade HCl was used without further purification.

The behavior of a given ion on the exchanger is given by Kraus and Moore[1] in terms of the elution constant, $E = Ad/V$, where d is the distance an absorption band travels in a column of cross-sectional area, A, on the passage of V cc. of eluant. With the present experimental set-up, several methods of evaluating E were successfully employed. A small sample (up to 0.5 cc. in most cases) of the desired activity dissolved in HBr of the appropriate concentration was allowed to seep into the top of the column, and this activity lamina then eluted with hydrobromic acid of the desired strength. By collecting fractions in calibrated test-tubes mounted on a rotary sample changer, and noting the point at which a new receiver was put into place on the strip chart recorder, a plot of volume *vs.* activity could be reconstructed from the sum of the eluant aliquots and the rate meter response.

Later experiments employed a photo-electric drop counter mounted on the tip of the outflow tube. The passage of each drop into the receiver was recorded as a small pip on the strip chart record, superimposed on the rate meter response. The total volume of eluate at the end of the experiment was determined either by weighing the total effluent and calculating the volumes from the known densities of the HBr solutions, or by collecting the effluent in a volumetric flask, filling to the mark from a buret and noting the added volume. Dividing the total eluate volume by the number of drops gave the drop volume, which in turn was used to calculate the volume corresponding to any given point on the strip chart record. The length, d, of the resin bed was determined by direct measurement. The term E_0, corresponding to no adsorption on the resin, was evaluated by the passage of 2.6y Na^{22} tracer through the column, and determining the volume at which the maximum activity appeared in the flow cell. The flow rates in these experiments were ~0.2–0.5 cc. min.$^{-1}$.

For each experiment, a plot of counting rate *vs.* volume was constructed from the raw data. The volume of eluate corresponding to the position of the activity maximum could be read from these graphs, and constituted the term V in the elution constant calculation. A typical activity *vs.* volume plot is shown in Fig. 1.

The Separation of Ni(II), Cu(II) and Zn(II).—One hundred mg. of copper foil was irradiated with 16 Mev. deuterons for five minutes at 30 μa. After a $^1/_2$-hour cooling period, the foil was dissolved in concentrated nitric acid, and the solution taken to dryness. The residue was dissolved in 5 cc. of 3 N HBr and again taken to dryness. The resulting residue was dissolved in 3.5 N HBr, transferred to a 50-cc. volumetric flask, made up to the mark with 3.5 N HBr and 5 cc. of this solution pipetted onto the top of the exchanger bed. Elution was started with 3.54 N HBr and, after the passage of the first activity peak, followed successively by 0.885 N HBr and H_2O. Fractions were collected on a rotary sample changer. The elution curve is given in Fig. 2.

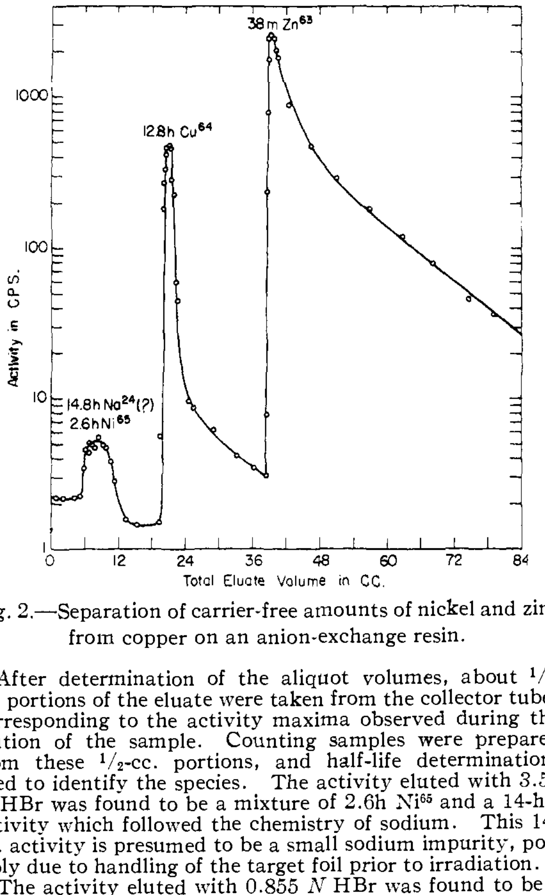

Fig. 2.—Separation of carrier-free amounts of nickel and zinc from copper on an anion-exchange resin.

