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ION EXCHANGE STUDIES IN CONCENTRATED SOLUTIONS

IV. The Nature of the Resin Sulfonate-Cation Bond in Strong Acid Solutions.

D. C. Whitney and R. M. Diamond

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ABSTRACT

A study has been made of the cation exchange of two labile ions, Fe(III) and Sc(III), and one non-labile ion, Cr(III), between strong acid solutions and both a sulfonic acid resin and a sulfonic acid "liquid ion-exchanger." The differences in exchange behavior in concentrated solutions are interpreted in terms of the differences in lability of the ions. The nature of the resin sulfonate-ion bond for both dilute and concentrated aqueous acid solutions is discussed.

INTRODUCTION

The distribution ratios of lanthanide elements between HCl solutions and sulfonic acid ion exchange resins were shown several years ago to pass through a sharp minimum at 4M HCl, followed by a very steep rise at higher concentrations.[3] The actinides, on the other hand, showed no, or a very slight, rise; the difference between the lanthanides and actinides was attributed to the formation of chloro complexes by the latter.[3] This was subsequently confirmed by the almost identical behavior of the lanthanides and actinides, including the sharp rise at high (> 4M) concentrations, in $HClO_4$ solutions, ClO_4^- being a non-complexing anion.[4]

However, no satisfactory explanation has been offered for the very great increases in distribution ratio, D, exhibited by these tripositive ions in concentrated acid solution, where the D may rise several orders of magnitude over the range of 4-10 M acid. A very strong interaction with the resin is implied, and the work reported in this paper is an attempt to determine the nature of this interaction.

The exchange of tracer alkali and alkaline earth ions with hydrogen ion in concentrated acid solutions has been treated in previous papers[5,6] and the selectivity of the resin was considered to be the outcome of a competition for the solvation of the cation between the resin sulfonate groups in the resin phase and the water and anions in the aqueous phase. For the tripositive ions, the existence of very high D's in concentrated acid implies very strong bonding to the resin sulfonate sites; the results given in this paper discriminate between simple electrostatic bonding between the RSO_3^- group and the cation, most probably via a H_2O bridge, and the actual entering of the RSO_3^- group into the coordination sphere of the cation.

This was accomplished through the use of two trivalent cations of essentially identical size but with coordination spheres greatly differing in lability, i. e., Fe(III) (0.64 Å), with essentially instantaneous ligand exchange, and Cr(III) (0.69 Å), with an approximately 32 hour half-life for H_2O exchange in strong acid solution.[7] By observing the behavior of these ions, the nature of their bonding to the resin from strong acid solutions has been elucidated.

It was subsequently determined that Fe(III) has somewhat anomalous behavior in dilute ($\leq$ 1M) $HClO_4$ solutions, so Sc(III) (0.81 Å), a somewhat larger but equally labile ion, was used to check the Fe results.

EXPERIMENTAL

Reagents. The Dowex 50W-X12 resin was 100-200 mesh and had a capacity of 5.2 meq/g dry resin; its treatment was discussed in a previous paper.[5] The dinonylnaphthalene sulfonic acid (DNNS) was obtained as a 39.1% solution in heptane and was diluted to 0.0697 M using 2,2, 4-trimethylpentane (iso-octane, Eastman Spectrograde). The $HClO_4$ was G. F. Smith reagent grade; the HCl and HNO_3 were Merck reagent grade. The radioactive tracers, their source and any chemical procedures used in their preparation are shown in Table I; no difference in the behavior of tracers purified by the different methods was noted.

Procedure. Dowex-50W. Exactly 0.100 g dry resin were shaken with 10.00 ml acid solution containing a known amount of tracer. Two 2.00-ml aliquots were withdrawn through a fritted-glass filter and γ-counted using a Na(Tl)I well crystal in conjunction with a single-channel analyzer. Distribution ratios were calculated as

$$D = \frac{100 \times \text{counts/min per 2.00 ml original solution} - \text{counts/min per 2.00 ml final sol.}}{\text{counts/ min per 2.00 ml final solution}}$$

where counting rates have been corrected for background.

