That more rapid carboxylate scrambling occurs in mixed carboxylates with high trichloroacetate: acetate ratios (in spite of the bulk of the CCl_3 group) is consistent with the relatively weaker donor properties of the trichloroacetate group and suggests a dissociative mechanism for the exchange process

$$Be_4O(RCO_2)_x(R'CO_2)_{6-x} \rightleftharpoons Be_4O(RCO_2)_x(R'CO_2)_{5-x}^+ + R'CO_2^-$$

We note here that the mass spectra of the mixed carboxylates indicated that for the process involving loss of carboxylate from $Be_4O(CH_3CO_2)_x(CCl_3CO_2)_{6-x}$, loss of CCl_3CO_2 occurred consistently 2.4 (±0.2) times the statistically calculated value. Thus for $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ one expects a 5:1 relative intensity ratio for $Be_4O(CH_3CO_2)_4(CCl_3CO_2)^+$:$Be_4O(CH_3CO_2)_5^+$ while a 1.9:1.0 ratio is observed. Once again these data are indicative of the relative ease of loss of trichloroacetate *vs.* acetate, although under quite different conditions with regard to nmr experiments.

In view of our observation of carboxylate scrambling the previous claim[10] for the preparation of pure acetate–monochloroacetate carboxylates simply by melting together appropriate amounts of starting materials appears untenable.

[10] A. V. Novoselenova and K. N. Semenko, *Zh. Neorg. Khim.*, **1**, 2344 (1956).

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Anion-Exchange Studies of Halo Complexes of Indium and Some Related Elements in Mixed Water–Alcohol Solutions

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The equilibrium distribution of anionic halo complexes of Au(III), In(III), and Ga(III) between solution and anion-exchange resin is profoundly affected by the addition of hydrophilic organic solvents. The solvents investigated were methanol, ethanol, 1-propanol, 1-butanol, and acetone. With Au(III) in aqueous HCl, the decrease in the distribution coefficient (K_d) is ascribed primarily to a change in the dielectric constant of the solution phase. For In(III), addition of the solvent affects the equilibria between the various species present in solution and K_d may increase, decrease, or go through a maximum depending on the halide present and on the solvent. With Ga(III), the results are similar to those for In(III). The results are in agreement with the previous solvent extraction studies of anionic In(III) complexes.

The use of anion exchange has provided much important information on the complexing behavior of positive ions in solution. For halide complexes, variations in the distribution coefficient (K_d) with hydrohalic acid concentration have been reported for a variety of elements in hydrofluoric,[1] hydrochloric,[2] and hydrobromic[3] acids. The values of K_d differ widely from element to element and often depend markedly on the acid concentration. The effect of adding electrolytes to the aqueous phase has been discussed by several authors, with special concern as to whether the observed changes in K_d arise from effects in the aqueous phase rather than in the resin.[4,5] There is much less information on anion exchange from nonaqueous solvents, or in mixed aqueous–nonaqueous systems; Korkisch and Janauer[6] have reviewed this field up to 1962, but with special reference to the behavior of uranium and thorium, and to the separation of these elements (see also ref 5).

The work described in this paper arose from a continuing interest in the nature of the indium(III) species present in aqueous solution. In particular, it is known that the extraction of anionic indium(III)–chloro complexes into basic oxygenated solvents is significantly less efficient than is the case for complexes of other tripositive elements. Results on the anion exchange of metal ions in aqueous hydrochloric acid solution[2] show a similar effect in that indium is removed from the solution phase less easily than other comparable elements. One possible explanation would be that indium(III) forms anionic complexes less strongly than the other elements in question. There are few reliable stability constant data[7] for the higher anionic complexes of elements such as indium, but in any case this explanation does not seem appealing when one compares (say) indium(III) and iron(III), since the available evidence shows that the complexing properties of these two elements are not very different quantitatively; in any case, the differences are not sufficient to explain fully the extraction and anion-exchange results.

An alternative explanation, advanced previously in connection with work on the extraction of indium by long-chain amines,[8] is that the predominant anionic

[1] J. P. Faris, *Anal. Chem.*, **32**, 520 (1960).

[2] K. A. Kraus and F. Nelson, *Proc. Int. Conf. Peaceful Uses At. Energy*, **7**, 113 (1956).

[3] R. H. Herber and J. W. Irvine, Jr., *J. Amer. Chem. Soc.*, **76**, 987 (1954); **78**, 905 (1956).

[4] F. Helfferich, "Ion Exchange," McGraw-Hill, New York, N. Y., 1962, p 220 ff.

[5] Y. Marcus and A. S. Kertes, "Ion Exchange and Solvent Extraction of Metal Complexes," Wiley, New York, N. Y., 1969.

[6] J. Korkisch and G. Janauer, *Talanta*, **9**, 957 (1962).

[7] "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964.