After determination of the aliquot volumes, about $^1/_2$-cc. portions of the eluate were taken from the collector tubes corresponding to the activity maxima observed during the elution of the sample. Counting samples were prepared from these $^1/_2$-cc. portions, and half-life determinations used to identify the species. The activity eluted with 3.54 N HBr was found to be a mixture of 2.6h Ni^{65} and a 14-hr. activity which followed the chemistry of sodium. This 14-hr. activity is presumed to be a small sodium impurity, possibly due to handling of the target foil prior to irradiation.

The activity eluted with 0.855 N HBr was found to be a single species, $t_{1/2}$ = 12.7 ± 0.2 hr., identified as Cu^{64}. The activity eluted with H_2O was also found to constitute only a single radioactivity, $t_{1/2}$ = 38 ± 1 min., identified as Zn^{63}.

The heights of the activity maxima in Fig. 2 have not been corrected for counting efficiencies of the various activities with the end-window counter, and are thus not directly indicative of the relative yields of the counted species.

The Partial Separation of Ni(II), Ga(II), Cu(II) and Zn(II).—The data obtained on the anion-exchange behavior

---

[4] J. W. Irvine, Jr., *J. Chem. Soc.*, S356 (1949); J. W. Irvine, Jr., and W. E. Bennett, "Annual Report," Laboratory for Nuclear Science, M.I.T., May 31, 1953, p. 86; K. A. Kraus and G. E. Moore, This Journal, **75**, 1460 (1953).

