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October 1963
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ABSTRACT

A study has been made of the ion-exchange behavior of Be, Ca, and Ba tracers in HClO$_4$, HCl, and HNO$_3$ solutions ranging from 0.1 to 10 M in concentration on a sulfonic acid resin, Dowex-50W. In dilute acid solutions the normal elution order is found and the values of the distribution ratios decrease as expected from the mass-action effect. With concentrated solutions an increase in the value of the distribution ratio with increase in acid concentration occurs in certain cases, leading to an inversion in the elution order of the ions. These results are interpreted in terms of the competition among the water molecules, aqueous anions, and resin sulfonate anions for solvating the cations. The results are compared with previous work on the alkali metal cations and with studies of other resins where the basicity of the resin groups was different.
INTRODUCTION

The previous papers in this series\(^3\) presented a study of the ion-exchange behavior of alkali metal cations at trace concentrations on both strong-acid and weak-acid resins in equilibrium with various acid and salt solutions ranging from 0.1 to \(~10\) M in concentration. The results were interpreted in terms of a proposed model for ion exchange selectivity which involves a competition among the water molecules, external-solution anions, and resin-anion groups to solvate the cations. Changes in the relative solvating abilities of these various agents were shown to lead to predictable effects on the distribution ratios of the alkali metal tracers. In this paper these studies are extended to include the alkaline earth cations, and thus further test the proposed model.

Several other studies of the alkaline earth cations in concentrated acid solutions have appeared previous to or concurrent with this work. A study of Ra, Ba, Sr, Ca, and Be tracers with HCl solutions ranging from 2.6 to 12.2 M was published by Diamond.\(^4\) Mann\(^5\) has reported data for Mg exchange in both HCl and HClO\(_4\), while Choppin and Dinius\(^6\) have published distribution data for Ba, Sr, and Ca in HClO\(_4\). As this report was being written, a preprint of a broad survey of cation exchange behavior of the elements in HCl and HClO\(_4\) solutions was received from Nelson, et al.,\(^7\) which included all the alkaline earths.
EXPERIMENTAL

Reagents. The cation exchange resin used was Dowex AG 50W-X12, 100-200 mesh, with a capacity of 5.2 meq/g dry resin; its treatment has been described in the previous paper. The HClO₄, HNO₃, and HCl solutions were prepared by volumetric dilution of reagent-grade material of known concentration. The Be⁷ tracer was purchased as the carrier-free isotope from Nuclear Science and Engineering Corp., Pittsburgh, Pa.; and the Ca⁴⁷ and Ba¹³³ (specific activities 21 and 1.1 curies/g, respectively) were purchased from Oak Ridge National Laboratories, Oak Ridge, Tenn.

Procedure. Batch measurements were made by placing 0.1000 g resin and 5.00 ml of acid solution of known tracer concentration in a 30-ml polyethylene bottle with a polyethylene screw top, and shaking for four hours. Two 2.00-ml samples were removed through fritted glass or glass wool filters and gamma-counted using a well-type Na(Tl)I scintillation crystal and a single-channel pulse-height analyzer. The distribution ratio was calculated as

\[ D = \frac{(\text{volume of equilibrated solution})}{(\text{weight of dry resin})} \]

where the solution volume is in milliliters, the resin weight is in grams, and the counts have been corrected for background. Variation of the shaking time over the period 4-12 hours showed no appreciable difference in D, establishing that equilibrium had been attained. All experimental work was done at room temperature, 22 ± 2°C.
RESULTS

In order to facilitate the comparison with the previous work on the alkalies\(^3\), the present results on Be\(^7\) were compared with Be\(^7\) elutions done on one of the cation exchange columns used for the alkalies and a suitable conversion factor between the batch and column experiments was determined. The present results are thus recorded as log-log plots of \(D'\) (corresponding to \(V(\text{ml})\) of the previous paper) vs. aqueous acid concentration and are given for Be, Ca, and Ba tracers with HClO\(_4\), HCl, and HNO\(_3\) acids in Figs. 1-3. In general, the agreement between the present data and those of the other workers cited in the introduction is quite good. The only exception is with the concentrated HClO\(_4\) data of Choppin and Dinius;\(^6\) this same disagreement was noted by Nelson, et al.,\(^7\) and was mentioned in the previous paper on the alkalies,\(^3\) also. No explanation is readily apparent for the discrepancy, but it is not severe.

