The heat of solution of the dichlorides at infinite dilution corresponds to the heat absorbed in the reaction

$$MCl_2(c) + \infty H_2O = MCl_2 \cdot \infty H_2O$$

$$\Delta H_{soln.} = \Delta H_1 - \Delta H_2 + \Delta H_3 - \Delta H_4 + \Delta H_5 - \Delta H_6$$

The standard heat of formation is the enthalpy change for the reaction

$$M(c) + Cl_2\,(g) = MCl_2(c)$$

when all the substances are in their standard states.

$$\Delta H^0_{f_{298.16}} = -\Delta H_1 - \Delta H_3 + \Delta H_4 - \Delta H_5 + \Delta H_7 - \Delta H_8$$

Table V lists the heats of solution and the heats of formation of the dichlorides.

That the oxidation of samarium(II) to samarium(III) by oxygen did not occur to any significant extent was evidenced by the data of Table I. There was no discernible difference between the results obtained in hydrogen-saturated acid and those obtained in air-saturated acid. The small value of the standard deviation obtained for the heat of reaction of ytterbium dichloride (Table II) also indicated that oxidation by oxygen did not take place to an appreciable extent.

TABLE V

HEATS OF SOLUTION AND HEATS OF FORMATION OF THE DICHLORIDES AT 298.16°K.

Substance	$\Delta H_{soln.,298.16}$	$\Delta H^{\circ}_{f_{298.16}}$
$SmCl_2$	-7 ± 6^a	-195.6 ± 1.0
$YbCl_2$	-15 ± 5^a	-184.5 ± 1.7

[a] The greatest uncertainty lies in the entropy estimation in the calculation of ΔH_2.

Acknowledgment.—The authors wish to express their gratitude to Dr. F. H. Spedding for supplying pure rare earth oxides; to Mr. Harry Eick for help in obtaining some of the calorimetric data; and to the U. S. Atomic Energy Commission for their financial support of the project.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Factors Influencing Ion-exchange Equilibria in Concentrated Solutions: Behavior of the Alkaline Earth and Alkali Ions[1]

BY R. M. DIAMOND[2]

RECEIVED DECEMBER 16, 1954

A study has been made of the elution behavior of beryllium(II), calcium(II), strontium(II), barium(II), radium(II), sodium(I), rubidium(I) and cesium(I), from a Dowex-50 (10–12% DVB) cation-exchange resin column, and of radium(II), strontium(II), cesium(I) and sodium(I) from nominal 2 and 16% DVB sulfonic acid resins with 2.6, 5.5, 8.7 and 12.2 *M* HCl solutions. The results cannot be explained by simple mass-action considerations, but postulation of ion dehydration, resin shrinkage, and non-exchange electrolyte absorption effects makes possible a reasonable interpretation.

The ion-exchange elution behavior of tracer quantities of rare earths from the sulfonic acid resin, Dowex-50, with hydrochloric acid of varying concentration as the eluant shows an interesting pattern.[3] As the hydrochloric acid concentration is raised above 1 *M*, the elution peak position, or volume of eluant at which the tracer ion concentration is a maximum, occurs at a smaller and smaller volume. Around 7 *M* HCl it is at a minimum, and with higher hydrochloric acid concentrations the elution peak volume increases. This behavior was attributed to the simultaneous operation in varying degree of some of the following factors influencing the exchange process, namely: 1, the mass-action effect of hydrogen ion; 2, complex ion formation of the metal ion with chloride; 3, disruption of the hydration shell of the metal ion; 4, shrinkage of the resin; 5, entrance of non-exchange electrolyte into the resin.

Since the interplay between so many factors makes interpretation difficult, it was felt that in studying families of ions of lower charge, such as the alkaline earth and alkali metal ions, where certain of the factors would be expected to be less important, confirmation might be obtained for the effects of the last three factors and simplifications introduced in estimating their relative importance.

Experimental

Resins.—The resins used were commercial Dowex-50 (*ca.* 10–12% DVB), 250–500 mesh, and two sulfonic acid exchangers of nominal 2 and 16% divinylbenzene content and of 50-100 mesh.[4] The exchange capacities of these resins are 5.1, 5.3 and 4.8 meq./g. of dry hydrogen-form resin, respectively, as determined by titration of the acid displaced from the hydrogen form resin with a large excess of sodium chloride solution. Before use the resins were washed thoroughly with concentrated hydrochloric acid and with water.

Tracers.—Na^{22}, Ca^{45} and Rb^{86} were obtained through the courtesy of Prof. J. Irvine, Jr., of the Massachusetts Institute of Technology. Cs^{137}, Sr-Y^{90} and Ba^{140} were purchased from Oak Ridge National Laboratory; Ra^{226} was kindly furnished by Prof. G. T. Seaborg, University of California; Be^7 was made using the Harvard synchrocyclotron.