DNNS. About 10^5 counts/ min of tracer were added to a glass-stoppered bottle containing 5.00 ml $HClO_4$ solution plus 5.00 ml DNNS solution. After shaking, the phases were separated by centrifugation and two 2.00-ml aliquots of each phase were removed and γ-counted. Distribution ratios were calculated as

$$D = \frac{\text{counts/min per 2.00 ml organic phase}}{\text{counts/min per 2.00 ml aqueous phase}}$$

counting rates again being corrected for background.

RESULTS

The experimental data are plotted using solid symbols as log D vs log M $HClO_4$ for Dowex-50W in Fig. 1 and DNNS in Fig. 2. Studies of the variation of D with time at a given $HClO_4$ concentration are shown using open symbols on the same graphs and listed in Tables II and III. The fact that the open symbols for Fe are coincident (within experimental error) with the closed ones indicates that equilibrium was established; the results with Cr are treated in the discussion section. Studies of the variation of D with time for Cr(III) with HCl and HNO_3 solutions are listed in Table IV.

DISCUSSION

It can be shown that the ion exchange behavior of a tracer cation of charge n in dilute aqueous acid solution can be described by the equation

$$\log D = -n\log[B] + \log K' \quad , \qquad (1)$$

where D is the distribution ratio, n is the charge on the tracer, and [B] is the aqueous acid concentration. Thus a plot of log D vs log [B] should yield a line of slope -n in the dilute solution region where activity coefficient ratios may be assumed to be constant.

Such a plot has been made in Fig. 1 and 2 for Fe(III), Cr(III), and Sc(III) tracers in $HClO_4$, and it is seen that a line of slope -3.0 is obtained for both Cr and Sc below 1M $HClO_4$ in both the Dowex-50W and the DNNS systems. Fe, however, exhibits a slope of 2.5 in both exchangers. This anomalous result was first ascribed to experimental error, but repeated determinations yielded essentially identical slopes.

Since the iron tracer was certainly in the tripositive state at the start of the exchange there is no apparent reason why it should fail to retain this charge throughout the experiment. One possible explanation is partial hydrolysis, although this seems highly unlikely in acid solution of 0.2 to 1M $HClO_4$. Another possible explanation is a partial reduction of the ferric ion by resin impurities, although these should not have been present in the DNNS, where the same behavior is observed. But since neither of these effects should take place at higher $HClO_4$ concentrations, and since the Fe curve seems to behave there like the Sc one, the iron was assumed to be tripositive and well behaved in the more concentrated acid region.

The general behavior and selectivity order of monovalent and divalent cations on Dowex-50W has been discussed in earlier papers,[5,6] and it can be seen in Fig. 1 that the ideas presented previously give at least qualitative agreement with the current data for these tripositive ions in dilute solution. In dilute acid solution the smaller ions, with their greater need of solvation, tend to prefer the aqueous phase more strongly than the larger, more weakly solvated ions, leading to resin selectivities in order of increasing crystallographic size. The point of interest is that since the tripositive ions fall into a normal selectivity order they must all be exhibiting the same type of bonding to the resin sites. Moreover, Boyd and Soldano[8] have shown that Cr(III) retains its primary hydration shell of six water molecules in the resin phase under such dilute solution conditions. This leads to the conclusion that all three of the ions in this study retain at least their first shell of water molecules inside the resin in dilute (< 1M) $HClO_4$, and that the cations, if bonding to a specific resin sulfonate group, do so through at least one H_2O "bridge" in their primary hydration shell.

Consider now the exchange resin behavior in more concentrated $HClO_4$ solutions. It is seen in Fig. 1 that the plots of D for Fe and Cr are essentially similar (provided the previously mentioned deviation in slope for Fe in dilute solution is neglected) up to about 2M $HClO_4$, and that Sc lies above, and parallel to, the Cr curve. At this point the Fe curve begins to deviate upward from a straight line, going through a minimum at 3.5M, after which it turns up sharply (the point at 9.8M $HClO_4$ is shown with an arrow because severe, possibly Fe-catalyzed, resin decomposition was noted in this sample, which would tend to lower the distribution ratio).

Scandium behaves in a similar manner, its curve being parallel to that of the Fe above 4M $HClO_4$. The values for Cr, on the other hand, keep on dropping until a more-or-less constant value of D is attained over the region of 4-10M $HClO_4$.