DISCUSSION

The mass-action expression applicable to dilute-solution ion-exchange was given in the first paper in this series,\(^3\) and only an outline of this process for dipositive ions with acid-form resins will be shown here. The equation for the exchange can be written as

\[
M^{+2} + 2H^+ = M^{+2} + 2H^+ \quad (2)
\]

where the superscript bar denotes the resin phase and ion hydration has been omitted. The corresponding equilibrium constant is
where parentheses denote activity and brackets concentration. If the aqueous acid concentration is reasonably dilute (<0.1 M), there will be negligible resin invasion by non-exchange electrolyte, and if $M^{+2}$ is in tracer concentration, \[ \frac{\gamma^2_{H^+}\gamma_{M^{+2}}}{\gamma_{M^{+2}}[H^+]^2\gamma^2_{H^+}} \] will remain essentially constant. In addition, \[ \frac{[M^{+2}]}{[M^{+2}]} \] is defined as $D$, the distribution ratio. Applying these simplifications to Eq. (3) results in

\[ K' = D[H^+]^2 \]  \hspace{1cm} (4)

and, taking logarithms,

\[ \log D = -2 \log [H^+] + \log K'. \]  \hspace{1cm} (5)

Thus a log-log plot of $D$ vs. $[H^+]$ should yield a straight line of slope -2 for the alkaline earth tracers from dilute solution, and indeed this is the observed results as shown in Figs. 1-3.

It may be noted, however, that all of these lines deviate from slope -2.0 as the concentration increases. This deviation marks a breakdown of the dilute solution assumptions made in the derivation of Eq. (5), and the causes and effects of this breakdown will be discussed later in this presentation.

It is first necessary, however, to discuss the reasons for the selectivity order which occurs in dilute solution, namely, Be < Mg < Ca < Sr < Ba < Ra.
We consider cation exchange as a competition among the water, aqueous anions, and resin anions for the solvation of the cation. In dilute solutions containing alkaline earth tracers and strong acids, the extent of cation interactions with the macro-anion is small compared to cation-water interactions, and thus dilute solution exchange simplifies to a competition between water and the resin anions for solvating the cations. Since the water in the dilute external phase is a better solvating agent than a concentrated solution of toluene sulfonic acid (considered as a model for the resin) cations will tend to prefer the aqueous phase in the order of their need for solvation. Thus the smaller ions, with their higher charge densities, will show the greatest tendency to be held in the aqueous phase and the larger ions, which require less solvation, will be forced into the resin by the solvation-(water-) seeking smaller ions—ín the present case, the hydronium ion. It can be seen in Figs. 1-3 that the values of the D's in dilute acid solutions are in the order of the crystallographic sizes of the ions; i.e., Ba > Ca > Be. Ra, Sr, and Mg all fall into the proper order in this series as shown by other workers for both HCl\(^4\)\(^-\) and HClO\(_4\)\(^-\).

We would like to stress again, as in the previous paper, that we believe this dilute solution order with a strongly acidic sulfonic-acid resin is not due primarily to a resin-phase ion-pairing of the sulfonate groups with the hydrated cations, as is often said or implied. We believe it is mainly a result of the more complete solvation possible to the ions in the dilute aqueous phase than in the resin phase. The cation which most needs solvation goes into the aqueous phase forcing the cation with the least need for solvation into the resin phase in the exchange.

This description of dilute solution selectivity will not be correct when dealing with weakly acidic resins. With such resins the stronger
interactions between the resin groups and the cations may become more important than the cation-water interactions in the dilute aqueous phase and so determine the direction of the exchange, i.e., the selectivity order. That is, the resin phase interactions do become dominant. In such a case we might expect that the cation most need of solvation would be preferentially picked up by the resin phase, leaving the less solvated ion to the now less desirable aqueous phase. The selectivity order would be reversed from that with a sulfonic-acid resin. It has already been noted that with a monobasic phosphoric-acid resin the alkali cations give smaller separations than with the stronger sulfonic-acid resins, and with carboxylate resins the alkalies are very close together in dilute solution exchange, although still in the same order. By going to a dibasic phosphonic-acid resin in alkaline media, the electrostatic interactions between the cations and the (doubly negative) resin groups are greatly enhanced and the dilute solution selectivity order of the alkalies does indeed reverse.