Procedure.—The technique employed was to study the variation in elution behavior of the tracer cations from resin columns when using 2.6, 5.5, 8.7 and 12.2 *M* HCl as eluting agents. The column of Dowex-50 resin contained 0.095 g. of dry resin and was 10 cm. long by 1.5 mm. in diameter; 0.418 g. of dry 2% DVB sulfonic acid resin was used in a column 10 cm. long (when in contact with 3 *M* HCl) and 4 mm. in diameter, and 0.184 g. of dry 16% DVB resin was used in a column 10 cm. long by 2 mm. in diameter. Before an elution the resin column was rinsed overnight with the

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[1] This work was supported by the U. S. Atomic Energy Commission.

[2] Baker Laboratory of Chemistry, Cornell University, Ithaca, New York.

[3] R. M. Diamond, K. Street, Jr., and G. T. Seaborg, THIS JOURNAL, **76**, 1461 (1954).

[4] These two sulfonic acid resins of nominal 2 and 16% DVB content were kindly furnished by Dr. K. S. Spiegler, Gulf Res. and Dev. Co.

hydrochloric acid solution to be used as the eluting agent. The tracer ions to be studied were placed on top of the resin bed in a volume of a few microliters, allowed to sink into the bed, and then the elution with hydrochloric acid was begun immediately. The elution of the tracer ions was followed by collecting fractions of the eluant in small test-tubes and counting these tubes in a scintillation counter using a well-type NaI(Tl) crystal, or by drying aliquots from these tubes on glass cover slides and counting these slides with an end-window Geiger counter. Whenever necessary, the activities were identified by their radiation characteristics and their half-lives. An example of a typical elution is shown in Fig. 1.

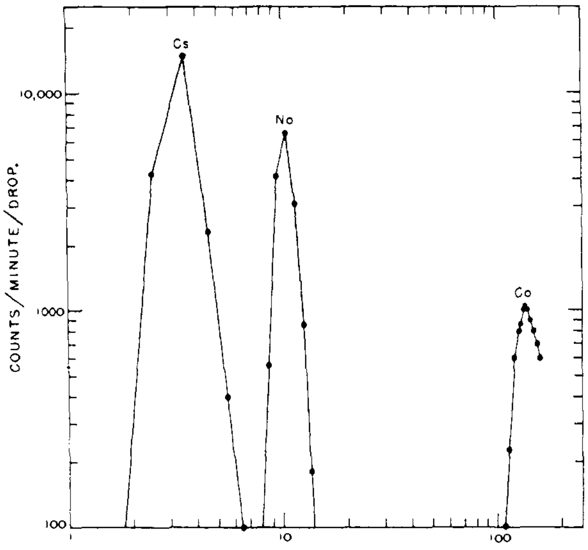

Fig. 1.—Typical elution: Cs, Na and Ca from 10 cm. by 1.5 mm. Dowex-50 (10–12% DVB, 250–500 mesh) column with 12.2 *M* HCl.

The linear flow rate in the columns was *ca.* 0.1–0.2 cm./min. That such a flow rate gives near equilibrium conditions in the three columns used was demonstrated by the symmetry of the elution peaks and by the fact that decreasing the flow rate by a factor of two did not change the elution peak position, nor did increasing the rate by a factor of three, though now some of the peaks tended to have a trailing edge.

As has been shown by Mayer and Tompkins,[5] the volume of the elution peak position in milliliters (disregarding the first free column volume) divided by the weight in grams of the resin in the column gives the value of the equilibrium distribution ratio, *D*, which for batch-type distribution experiments is defined as

$$D = \frac{\text{fraction of metal ion/g. of resin}}{\text{fraction of metal ion/ml. of soln.}} \qquad (1)$$

The results of the present work are shown in Figs. 2, 3, 4 and 5 as plots of this quantity, *D*, against the molarity of the hydrochloric acid used as eluant. Each experimental point is the result of one to five determinations, most being the average of two. The results were reproducible to about 10%, or a little better. As the elutions were performed at room temperature, which varied several degrees in the course of the work, part of the cause for the spread in values may be due to this variation in temperature. However, previous experiments[3] had shown this was not a serious factor.