Since Fe and Cr are of substantially identical size and are both hexaquo ions, any explanation of the difference in their behavior must be connected with the difference in the labilities of the aquo-ions. The relatively long half-life for water exchange by $Cr(H_2O)_6^{+++}$ means that in our distribution experiments this ion will exist primarily as the hexaquo complex even in concentrated $HClO_4$. On the other hand, $Fe(H_2O)_6^{+++}$ will tend to surrender some of its waters of hydration in the dehydrating atmosphere of the concentrated $HClO_4$ solutions, even though its high charge density strongly requires coordination (solvation) by basic (electron-donating) species. One possible explanation, then, for their difference in exchange resin behavior in concentrated $HClO_4$ solutions is that the shrinkage of the resin in such solutions closes down the pores of the resin to the point where the $Cr(H_2O)_6^{+++}$ ion cannot enter the resin phare as easily as the partially dehydrated, and thus smaller, Fe ion. In order to test for any such steric effects owing to the size of the resin pores, the experiments were repeated using a 0.0669M solution of dinonylnaphthalene sulfonic acid (DNNS) in a mixture of heptane and iso-octane, a so-called "liquid ion-exchanger". Almost identical behavior to that found for the resin is shown when the exchanger is DNNS (Fig. 2), with the exception that the distribution ratio for Cr, instead of remaining constant, falls off very rapidly as the $HClO_4$ concentration increases, and the rise of the Fe curve is not so steep. Since pore size considerations cannot be very important with dilute

DNNS solutions there must be another explanation for the difference in behavior between Fe and Cr. It might be expected that with the low water activities of concentrated $HClO_4$ solutions tripositive ions (except very small ones such as Al) would become partially dehydrated, especially if there is some other solvating agent, such as a resin sulfonate anion, present to replace the solvation lost by the dehydration. (An example of this effect is seen with the alkalies, where the selectivity order on Dowex-50W becomes reversed due to the enhanced ability of the resin sulfonate ion to compete for the smaller ions in solutions which have low water activities.) Uner these conditions, it seems reasonable that the labile ions, seeking solvation, would enter the resin phase and use sulfonate ions to complete their primary solvation shells, forming bonds directly between the cation and the resin sulfonate anion. This solvation by the resin results in a rise in the D's for most tripositive ions in concentrated $HClO_4$ solutions. On the other hand, the $Cr(H_2O)_6^{+++}$ ion, because of the slow kinetics of its water exchange, would keep its hydration shell during the period of time of these experiments, even in very concentrated acid solutions. Thus $Cr(H_2O)_6^{+++}$ would tend to remain in the aqueous phase to a greater extent than would the labile cations.

The case is more clear-cut when DNNS solutions in octane are the exchanger, since they are more weakly acidic than Dowex-50. Also such complications as resin invasion (entrance of non-exchange electrolyte), secondary ion hydration, and non-bonded water would be expected to be minimized because of its more organic-solvent-like nature. With DNNS solutions the behavior of Fe and Cr is again similar below $4\underline{M}$ $HClO_4$ where both ions still retain their hydration shells, but above $4\underline{M}$ $HClO_4$ the dehydration of the Fe causes it to seek solvation very strongly in the

DNNS solution phase, while the hydrated Cr remains in the aqueous phase. As the acid concentration rises, the protons, also seeking solvation in the DNNS phase, cause the $Cr(H_2O)_6^{+++}$ to be rejected more and more strongly by the DNNS, with a consequent sharp drop in D, and even the Fe begins to become affected at 10M $HClO_4$.

The foregoing ideas can be checked by carrying out a study of the change in distribution ratio with time. Since the $Cr(H_2O)_6^{+++}$ does slowly undergo exchange of its waters of hydration, it would be expected that in solutions of low water activity another solvating group, specifically a resin sulfonate anion, could replace a water molecule if given enough time. Thus it might be predicted that the distribution ratio of Cr tracer would gradually increase with time, as resin sulfonate groups gradually entered the first hydration shell of more and more chromium ions, until values of the distribution ratio approaching those for Fe were obtained. Since only those few exchanges which occurred between the sulfonate groups and the H_2O molecules coordinated to the Cr ion would give an increase in D, this process would most probably take weeks to approach completion; however, the trend should be evident over a shorter period of time, i.e., a few days. Scandium and iron, on the other hand, would be expected to maintain the same D over these periods of time, since they are undergoing continuous exchange between H_2O and sulfonate groups in a state of dynamic equilibrium.