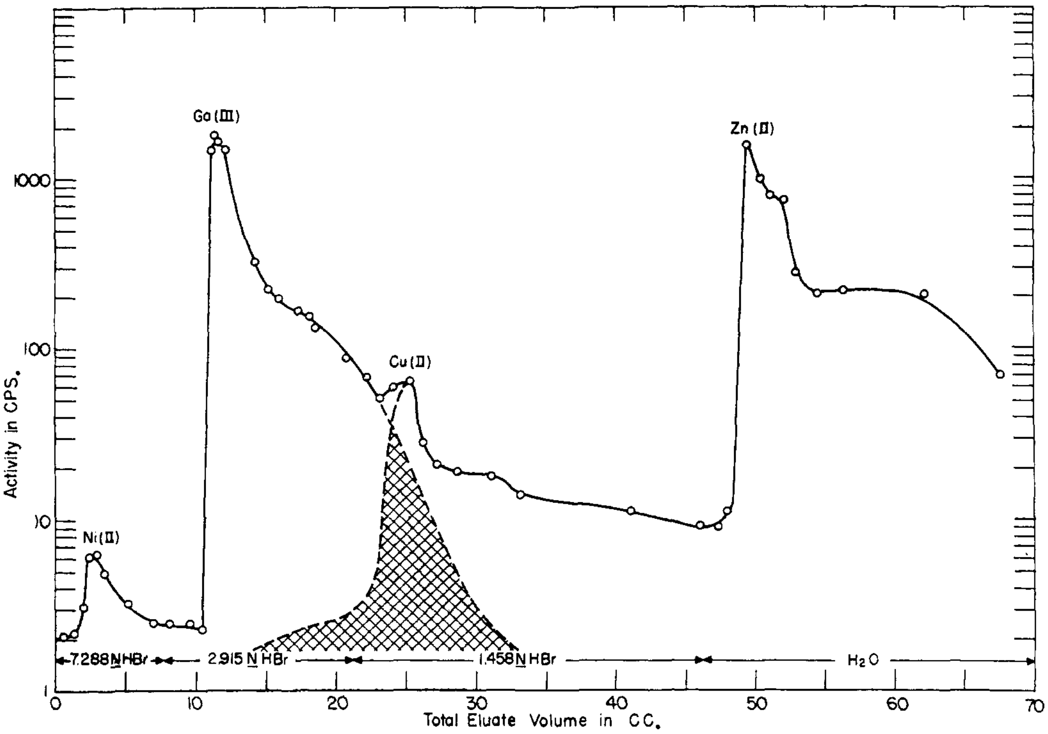

Fig. 3.—The partial separation of Ni(II), Ga(III), Cu(II) and Zn(II).

of Ga(III), using the separated activity column technique, seemed to indicate (see below) that at least a partial separation of Cu(II) and Ga(III) on a column was possible using HBr as the complexing agent. To test this prediction a zinc plated copper foil was bombarded with 16 Mev. deuterons for 5 μah., and the target dissolved in nitric acid. The solution was fumed to dryness, and the residue twice dissolved in 7.3 N HBr and taken to dryness. The residue from this treatment was dissolved in 5 cc. of 7.3 N HBr, and 0.1 cc. of this solution adsorbed on the top of the exchanger bed.

Elution of the activity lamina was then started with 7.29 N HBr, and an activity peak (Fig. 3) was washed out, and identified by a half-life measurement to be 2.6h Ni^{65}(II). The elutriant was then changed to 2.9 N HBr and a large activity maximum came off the column and was shown to be 9h Ga^{66}(III). During the gallium elution, the blue copper complex was seen to move slowly down the column, and finally to appear in the eluate, giving rise to the cross-contamination indicated in Fig. 3. The elutriant was then changed to 1.46 N HBr and the Cu(II) removed from the column. After washing the column with 20 cc. (~8 column volumes) of 1.46 N HBr, the remaining activity, identified as 38m Zn^{63}(II), was removed by washing the column with water.

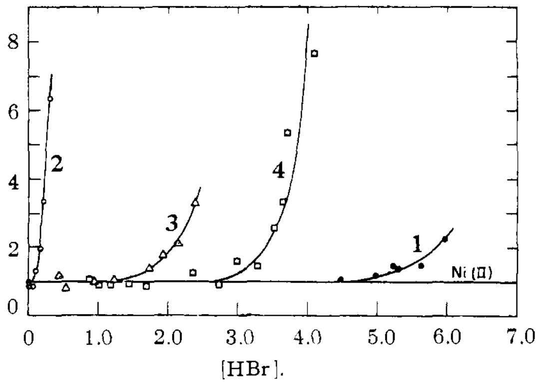

Fig. 4.—The anion-exchange behavior of some transition bromide complexes: ● (1), Co(II)-HBr; ○ (2), Zn(II)-HBr; △ (3), Cu(II)-HBr; □ (4), Ga(III)-HBr.

Results and Discussion

The ion-exchange behavior of Co(II), Zn(II), Cu(II) and Ga(III) in aqueous HBr solutions is summarized in Figs. 4 and 5.

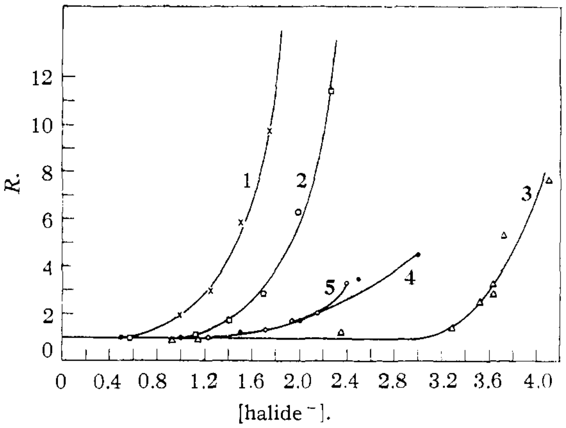

Fig. 5.—Comparison of anion-exchange behavior of Cu(II) and Ga(III) bromide and chloride complexes: 1, Ga(III)-Cl batch; 2, Ga(III)-Cl column; 3, Ga(III)-Br column; 4, Cu(II)-Cl batch; 5, Cu(II)-Br column.