Results and Discussion

The ion-exchange process

$$_{(w)}M(H_2O)_n{}^{++} + 2\,_{(r)}H(H_2O)_{m'}{}^{+} \rightleftharpoons {}_{(r)}M(H_2O)_{n'}{}^{++} + 2\,_{(w)}H(H_2O)_m{}^{+}$$

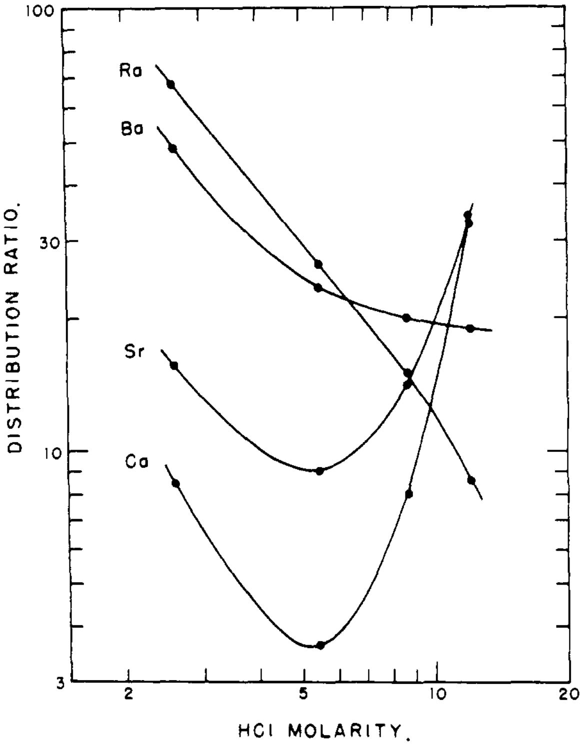

Fig. 2.—Variation with concentration of the hydrochloric acid eluant of the distribution ratios of the alkaline earth ions, Ra, Ba, Sr and Ca.

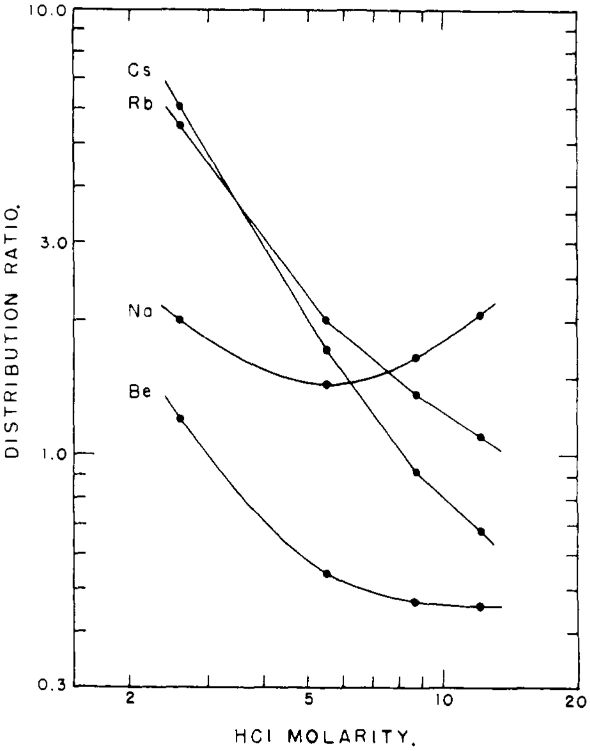

Fig. 3.—Variation with concentration of the hydrochloric acid eluant of the distribution ratios of the alkali ions, Cs, Rb, Na and of Be.

may be treated as a two-phase equilibrium of the two diffusible species, MCl_2 and HCl. For this

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[5] S. W. Mayer and E. R. Tompkins, THIS JOURNAL, **69**, 2866 (1947).

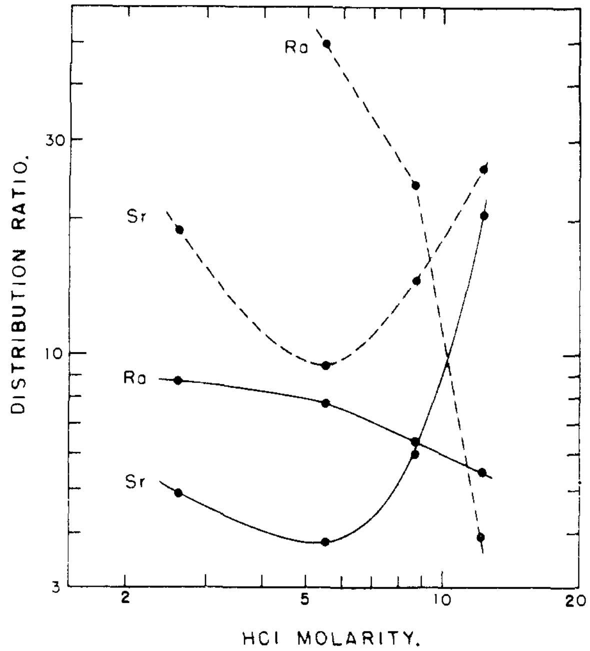

Fig. 4.—Variation with concentration of the hydrochloric acid eluant of the distribution ratios of Ra and Sr with 16% DVB resin ---, and with 2% DVB resin ——.