Distribution ratios at several different acid molarities taken over a period of several weeks are shown in Figs. 1 and 2 using open symbols and are listed in Tables II and III. It can be seen that essentially no differences occur in any of the points with the exception of those for Cr tracer in 7.5M $HClO_4$, where a roughly exponential increase with time

occurs for the first week; results for longer times are probably incorrect (on the low side) due to degradation of Dowex-50W by the $HClO_4$. But the increase with time certainly confirms the ideas expressed above.

In order to show that the variation of D with time for Cr is not specifically associated with the ClO_4^- anion, time studies were also carried out with HCl and HNO_3 solutions. On the basis of the foregoing analysis, it would be expected that HNO_3 solutions, involving a relatively poorly complexing anion, would yield similar results as $HClO_4$, but with a less marked increase, while with HCl solutions the distribution ratio would fall with time, as chloro-complexes of Cr(III) gradually formed. As can be seen in Table IV, these are exactly the results obtained although the low values of D in the HCl solutions makes for rather large experimental errors.

It thus appears that some rather definite conclusions can be made about the bonding of tripositive ions such as Sc, Fe, the lanthanides and actinides, etc., to sulfonic acid ion exchange resins. In dilute solutions, the ions retain their primary hydration shell and to whatever extent they are actually bonded to the resin sulfonate groups, this must be through at least the primary hydration shell. As the water activity falls, and in the absence of complexing anions in the aqueous phase, those ions which lose at least one of their first-shell waters of hydration may replace it with a resin sulfonate group, forming a cation-sulfonate group bond and thus yielding very high distribution ratios. Those ions which, under the conditions of the experiment do not lose their primary hydration shell, whether for kinetic reasons or because of the strength of the water-ion bond, will not go as strongly into the resin phase and so will exhibit lower distribution ratios than the former ions. Exactly the reverse behavior will occur in the presence of strongly complexing anions.

Table I. Preparation of Radiochemical Tracers.

Tracer	$T_{1/2}$ (a)	Chemical Form	Source (b)	Processing
Sc^{46}	85d	$ScCl_3$ in HCl	ORNL	Evaporated to dryness and dissolved in $HClO_4$
Cr^{51}	27d	$CrCl_3$ in HCl	ORNL	Evaporated to dryness with $HClO_4$ and dissolved in $HClO_4$, allowed to stand for two weeks before use to permit Cl-H_2O exchange.
		$Cr(ClO_4)_3$	GETR	Dissolved in $HClO_4$, treated with H_2O_2 to reduce Cr_2O_7, and boiled to remove excess H_2O_2.
		CrO_3	GETR	Same as above.
Fe^{59}	45d	Fe filings	GETR	Dissolved in $HClO_4$, evaporated to dryness and redissolved in $HClO_4$
		$Fe_2(SO_4)_3$	GETR	Dissolved in $HClO_4$, treated with $K_2S_2O_8$ to oxidize Fe(II) and boiled to decompose excess $K_2S_2O_8$.

(a) All half-lives taken from the "General Electric Chart of the Nuclides", fifth edition, Knolls Atomic Power Laboratory, April, 1956.

(b) ORNL - Oak Ridge National Laboratory, Oak Ridge, Tenn.
GETR - Material irradiated at General Electric Test Reactor (Vallecitos), Pleasanton, California

Table II. Time Studies of the Distribution of Trivalent Tracers Between Dowex-50W and $HClO_4$.