In a direct analogy to the last example given above, it might be expected that the dipositive alkaline earth cations would show enhanced interactions over the monopositive alkali ions with a resin group. In fact, the former ions do show an inverted selectivity order with the monobasic phosphoric acid resin that yields a normal, though compressed, order with the alkalies. But with as weakly basic a resin group as the sulfonate used in the present study, this effect is not very marked, at least in dilute solution, as a normal order for the alkaline earth tracers is observed. Apparently with the Dowex-50 resin in dilute solution exchange the ion-water interactions are still more important for the direction of the exchange than the resin anion-cation interactions, and so the much greater hydration of the dipositive ion in the aqueous
phase holds it there with respect to the unipositive ion. Also, with sulfonic-acid resins, the alkaline earth ions show fairly wide separations in the normal order, Be < Mg < Ca < Sr < Ba < Ra, again suggesting that the cation-water interactions dominate in dilute solution exchange over the resin anion-cation interaction in determining the order.

However, as the external acid concentration is increased, the amount of water available to hydrate each ion diminishes, and the relative importance of the cation-anion interactions in both the aqueous and resin phases increases. This result and the entrance of non-exchange electrolyte into the resin phase at high external solution concentration appear to the authors to be the origins of the deviations from mass-action law behavior shown by the ions in concentrated solutions. The latter effect, resin invasion by non-exchange electrolyte, acts to a first approximation as additional anionic sites for the cations. Such additional sites contribute to a gradual increase above the "ideal mass-action line" of slope -2.0 for all the tracer cations. More important, however, to the changes in selectivity order are the increasingly stronger cation-anion interactions in both phases as the water activity decreases. With most alkali earth cations and simple univalent anions these interactions are not like the usual chemical complexing that can occur with higher charged ions, e.g., FeCl\(^{++}\), AuCl\(_4^-\), etc., but are more ephemeral forms of association. Two such related types of electrostatic interactions, a transitory ion-pairing of the bare ions and an association through one, or more, polarized water molecules (localized hydrolysis\(^{10}\)) have been discussed in the previous paper;\(^3\) the actual nature of the "complexing" is less important to the present discussion than the fact that there is some such interaction. The effect shows up in the order of the activity coefficients of the alkali and alkaline earth salts, and in fact, it was to explain the order of the coefficients of the alkali
acetates and hydroxides that the localized hydrolysis hypothesis was developed. For simple monatomic cations the strength of these cation-anion interactions decreases with increasing basicity or size. So for the alkaline earths they decrease from Be to Ra. For the anions, the order is roughly that of decreasing basicity, i.e., $\text{ROC}_2 > \text{toluene} > \text{SO}_2^- > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{ClO}_4^-$. Nitrate ion is exceptional; although it is a stronger base than $\text{Cl}^-$, it appears to associate appreciably only with the largest cations. More will be said about this later.

As the external aqueous phase concentration is increased, the number of water molecules per ion decreases, and a cation by necessity becomes less well hydrated. Its solvation by water molecules must gradually become partially replaced with solvation (complexing) by anions in either the resin or aqueous phase. If the interactions with the resin group are stronger than those with the aqueous phase anion, the cation will increasingly prefer the resin phase, and conversely, if the aqueous phase anion interactions are the stronger, the cation will go preferentially into that phase. Since the smaller alkaline earths have stronger electrostatic interactions with anions than the larger ones, the smaller cations will usually determine the change in the direction of the equilibrium of Eq. (2) with increasingly concentrated solutions. If the resin anion affords better solvation than the aqueous phase anion, the smaller cation will go into the resin phase and force the larger cation into the aqueous phase, and vice-versa. In an ion-exchange reaction we must consider the way in which the solvation of the system as a whole is made optimum, that is, in which the solvation of both ions is maximized, in order to determine the change in the ion-exchange equilibrium.

With these ideas in mind, we may now take up the behavior of the alkaline earth tracer cations in concentrated acid solutions. Consider first the
behavior of the alkaline earths in HClO$_4$. Since ClO$_4^-$ is a much more poorly complexing anion than RSO$_3^-$, only the competition between the water and the resin sulfonate ions is important in determining values of D. But as the HClO$_4$ concentration increases, the water activity falls rather steeply and the resin sulfonate anion is increasingly better able to compete with water for solvating the cations, tracer cations as well as the hydrogen ions from the macro-acid, as the availability of water decreases.