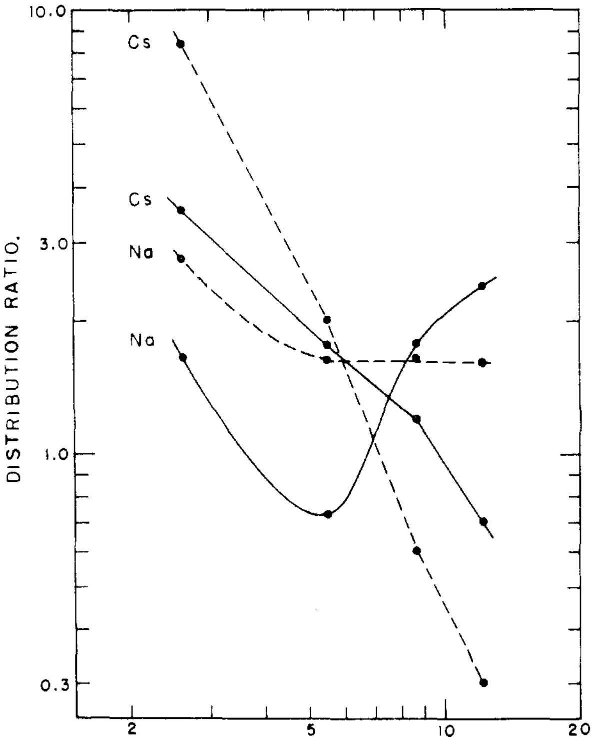

Fig. 5.—Variation with concentration of the hydrochloric acid eluant of the distribution ratios of Cs and Na with 16% DVB resin ----, and with 2% DVB resin ——.

the chemical potential of each species in the two phases must be equal. Assuming the same standard state for a species in both the resin and aqueous phases leads to the activities in the two phases being equal, and dividing this relationship for one species by the similar equation for the other results in

$$\frac{{}_{\mathrm{r}}(\mathrm{MCl_2})_{\mathrm{w}}(\mathrm{HCl})^2}{{}_{\mathrm{w}}(\mathrm{MCl_2})_{\mathrm{r}}(\mathrm{HCl})^2} = 1 \qquad (2a)$$

where the parentheses ( ) represent activities in the resin, r, or water, w, phase. Inclusion, as an osmotic free-energy term, of the effect of the swelling of the resin on contact with aqueous solutions modifies this equation to[6,7]

$$\frac{{}_{\mathrm{r}}(\mathrm{MCl_2})_{\mathrm{w}}(\mathrm{HCl})^2}{{}_{\mathrm{w}}(\mathrm{MCl_2})_{\mathrm{r}}(\mathrm{HCl})^2} = e^{\Pi(2\bar{v}_{\mathrm{H}} - \bar{v}_M)/RT}$$

Π is the swelling pressure in the resin, and $\bar{v}_{\mathrm{H}}$ and $\bar{v}_{\mathrm{M}}$ are the partial molal volumes of H^+ and M^{++} in the resin phase. Several investigators have shown that this exponential factor, however, does not provide the whole answer to resin selectivity,[8,9] and under the conditions of the present experiments, where the resin is in contact with rather concentrated solutions of electrolyte, the value of the factor is close to one. It will be taken as one, as the effects of resin swelling and ionic volume will be considered explicitly, though qualitatively, in the discussion to follow.

Equation 2a may be rearranged to

$$\frac{{}_{\mathrm{r}}[\mathrm{M}^{++}]}{{}_{\mathrm{w}}[\mathrm{M}^{++}]} = \frac{{}_{\mathrm{r}}[\mathrm{H}^+]^2\ {}_{\mathrm{r}}\gamma^2_{\mathrm{HCl}}\ {}_{\mathrm{w}}\gamma_{\mathrm{MCl_2}}}{{}_{\mathrm{w}}[\mathrm{H}^+]^2\ {}_{\mathrm{w}}\gamma^2_{\mathrm{HCl}}\ {}_{\mathrm{r}}\gamma_{\mathrm{MCl_2}}} \qquad (2b)$$

with the brackets, [ ], indicating molalities, *i.e.*, moles per 1000 grams of water. This equation may be combined with one expressing the electroneutrality of the resin

$$2\ {}_{\mathrm{r}}[\mathrm{M}^{++}] + {}_{\mathrm{r}}[\mathrm{H}^+] = {}_{\mathrm{r}}[\mathrm{R}^-] + {}_{\mathrm{r}}[\mathrm{Cl}^-] \qquad (3)$$

to yield

$$\frac{{}_{\mathrm{r}}[\mathrm{M}^{++}]}{{}_{\mathrm{w}}[\mathrm{M}^{++}]} = \frac{{}_{\mathrm{r}}[\mathrm{R}^- + \mathrm{Cl}^- - 2\mathrm{M}^{++}]^2\ {}_{\mathrm{r}}\gamma^2_{\mathrm{HCl}}\ {}_{\mathrm{w}}\gamma_{\mathrm{MCl_2}}}{{}_{\mathrm{w}}[\mathrm{H}^+]^2\ {}_{\mathrm{w}}\gamma^2_{\mathrm{HCl}}\ {}_{\mathrm{r}}\gamma_{\mathrm{MCl_2}}} \qquad (4)$$