The ratios of the elution constants for no interaction of the tracer ion with the resin, E_0, determined from Na^{22} runs, compared to the constant at a given acid concentration, is given by $R = E_0/E$. It is seen that large values of R correspond to strong adsorption, whereas a value of unity corresponds to no interaction of the tracer ion with the resin except for Donnan adsorption and diffusion.

For ease in comparing elution constants determined from columns differing slightly in diameter and bed depth in the present study, and with the data of Moore and Kraus, the ratio $R = E_0/E$ has also been tabulated (Table I), and is presented graphically in Fig. 4. Nickel was found to be unadsorbed by the resin up to acid concentrations of 7 M. Two points of interest arise from these data. It seems clear that the order of decreasing complex strength for the monovalent bromide anion complexes is Zn > Cu > Ga > Co > Ni corresponding to the order found for the chloride complexes, and agreeing for the Zn–Cu–Co triplet with the "average stability constant" data of Bjerrum.[5]

TABLE I

COMPARISON OF R VALUES FOR HCl AND HBr COMPLEXES OF Cu(II), Co(II) AND Ga(III)

	Cu(II)		Co(II)		Ga(III)	
N acid	R_{HCl}	R_{HBr}	R_{HCl}	R_{HBr}	R_{HCl}	R_{HBr}
0.5	1.2	1.0	1.0	1.0	1.0	1.0
1.0	1.4	1.0	1.0	1.0	1.0	1.0
1.5	1.8	1.2	1.0	1.0	2.1	1.0
2.0	2.3	1.75	1.1	1.0	5.9	1.0
2.5	3.6	3.5	1.3	1.0		1.0
3.0	4.7		1.4	1.0		1.0
3.5						2.4
4.0			1.9	1.0		7
5			3.9	1.2		
6			14	2.5		

It is also evident that, with the exception of Ga(III), the R value for the chloride complex is only slightly larger than the value of this constant for the bromide complex at the same halogen acid concentration, indicating a somewhat greater retention of the chloride complex by the resin.

The anion-exchange behavior of Cu(II) and Ga(III) in HCl and HBr solutions is summarized in Fig. 5. Curve 1 is a rough extrapolation from batch experiment data on the system Ga(III)–HCl, investigated by Kraus, *et al.*,[6] while curve 2 represents the column experiment data on the system Ga(II)–HCl of the present work, which are summarized in Table II.

TABLE II

SUMMARY OF Ga(III)–HCl COLUMN EXPERIMENTS

N_{HCl}	V_{max}	E	$E_0/E = R$
0.5655	2.338	1.439	0.9652
1.131	2.808	1.198	1.159
1.414	4.212	0.799	1.739
1.697	6.959	.483	2.873
1.979	15.426	.218	6.369
2.262	27.762	.1212	11.462

Curve 3 summarizes the column experiment data on the system Ga(III)–HBr. It is evident that the chloride anion complex is formed at much lower halide ion concentrations than the bromide homolog, and that gallium—in contrast to the other transition elements so far investigated—displays markedly different anion exchange behavior in bromide and chloride solutions.

Curve 4 is an extrapolation of the batch experiment data on the system Cu(II)–HCl, reported by Kraus and Moore. Curve 5 summarizes the present column data on the system Cu(II)–HBr, the marked similarity in behavior being at once evident from the near superposition of the initial portions of the two curves.

From these data it appeared that although a separation of a small amount of Ga(III) from a large quantity of Cu(II) would be unfavorable in the chloride system, in the case of HBr as a complexing agent, this separation might become more feasible due to the large variation of the Ga(III) R factor between the two systems.