Ba, the largest of the three cations shown in Fig. 1, has the least need for solvation and does not compete quite as well as the proton for the available means of solvation. As the water activity falls, ions tend to lose their hydration and the protons from the HClO$_4$ will preferentially move into the resin phase to replace water molecule interactions with sulfonate ion interactions. This causes the less strongly solvated Ba ions to remain in the aqueous phase to a greater extent than predicted from Eq. (5). Thus its D's begin to fall below those corresponding to a straight line of slope -2. However, as the HClO$_4$ concentration continues to increase, the amount of resin invasion by non-exchange HClO$_4$ begins to become appreciable. Since to a first approximation this non-exchange ClO$_4^-$ acts as additional resin sites, the effect is to eventually raise all of the distribution ratios; thus the curve for Bashows an upward deviation above 6 M HClO$_4$.

Ca, being smaller than Ba, is a stronger seeker of solvation and thus competes better with the protons for solvation by the water molecules and by the resin sulfonate groups. As the water activity falls in concentrated HClO$_4$ solutions, the Ca begins to lose its primary water shell, and so tends to go into the resin phase to compensate for its loss in hydration by resin sulfonate interactions. Its high charge density permits it to compete very favorably with the H$_3$O$^+$ ion for the resin sites, and above about 4 M HClO$_4$, the sharp
upturn of the curve signifies that as less and less water is available for the ions in the aqueous solution, the Ca increasingly turns to the resin sulfonate groups to satisfy its need for coordination. There is thus a reversal in the elution order of the heavier alkaline earths from the normal dilute solution sequence of \( \text{Ca} < \text{Sr} < \text{Ba} < \text{Ra} \) to \( \text{Ra} < \text{Ba} < \text{Sr} < \text{Ca} \) in concentrated \( \text{HClO}_4 \), as the best solvating medium for the ions gradually changes from the external aqueous phase to the resin phase.

It might be expected, then, that Be would show very high D's in concentrated \( \text{HClO}_4 \) solutions. But Be is such a small ion with such a high charge density that it is able to retain its primary hydration shell even at very low water activities, and thus remains in the aqueous phase, at least up to 9 M \( \text{HClO}_4 \). But the relatively greater upward deviation of Be as compared with Ba at 5-9 M \( \text{HClO}_4 \) suggests that in these highly dehydrating solutions even Be is beginning to lose some of its water of hydration and is starting to solvate with the resin sulfonate groups. In an even more strongly dehydrating solution we suspect Be would show an extremely steep rise, crossing both Ca and Ba and yielding the inverted order as previously found for the alkalies.³ That is, for very small, highly charged ions which hold onto their water very strongly, the sharp rise in the distribution ratio and consequent inversion in elution order is delayed to very strongly dehydrating conditions. Probably Mg would show a similar behavior to that of Be, but would go into the resin phase under somewhat less dehydrating conditions.

The next solution to be studied, HCl (Fig. 2), shows the effect of introducing an anion, namely \( \text{Cl}^- \), which, as the water activity falls, is able to compete with the resin group in solvating the cations, that is, in replacing complexing by water by anion complexing. This interaction with \( \text{Cl}^- \) tends
to hold the cations more strongly in the aqueous phase than with concentrated HClO₄ solutions, and so should delay the inversion of the elution order to higher concentrations of acid. The higher water activity in HCl solutions compared to HClO₄ also delays the transition to anion complexing, with similar effect, and so inversion should occur at a markedly higher concentration with HCl. Whether an individual alkaline earth tracer shows a higher or lower D in concentrated HCl relative to its value in HClO₄ depends upon whether it is less or more strongly complexed by Cl⁻ than is the macro-cation, H₂O⁺.

Again looking first at the Ba curve, it is seen that the values for the D's in HCl are similar to those in HClO₄, even in concentrated acid. Since in 10 M HCl some of the protons are certainly associated with the chloride ions, the implication is that some of the Ba ions must also be associating with the chloride ions, and to about the same extent as the HCl.

This type of association should be stronger with the smaller Ca ion than with Ba. It can be seen (Fig. 2) that although the Ca points in dilute HClO₄ and HCl are practically identical, the Ca curve in HCl falls below that in HClO₄ as the HCl concentration increases above 2 M. This is due to the greater complexing of Ca⁺⁺ than H₂O⁺ in the aqueous phase by Cl⁻. It may be noted, however, that the Ca curve, for the same reasons as in HClO₄ solutions, passes through a minimum (at 6 M HCl) and rises steeply thereafter, crossing the Ba curve. But as expected, this occurs at a higher concentration than in HClO₄.