The distribution ratio, D, as defined in equation 1 would be exactly proportional to ${}_{\mathrm{r}}[\mathrm{M}^{++}]/{}_{\mathrm{w}}[\mathrm{M}^{++}]$ if the amounts of water in a gram of (initially dry) resin and in a milliliter of solution stayed constant, or varied in the same proportion, with increasing hydrochloric acid concentration in the contacting solution. D actually is roughly proportional, since the quantities of water in both cases decrease, although that in the gram of resin decreases the faster especially for resins of lower DVB content. Thus, in a plot against the external hydrochloric acid concentration, D will show a somewhat more negative slope than the molality ratio, ${}_{\mathrm{r}}[\mathrm{M}^{++}]/{}_{\mathrm{w}}[\mathrm{M}^{++}]$, and this difference will be larger, the lower the DVB content of the resin. As we are interested in only a qualitative discussion of the trends in D, we shall set D proportional to the molality ratio, and keep in mind that the constant of proportionality, K, is really not constant but a slowly decreasing function of the hydrochloric acid concentration, and that this decrease is greater, the lower the cross-linking of the resin.

$$D = K\,\frac{{}_{\mathrm{r}}[\mathrm{R}^- + \mathrm{Cl}^- - 2\mathrm{M}^{++}]^2\ {}_{\mathrm{r}}\gamma^2_{\mathrm{HCl}}\ {}_{\mathrm{w}}\gamma_{\mathrm{MCl_2}}}{{}_{\mathrm{w}}[\mathrm{H}^+]^2\ {}_{\mathrm{w}}\gamma^2_{\mathrm{HCl}}\ {}_{\mathrm{r}}\gamma_{\mathrm{MCl_2}}} \qquad (5a)$$

With the metal ion present only in trace quantity

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(6) F. G. Donnan, *Z. physik. Chem.*, **168A**, 369 (1934).

(7) H. P. Gregor, This Journal, **73**, 642 (1951).

(8) G. E. Boyd and B. A. Soldano, *Z. Elektrochem.*, **57**, 162 (1953).

(9) E. Glueckauf, *Proc. Roy. Soc.* (*London*), **214A**, 207 (1952).

as a radioactive species, and comparatively overwhelming amounts of acid as the macro-component ($[M^{++}] \ll [H^+]$, ${}_r[M^{++}] \ll {}_r[R^-]$) the actual exchange will not affect the composition of the resin appreciably, and with the usual commercial resins of 10–12% DVB content in contact with dilute hydrochloric acid solutions, the concentration of non-exchange chloride ion in the resin is small, (${}_r[Cl^-] \ll {}_r[R^-]$) so that the hydrogen ion concentration in the resin phase is essentially a constant equal to ${}_r[R^-]$. Then the ratio ${}_r\gamma^2_{HCl}/{}_r\gamma_{MCl_2}$ is also a constant, and the activity coefficient ratio in the dilute external solution, ${}_w\gamma_{MCl_2}/{}_w\gamma^2_{HCl}$ is only a slowly varying function of the hydrochloric acid concentration, so

$$D = K'/_w[H^+]^2 \tag{5b}$$

This expresses the "mass-action" effect listed earlier and is a well-known feature of the exchange process in dilute solution when the metal cation is a microcomponent. This decrease of D with increasing hydrochloric acid concentration can still be seen from 3 to 6 M HCl in Fig. 2 for the alkaline earth ions studied, though the other factors to be discussed in this paper are becoming increasingly important.

Three other features of the results shown in Fig. 2 are to be noticed: 1, the order of elution of the alkaline earth ions in dilute hydrochloric acid; 2, their order of elution in 12 M HCl; 3, the minimum in D around 6 M HCl for strontium(II) and calcium(II). The first item, the order of elution in dilute acid, is just that to be expected from the order of their hydrated radii in dilute solution, assuming that the largest hydrated ion is bound the least tightly and so will elute first. The hydrated radii go in the order beryllium(II) > calcium(II) > strontium(II) > barium(II) > radium(II), as is indicated by the values of the equivalent conductances for these ions in dilute solution[10] and by the volumes of the water swollen resins in the different salt forms.[11]