Tracer	Acid Molarity	Time	$(c/m)_{orig.}$	$(c/m)_{final}$	D
Fe(III)	.226	15 m	9.5×10^4	1.7×10^3	5.5×10^3
	.226	4 h	1.1×10^5	1.9×10^3	5.7×10^3
	.226	7 d	7.2×10^4	1.8×10^3	4.0×10^3
	1.63	15 m	9.6×10^4	6.6×10^4	4.6×10^1
	1.63	4 h	1.1×10^5	7.1×10^4	5.2×10^1
	1.63	7 d	7.1×10^4	5.1×10^4	4.0×10^1
	7.47	4 h	1.1×10^5	6.1×10^4	8.2×10^1
	7.47	7 d	7.3×10^4	4.2×10^4	7.4×10^1
Cr(III)	.226	15 m	2.0×10^5	1.2×10^3	1.6×10^4
	.226	4 h	3.1×10^5	2.2×10^3	1.4×10^4
	.226	7 d	1.9×10^5	1.1×10^3	1.7×10^4
	1.63	15 m	2.04×10^5	1.37×10^5	4.8×10^1
	1.63	4 h	3.07×10^5	2.10×10^5	4.8×10^1
	1.63	7 d	1.96×10^5	1.31×10^5	4.9×10^1
	7.47	15 m	2.41×10^5	2.38×10^5	5.2×10^0
	7.47	4 h	2.90×10^5	2.72×10^5	6.7×10^0
	7.47	24 h	2.91×10^5	2.68×10^5	8.9×10^0
	7.47	4 d	2.35×10^5	2.08×10^5	1.3×10^1
	7.47	5 d	2.70×10^5	2.35×10^5	1.5×10^1
	7.47	7 d	2.38×10^5	2.00×10^5	1.8×10^1
	7.47	14 d	1.71×10^5	1.43×10^5	2.0×10^1
	7.47	28 d	7.54×10^4	6.26×10^4	2.1×10^1

Table III. Time Studies on the Distribution of Trivalent Tracers Between 0.0697M DNNS and 7.47M $HClO_4$.

Tracer	Time	$(c/m)_{orig.}$	$(c/m)_{aq.}$	D
Sc(III)	30 m	4.8×10^4	8.0×10^3	6.0×10^0
	7 d	6.8×10^4	1.1×10^4	6.2×10^0
Cr(III)	30 m	1.7×10^3	1.5×10^5	1.1×10^{-2}
	2 d	3.6×10^3	1.9×10^5	1.9×10^{-2}
	5 d	4.3×10^3	1.6×10^5	2.6×10^{-2}
	8 d	6.1×10^3	1.7×10^5	3.5×10^{-2}
	15 d	5.1×10^3	1.3×10^5	3.9×10^{-2}

Table IV. Time Studies of Distribution of Cr(III) Between Dowex-50W and HCl and HNO_3.[a]

Acid	Time (hrs)	$(c/m)_{orig.}$	$(c/m)_{final}$	D
7.7M HNO_3	4.5	1.02×10^5	8.0×10^4	2.7
	27.8	9.9×10^4	7.7×10^4	2.9
	75.5	9.5×10^4	7.3×10^4	3.0
	220	8.2×10^4	6.3×10^4	3.0
	7200	8.0×10^4	6.0×10^4	3.3
8.7M HCl	4.5	8.78×10^4	8.32×10^4	$0.5_5 \pm 0.2$
	27.8	8.62×10^4	8.20×10^4	0.5 ± 0.2
	75.5	8.17×10^4	7.75×10^4	$0.5_5 \pm 0.2$
	220	7.14×10^4	6.89×10^4	0.35 ± 0.2
	7200	6.94×10^4	6.86×10^4	0.1 ± 0.2

(a) Because of the low D's involved, 1.000 g of resin were used in these studies.