The experiment in which an attempt was made to separate carrier-free quantities of Ni(II) and Ga(III) from mg. amounts of Cu(II) and Zn(II) is summarized graphically in Fig. 3. The rather pronounced trailing of the gallium activity leads, as is indicated in the figure, to a certain amount of cross-contamination between Cu(II) and Ga(III), although the separation is significantly better than would be possible had HCl been used as an elutriant.

Summary and Conclusions

From the above results it seems clear that, in general, the anion-exchange behavior of the transition group bromide and chloride complexes is quite similar, the observed differences lying within the experimental errors of the experiments. A definite exception to this generalization seems to obtain in the case of Ga(III), for which the bromide complexes interact to a much smaller extent with the resin, than do the chloride homologs.

Just as in the case of the chloride studies reported by Kraus and his co-workers, the differences in the elution constants between Ni(II), Co(II), Ga(III), Cu(II) and Zn(II) bromide complexes permits the separation of these elements from each other.

Experiments on Cu(II), Co(II) and Ni(II) have shown that the migration rate of a given ionic species through the exchanger is not a function of the concentration of that species, and that carrier-free amounts of radiotracers (less than 10^{-8}mg.) behave in all cases similar to mg. quantities. Again, Ga(III) appears to be an exception to this rule, the distribution coefficient of this ion between the solid resin phase, and the aqueous portion of the system being a function of the Ga(III) concentration. This effect also has been observed by Bennett and Irvine[7] in their study of the extraction of Ga(III) from HCl solutions by various ethers, and the dependence of the distribution coefficient of gallium between aqueous HBr and HCl solutions and anion-exchange resins is being studied further.

The present bromide complex studies could not be extended beyond ~7 M HBr due to chemical interaction between the resin and the elutriant. When using concentrated solutions (>6 M) it was found that to the initial few millimeters of the resin bed was imparted a yellow coloration, whereas the remainder of the resin was a light tan. This yellow coloration persisted even after the resin had been extensively washed with distilled water, under

---

[5] J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

[6] We are greatly indebted to Dr. Kraus for furnishing us with a prepublication summary of these data.

[7] W. E. Bennett and J. W. Irvine, Jr., "Annual Report," Laboratory for Nuclear Science, M.I.T., May 31, 1953, p. 86.

which conditions the remainder of the resin is a pale yellow, and is thought to be due to the action of a small amount of bromine produced from the concentrated bromide solution by air oxidation.

From this it appears, then, that with the exception of Ga(III), the anion separation of the bromide complexes of the transition elements studied offers no advantage over the more convenient chloride complex separation, while placing an upper limit of ~7 *M* on the anion concentration which can be employed in the separation.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Specific Effects in Acid Catalysis by Ion Exchange Resins. III. Some Observations on the Effect of Polyvalent Cations[1]

BY SIDNEY A. BERNHARD, EUGENE GARFIELD AND LOUIS P. HAMMETT

RECEIVED SEPTEMBER 14, 1953

The catalytic effectiveness for the hydrolysis of ethyl acetate and of ethyl hexanoate of the hydrogen ions of a lightly cross linked polystyrene sulfonic acid is unaffected when the resin contains a considerable proportion of magnesium ions as well as the hydrogen ions. Replacement of part of the hydrogen ions of the sulfonic acid by ethylenediammonium ions, however, reduces the catalytic effectiveness of the remaining hydrogen ions by a factor which is twice as large for the hexanoate as for the acetate.

The ratio $r = q_1/q_2$ of the efficiencies of an ion exchange resin for the hydrolysis of two carboxylic esters 1 and 2 is in 70% aqueous acetone strongly dependent on the degree of cross linking of the resin.[2] This ratio, which we shall call the specificity ratio of the resin relative to the two esters, measures the difference between the standard free energies of transfer of the transition states for the two esters from homogeneous solution to the environment prevailing in the resin.[2] One way in which increased cross linking affects this environment is merely by squeezing out solvent, so that the environment is more like an aromatic hydrocarbon and less like an aqueous solution. But the solvent content of the resin may also be reduced by partial replacement of the hydrogen ions of the cross-linked polystyrene sulfonic acid by other cations and especially by polyvalent cations.