As the concentration of the hydrochloric acid eluant increases, the values of D for the alkaline earth ions approach each other, and by 12 M HCl, the elution order has reversed, with the exception of beryllium. Disregarding beryllium for the moment, the reversal in elution order suggests that the order of the effective (hydrated) radii of the alkaline earth ions has altered. This is not too surprising considering the change in their environment. In 3 M HCl there are 3 moles of hydrogen and chloride ions for about 52 moles of water, so each ion can be quite hydrated. There is experimental evidence for the coördination, at moderate electrolyte concentrations, of 5 molecules of water per hydrogen ion,[12,13] probably one to form the hydronium ion, and four more water molecules to form the inner solvation shell for this ion. Different experimental methods give different values for the hydration numbers of an ion, but methods which seem to measure primarily the first solvation shell give about the same results. An unambiguous case is the hexahydration of chromic ion, demonstrated by Plane and Taube[14] through the slow exchange of inner shell water molecules with those in solution, using O^{18}-labeled H_2O. For other ions the primary hydration numbers in dilute solution vary from less than 1 to 8,[15] and chloride ion is usually assigned 2–4 water molecules. Theoretical calculations of heats and entropies of hydration[16,17] require such an inner solvation shell to achieve agreement with experimental values, so it seems that in dilute solution a mole of aqueous HCl ties up in the first solvation shell of the ions on the order of 9 moles of water.

But by 12 M HCl, there are only about 42 moles of water per 12 moles of HCl. Even granting that some of the HCl is undissociated,[18] and that the hydrogen and chloride ions may share some of the water molecules, all the water left is not enough to satisfy even the primary hydration shells of the ions. So the hydration shells are necessarily diminished, and, consequently, so are the effective hydrated radii. Naturally other ions present in this solution will suffer the same fate. This effect is even more important inside the resin phase, as the solution there is at a higher ionic strength than the external solution. For example, for a typical commercial Dowex-50 resin, (10–12% DVB) when the outside solution is 6 molal hydrochloric acid, the resin phase is about 7.5 molal in sulfonate groups and almost 1 molal in non-exchange hydrochloric acid. A similar situation exists at higher external concentrations, and because of this scarcity of water in the resin phase, disruption of an ion's solvation shell becomes an important effect. This partial dehydration of the alkaline earth ions explains the reversal in their elution order with concentrated hydrochloric acid as it brings their effective radii into the order of their crystallographic radii, *i.e.*, calcium < strontium < barium < radium.

Some 28 years ago, Wiegner and Jenny,[19] working with artificial and natural colloidal aluminum silicates, pointed out the importance of considering the hydrated radii of ions in the ion-exchange process, and explained changes in the elution order of the alkali ions in 80% alcohol solutions from that in water as due to dehydration of the ions and hence a change in the order of their effective radii. More recently, Gregor and Bregman[20] have observed changes in the normal elution order of the alkalies when using sulfonic acid resins of high cross-linking, and have suggested that with increasing cross-linking and consequent decreasing amount of water in the resin, dehydration of the ions in the resin phase will occur with corresponding changes in the elution order of the ions.

Small, originally highly hydrated, ions have more water to lose than large ions which are more weakly

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[10] "International Critical Tables," Vol. VI. p. 233, McGraw-Hill Book Co., New York. N. Y., 1929.

[11] H. P. Gregor, F. Gutoff and J. I. Bregman, *J. Colloid Sci.*, **6**, 245 (1951).

[12] K. W. Pepper and D. Reichenberg, *Z. Elektrochem.*, **57**, 183 (1953).

[13] E. J. Goon, Ph.D. Dissertation, Rensselaer Polytechnic Institute, 1953.

[14] R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

[15] J. O'M. Bockris, *Quart. Rev.*, **3**, 173 (1949).

[16] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

[17] D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, **34**, 1093 (1938).

[18] A. M. Posner, *Nature*, **171**, 519 (1953).

[19] G. Wiegner and H. Jenny, *Kolloid-Zeit.*, **42**, 268 (1927).

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

hydrated and so have less solvation water from the start. In this connection, it is interesting to note that the position of barium reverses with that of radium before 9 *M* HCl, strontium catches up with barium shortly after 9 *M* HCl, and calcium is just barely held more tightly than strontium at 12 *M* HCl. This is possibly an indication that the behavior of beryllium is due merely to the fact that it is still holding very tightly to its hydration shell and more vigorous dehydrating conditions are required before it will show an increase in *D*. However, it seems more likely that the monotonic decrease in *D* with increasing hydrochloric acid concentration observed for beryllium is due to complex ion formation with chloride ion. This probably would not be anionic complex formation as beryllium shows no significant tendency in hydrochloric acid solutions to stick to strong base anion-exchange resins, Dowex-1[21] or Dowex-2,[22] but might be cationic chloro complexes, possibly polynuclear ones.

The extent to which the other alkaline earth ions associate and complex with chloride ion is no better known than for beryllium, but presumably is less than with that ion. Certainly this cannot be a very important factor with these ions since such behavior would cause *D* to decrease rather rapidly with increasing hydrochloric acid concentration, and the remaining feature to be explained in Fig. 2 is just the converse, namely, the minimum of *D* around 6 *M* HCl for strontium and calcium and the subsequent large values in 12 *M* HCl.