FOOTNOTES AND REFERENCES

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

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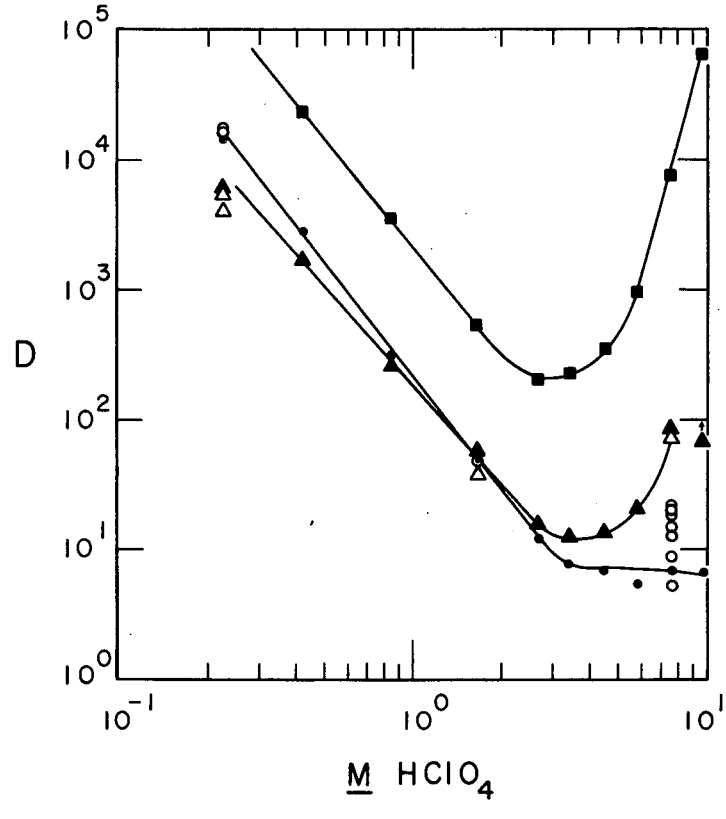

Fig. 1. Variation of distribution ratio on Dowex-50W with $HClO_4$ molarity for the tripositive ions: ▲, Fe; ●, Cr; ■, Sc. Open symbols are time studies, see Table II and text.

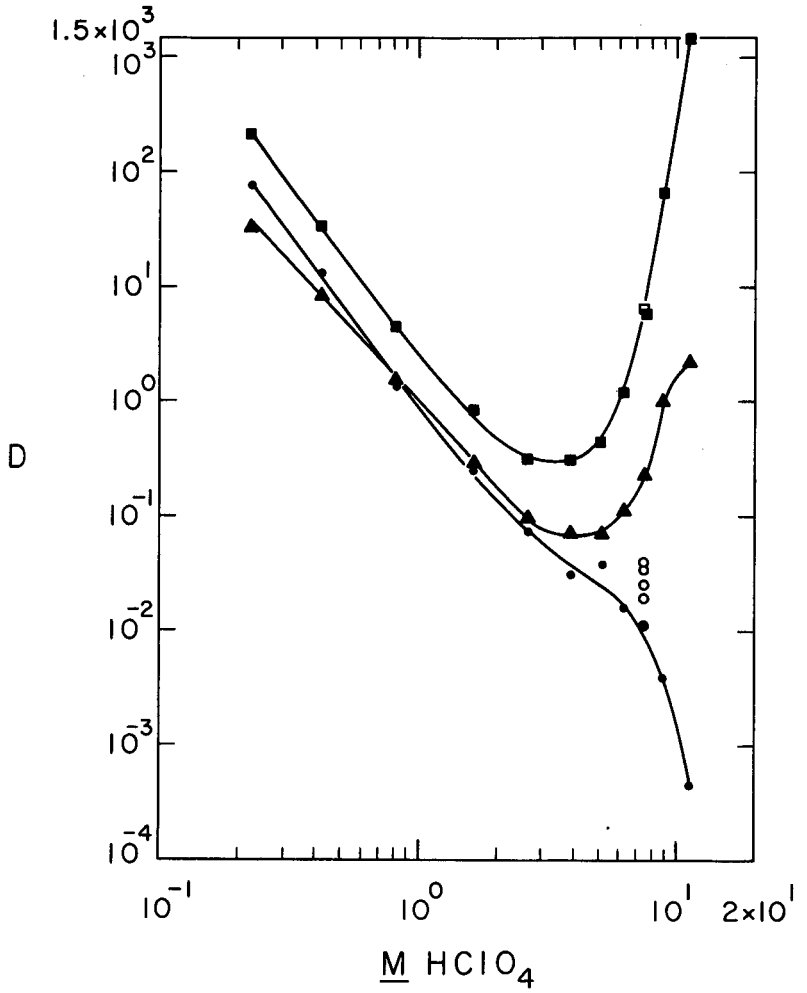

Fig. 2. Variation of distribution ratio into 0.0697M DNNS with $HClO_4$ molarity for the tripositive ions: ▲, Fe: ●, Cr; ■, Sc. Open symbols are time studies, see Table III and text.