The behavior of Be is very similar to that in HClO₄ up to 1-2 M HCl. However, instead of showing a slight upturn in more concentrated acid, the Be curve deviates downward from the mass-law slope. As with Ca, this lowering of D over the HClO₄ case can be explained by the fact that Be is complexed more strongly by chloride than are the protons, so that it is held even more strongly in the aqueous phase than in the HClO₄ case. In fact, Be has been
shown to exist in concentrated HCl solutions as an uncharged or even negative ion. 12,13

In Fig. 3 are shown the results of the exchange between HNO₃ and the alkaline earth tracers. The most interesting feature of these curves is the fact that they tend to fall below the HClO₄ curves, somewhat for Ca and especially for Ba. The deviation is greater, the larger the cation. Since HNO₃ is a much weaker acid than HClO₄, becoming about 50% associated at 10 M, it would be expected that the HNO₃ curves would rise above those for HClO₄ due to the effective decrease in the mass-law concentration of the hydrogen ions. Also, because of the higher water activity in a HNO₃ solution compared to an HCl or HClO₄ solution of the same concentration, it might be expected that the Ba-Ca reversal would occur at a still higher concentration with HNO₃ than with even HCl. Instead, the opposite is true for both expectations. Upon inspecting the HClO₄, HCl, and HNO₃ figures, the origin of this behavior seems to be principally due to the Ba curve, and seems to suggest an interaction between the alkaline earth cations and the nitrate ion which increases in importance with increasing size of the cation. To a smaller extent, these effects were noticed earlier with the alkali tracers also. 3 We can offer no explanation which will readily account for such behavior. But we might note that the order of elution of rare earth tracers on a anion exchange resin with LiNO₃ solutions 14 is such as to again indicate that the larger the cation, the more strongly it is complexed by NO₃⁻. Finally, the sharp upturns in the curves in Fig. 3 for all ions, including Be, in concentrated HNO₃ solutions occurs because of the association of the acid and consequent reduction in availability of hydrogen ions for exchange.
CONCLUSIONS

In a cation exchange resin system there exists a competition among the water, aqueous anions, and resin anions for solvating the exchanging cations, and there is a competition among the cations to go into the best solvating phase. In cases where complexing by the aqueous phase anions is relatively unimportant, the competition is mainly between water and the resin anions. So for dilute solutions and strong acid resins, such as those used in this study, it is found that the cations which most strongly need solvation (for monatomic cations, this would be the smaller ones) will interact preferentially with the stronger solvating agent, namely, water, and so prefer the aqueous phase. The larger monatomic cations will not show such a strong preference and thus will be forced into the resin phase in the exchange. Thus the dilute solution selectivity of alkali and alkaline earth ions with strongly acidic sulfonic resins is explainable as a predominantly aqueous phase effect.

But if strongly dehydrating solutions, such as concentrated HClO₄, are used, it is possible to reduce the water activity to the point where the smaller ions do not receive adequate solvation from the water molecules, and so increasingly tend to go into the resin phase where they can interact with the resin anion, RSO₃⁻. The result is a reversal in the selectivity order for all cations except the very smallest, e.g., Be²⁺ and Mg²⁺, which, with a very high charge density, are able to hold onto their primary hydration shell and so remain in the aqueous phase.

If the aqueous phase anion is a strong enough complexing agent to compete with the water and resin anion for solvating the cations, the distribution ratios will now also be a function of the relative extent of interaction between the various cations and anions in the aqueous phase. If the metal cations interact more strongly with the aqueous anion than does the hydrogen
ion, or if the solution is not as strongly dehydrating, the reversal in the elution order of the metal cations is delayed to higher concentrations of the macro-acid. This situation is exemplified by the case of the HCl systems. On the other hand, association of the aqueous anion preferentially with the macro-hydrogen ion effectively holds the latter in the aqueous phase and forces all other cations more strongly into the resin phase, that is, raises the value of their distribution ratios. This behavior is certainly occurring above 7 M HNO₃.
FOOTNOTES AND REFERENCES

(1) This work was supported in part by the U.S. Atomic Energy Commission.

(2) Present address: Shell Development Co., Emeryville, California.

(3) D. C. Whitney and R. M. Diamond, UCRL-10595, UCRL-10602, accepted for publication in combined form in Inorganic Chemistry.


Fig. 1. Distribution ratios on Dowex-50W vs HClO₄.
Fig. 2. Distribution ratios on Dowex-50W vs HCl.
Fig. 3. Distribution ratios on Dowex-50W vs HNO₃.
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