Dehydration of the alkaline earth ions has been discussed as a possible cause for the reversal in their elution order; however, to determine the actual trend of *D* of an ion with increasing hydrochloric acid concentration in the eluant, that is, whether *D* is increasing or decreasing, and not just its relative position to the other alkaline earth ions, the dehydration of the exchanging cation, in this case H^+, or more properly H_3O^+, must also be considered. If the hydronium ion should desolvate very readily, it would be attracted much more strongly by the resin and so would tend to displace the alkaline earth ion more easily, decreasing the value of the latter ion's *D*. (This corresponds to ${}_r\gamma^2{}_{HCl}$ increasing less rapidly than ${}_r\gamma_{MCl_2}$ in equation 5a.) Or conversely, if H_3O^+ should desolvate much less readily than the alkaline earth ions, the latter would be favored on the resin and would show a slower decrease in *D* with increasing hydrochloric acid concentration than otherwise. (${}_r\gamma_{MCl_2}$ increases less rapidly than ${}_r\gamma^2{}_{HCl}$ in equation 5a.) Conceivably this might even lead to a rise in *D*, as is observed with calcium and strontium. However, such an increase has also been noted with the rare earth ions,[3] and since it seems unlikely that the hydronium ion should retain its water of hydration more strongly than the dipositive ions, certainly not more strongly than the tripositive ones, it would appear that this is not the cause of the minimum in *D*; other factors must be involved.

It is suggested that the shrinkage of the resin and the absorption of non-exchange electrolyte with increasing concentration of hydrochloric acid in the eluting solution can account for the observed minima. The reasoning and experimental justification for this are given in the next few paragraphs, but a conclusion from that discussion is that the effect of these factors should be less for univalent ions than for polyvalent ones. Since chloro-complexing should also be less with the alkali ions than with the alkaline earth ions, a study of the elution behavior of the former should show predominantly the "mass-action" and "desolvation" effects. A reversal of elution order would be expected, and since the alkalies are less strongly hydrated than the corresponding alkaline earths, it might be expected to take place earlier, that is, at a lower hydrochloric acid concentration.

The experimental results for sodium(I), rubidium(I) and cesium(I) are shown in Fig. 3. The elution order in dilute hydrochloric acid is that predicted from the order of the hydrated radii in dilute solution, but this order is reversed in 12 *M* HCl. As expected, the reversal occurs earlier than with the alkaline earths; rubidium and cesium reverse the order of their positions before 6 *M* HCl, and sodium has become more tightly bound than either of these by 9 *M* HCl. As with the alkaline earths, the (crystallographically) smaller ions show a minimum value of *D* near 6 *M* HCl and then an increase. But here the increase is smaller than in the case of the dipositive ions; the effect of resin shrinkage and of absorption of non-exchange electrolyte is smaller with the monopositive ions.

The resin shrinks with increasing hydrochloric acid concentration in the contacting solution because of loss of water to that solution as the activity of water decreases. The contraction of the resin results in an increase in the concentration of its sulfonate groups and of the cations in the resin phase. For a univalent ion–hydrogen ion exchange this increase in concentration has little effect, but for a polyvalent ion–hydrogen ion exchange the equilibrium is shifted in favor of the more highly charged ion, as can be seen from equation 5a.

The effect of shrinking and swelling of the resin can be studied by observing the behavior of an ion on resins of different divinylbenzene content as the acid concentration of the external solution is varied. A highly cross-linked resin will swell little as the external hydrochloric acid concentration is decreased and so should show a small effect, while a low cross-linked resin which swells considerably should show a marked effect on the trend of *D*. The nominal 16 and 2% cross-linked resins used in this study showed virtually no change in volume, and a doubling of volume, respectively, when the hydrochloric acid concentration in the contacting solution was varied from 12 to 3 *M*. Plots of *D* against hydrochloric acid concentration for the ions sodium(I), cesium(I), strontium(II) and radium(II) with these two resins are shown in Figs. 4 and 5.

Consider the large, weakly hydrated radium ion. With the 16% cross-linked resin the major factor in its behavior should be the "mass-action" effect, and *D* should increase rather rapidly with decreasing acid concentration. With the 2% cross-linked resin the rate of increase should be smaller for, as the concentration of the external solution decreases,

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

(22) R. M. Diamond, unpublished work.

the resin absorbs water and swells, decreasing the concentration of the sulfonate groups ($[R^-]$ in equation 5a) and hence the selectivity of the resin for radium. This is what is observed experimentally, as shown in Fig. 4 where the plot for radium ion with the 2% DVB resin increases much less rapidly with decreasing hydrochloric acid concentration than that of radium and the highly cross-linked resin. A similar effect is observed for cesium, and likewise for sodium and strontium where the plots of D go through minima, but still increase less rapidly for the lower cross-linked resin than for the higher with decreasing acid concentration.