Thus a very lightly cross linked resin (prepared with only 0.5% of divinylbenzene in the initial polymerization mix) which in the form of the air-dry acid swells 40-fold on immersion in water shrinks by a factor of 2 when the swollen acid is converted to the fully hydrated magnesium salt and by a factor of 3 when the acid is converted to the salt of the ion $H_3\overset{+}{N}CH_2CH_2\overset{+}{N}H_3$. A smaller but still considerable shrinkage must be expected when only part of the hydrogen ions in the acid are replaced by the polyvalent ion.[3] With these considerations in mind we have determined the effect on the catalytic properties for the hydrolysis of ethyl acetate and of ethyl hexanoate of replacing part of the hydrogen ions in this resin by magnesium ion or by the diquaternary ion $Me_3\overset{+}{N}CH_2CH_2\overset{+}{N}Me_3$. The results are reported in Table I. The column headed H^+, % lists the percentage of the hydrogen ion of the original resin which has not been replaced by another cation. *k* is a second-order specific rate with time in minutes computed by dividing the first-order specific hydrolysis rate by the number of moles of hydrogen ions available from the resin per liter of solution. The specificity ratio, *r*, defined in the first paragraph, ester 1 being the hexanoate, ester 2 the acetate, was calculated using the data of Haskell and Hammett[4] on hydrolysis rates in homogeneous solution at 25° on the basis that the energy of activation for the homogeneous reaction is 16.3 kcal. for both esters.[5]

TABLE I

SPECIFIC RATES AND SPECIFICITY RATIOS IN 70% AQUEOUS ACETONE AT 40° FOR RESINS WITH PARTIAL REPLACEMENT OF HYDROGEN IONS BY POLYVALENT CATIONS. TIME IN MIN.

Replacing ion	H^+, % remaining	10^5 *k* for Ethyl acetate	10^5 *k* for Ethyl hexanoate	*r*
None	100	12.2	2.62	0.65
Mg^{++}	66	12.6	2.60	.63
$Me_3\overset{+}{N}CH_2CH_2\overset{+}{N}Me_3$	42	9.8	1.30	.40
$Me_3N^+CH_2CH_2N^+Me_3$	29	8.1	0.85	.32

Two features of these results are of particular interest. One is the contrast between the effects of magnesium ion and of the diquaternary ion. Replacement of hydrogen ion by either of these ions shrinks the resin strongly, yet in the presence of magnesium ion the remaining hydrogen ions are unchanged in catalytic properties for both esters while the diquaternary ion retards the hydrolysis of both esters and alters the specificity ratio considerably. The other is the fact that if the resin in the fully acid form had been altered by increasing the degree of cross linking to such an extent as to reduce the hydrolysis rate of ethyl acetate to 8.1×10^{-5} the specificity ratio would have been decreased to 0.19 instead of to the 0.32 observed.[6]

---

[1] The work reported herewith was carried out as project NR 056-062 under contract N6onr-271 between the Office of Naval Research and Columbia University. Reproduction in whole or in part permitted for any purpose of the United States Government.

[2] S. A. Bernhard and L. P. Hammett, THIS JOURNAL, **75**, 1798 (1953).

[3] D. K. Hale, D. I. Packham and K. W. Pepper, *J. Chem. Soc.*, 844 (1953).

[4] V. C. Haskell and L. P. Hammett, THIS JOURNAL, **71**, 1284 (1949).

[5] (a) G. Davies and D. P. Evans, *J. Chem. Soc.*, 399 (1940); (b) H. A. Smith and J. H. Steele, THIS JOURNAL, **63**, 3466 (1941).

[6] This figure is based on data on the effect of cross linking on hydrolysis rates at 40° contained in a forthcoming article by Riesz and Hammett; see also paper IV, p. 992.