It may be noted that in 12 M HCl the values of D for the ions studied were greater with the 2% DVB resin than for the 16% DVB resin (not true for strontium with 12 M HCl, but from Fig. 4 indicated to be true at a slightly higher acid concentration) though at lower concentrations the reverse is true as would be expected from the lower sulfonate concentration in the 2% DVB resin. It is believed that this behavior is caused by the fifth factor mentioned earlier, the amount of non-exchange electrolyte present in the resin.[23] When the external solution is dilute, this is a negligible quantity and so has little effect on D, but as the external HCl concentration is increased, the amount absorbed by the resin phase increases rapidly. This non-exchange electrolyte consists of both HCl and MCl_2, and so, like the resin shrinkage itself, contributes to an increase in D with increasing electrolyte concentration in the contacting solution, as can be seen in equation 5a by increasing $_r[Cl^-]$. Since a less cross-linked resin takes up non-exchange electrolyte more readily than a highly cross-linked one, the values of D for the 2% DVB resin should show a slower decrease, or a faster increase, with increasing hydrochloric acid concentration than those for the 16% DVB resin, and if the excess of non-exchange electrolyte in the 2% DVB resin over that in the 16% DVB resin beomes large enough, the values of D for the former resin might become larger than those of the latter. In contact with 12 M HCl the 2% DVB resin becomes 10–11 M in HCl while the 16% DVB resin becomes only about 3–4 M; although the non-exchange MCl_2 in the two resins may not be in this same ratio, apparently the amount in the 2% DVB resin is enough in excess of that in the 16% DVB resin to cause a larger value of D at 12 M HCl than for the higher cross-linked resin.

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[23] The author gratefully acknowledges helpful discussion on this topic with Dr. G. E. Boyd, Oak Ridge National Laboratory.

[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Heat Capacities and Entropies of Sulfuric Acid Tri- and Tetrahydrates[1]

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RECEIVED FEBRUARY 4, 1955

The heat capacities of sulfuric acid tri- and tetrahydrates have been measured from 15 to 300°K. The heats of fusion are 5736 and 7322 cal. mole^{-1} at their respective melting points, 236.77 and 244.89°K. The peritectic temperature, where the trihydrate is in equilibrium with tetrahydrate and solution, was found to be 236.72°K. The unstable melting point was estimated to be 0.05° above this temperature. The values of the entropies at 298.16°K. are 82.55 cal. deg.$^{-1}$ mole^{-1} for the trihydrate and 99.07 cal. deg.$^{-1}$ mole^{-1} for the tetrahydrate. The entropies of formation of these two hydrates have been calculated from isothermal data and the values agree closely with those obtained by means of the third law of thermodynamics. This indicates that there is no residual disorder due to hydrogen bonding or other effects at limiting low temperatures. It has been shown that sulfuric acid tetrahydrate crystallizes as $H_2SO_4\cdot(4.0000 \pm 0.0001)H_2O$.

This is one of a series of investigations on the thermodynamics of the sulfuric acid–water system. We are concerned with the general problem of possible structural disorder, particularly hydrogen bond disorder, in crystals at limiting low temperatures as evidenced by residual entropy. It is important to know more about the extent and circumstances of such possible disorder, not only in connection with the application of the third law of thermodynamics, but also in connection with the interpretation of solid state phenomena at low temperatures. It has been shown previously[2,3] that ice retains hydrogen bond disorder at low temperatures. It is desirable to investigate a wide variety of chemical substances. The sulfuric acid–water system has been investigated partly because of the connection of these substances with many paramagnetic hydrated sulfates of interest at very low temperatures, and partly because of its widespread chemical importance.

Sulfuric acid tetrahydrate has been investigated previously in this Laboratory by Rubin and Giauque.[4] Their experiments, which were completed in 1940, showed discordant thermal behavior in the region below the melting point. The effects, which could not be interpreted at that time, made it impossible to obtain a reliable value of the heat of fusion from their data. Later a freezing point investigation of Gable, Betz and Maron[5] disclosed the existence of a previously undiscovered trihydrate of sulfuric acid and it became evident that a small amount of this material had crystallized with the tetrahydrate and was responsible for the abnormal thermal behavior. For this reason the results were withheld from publication and the re-

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[1] This work was supported in part by the Office of Naval Research, United States Navy, and by the National Science Foundation.

[2] L. Pauling, THIS JOURNAL, **57**, 2680 (1935).

[3] W. F. Giauque and J. W. Stout, *ibid.*, **58**, 1144 (1936).

[4] T. R. Rubin and W. F. Giauque, *ibid.*, **74**, 800 (1952).

[5] C. M. Gable, H. F. Betz and S. H. Maron, *ibid.*, **72**, 1445 (1950).