[8] D. G. Tuck and E. J. Woodhouse, *J. Chem. Soc.*, 6017 (1964).

indium(III) complex in aqueous solution is the singly charged species $InX_4(H_2O)_2^-$, which cannot be extracted into the organic phase as such because of its strong hydration. The dissociation equilibrium

$$InX_4(H_2O)_2^- \rightleftharpoons InX_4^- + 2H_2O$$

which must precede extraction lies well to the left.[8] The predominant anionic complexes for other elements are presumably species which are more easily removed from aqueous solution (see below).

The position of the above equilibrium will obviously depend, *inter alia*, on the thermodynamic activity of H_2O in the solution in question. The nature of two-phase solvent extraction systems does not allow the water activity to be varied by the addition of hydrophilic solvents such as aliphatic alcohols, since these render the organic extractant partially or completely miscible with the aqueous phase. This does not hold for anion exchange, although the presence of an organic solvent in the aqueous phase must necessarily have some effect on the resin (see Discussion). The present paper reports results on the anion exchange of indium(III) and gold(III), and in less detail of gallium(III), from aqueous hydrohalic acid solutions containing methanol, ethanol, 1-propanol, 1-butanol, or acetone. The results are in agreement with earlier views on the nature of indium complexes in aqueous solution.[8]

Experimental Section

Materials.—Organic solvents were reagent grade and were suitably dried and distilled before use. Acid solutions were prepared by dilution of reagent grade materials; hydriodic acid was pretreated with tri-*n*-butyl phosphate before use to remove iodine.[9]

Two strongly basic ion exchangers were used in this work, Amberlite 400 and Dowex 1-X8 (50–100 mesh). In both cases, the resin was conditioned by treatment alternatively with 3 *M* aqueous sodium hydroxide and 3 *M* hydrohalic acid. The final product, in the halide form, was washed extensively with deionized water to remove "fines" and dried at 60°. The two different resins gave essentially the same results in terms of the dependence of K_d on alcohol concentration. The results quoted for each series of experiments refer to measurements involving samples of the same resin.

Radiochemical Procedures.—Radioactive indium (^{114}In, $t_{1/2}$ 49 days) and gold (^{198}Au, $t_{1/2}$ 2.70 days) were produced by neutron bombardment of the metal. In each case, the active metal was dissolved in aqueous hydrochloric acid, and the stock solution so obtained diluted as required for experiments in chloride systems. In the bromide and iodide work, a portion of the initial hydrochloric acid solution was evaporated to dryness, and the residue was dissolved in concentrated hydrobromic or hydroiodic acid; the resultant solution was then evaporated three times with excess acid, followed by final dilution.

Radioactive gallium (^{67}Ga, $t_{1/2}$ 78 hr) was prepared by deuteron bombardment of metallic zinc in the cyclotron of the University of Birmingham. The target was dissolved in 6 *M* hydrochloric acid, gallium carrier was added, and the solution was extracted with diethyl ether. Gallium was then back-washed from the extract solution with 1 *M* hydrochloric acid, which was evaporated almost to dryness to remove any dissolved ether. The resultant solution was diluted with 1 *M* hydrochloric acid, and aliquots of this were used in the ion-exchange work.

The specific activity of solutions was measured by counting samples (1–2 ml) in a well-type NaI(Tl) scintillation counter. In all measurements, sufficient counts were recorded to give a statistical accuracy of better than 1%. Since our interest is in changes in K_d, rather than in absolute values, and since these changes are in practice quite large (see Results), no attempt was made to correct the experimental activities for the different radiation absorption characteristics of the various solutions investigated, since the correction factors involved would have been small compared with the observed changes in K_d.

Determination of Distribution Coefficients.—In each experiment, a weighed quantity of resin (usually 25–500 mg) was added to 20 ml of solution of known acidity and alcohol content, and the mixture was allowed to stand for about 30 min to allow the resin to come to equilibrium with the solution. A small aliquot of the stock tracer solution (usually ~0.1 ml) was then added, and the mixture was shaken mechanically for several hours. The resin was then allowed to settle out, after which aliquots of the solution were withdrawn for counting; because the "fines" had been previously removed, the solution was not centrifuged before sampling. All experiments were carried out at 20 ± 0.2°. The metal concentration in the initial solution before exchange was approximately 1.25 m*M*.

The distribution coefficient was calculated as $K_d = (C_{In})_R/(C_{In})_{aq}$, where the equilibrium concentrations are in moles per kilogram in the resin phase and moles per liter in the aqueous phase. The experimental conditions were chosen so as to give values of the activity ratio $(I_0 - I_x)/I_x$ close to unity.

The importance of changes in the swelling factor in ion exchange from mixed aqueous–nonaqueous media has been emphasized.[10] We have measured the swelling factor (δ) for Dowex 1-X8 over the range of solution conditions used in the anion-exchange work. The results, based on direct microscopic measurement of the diameter of resin beads, are given in Table I. There are some obvious correlations; δ increases in the order Cr < Br < I and methanol < ethanol < 1-propanol, and for a

TABLE I

SWELLING FACTOR (δ) FOR DOWEX 1-X8 RESIN UNDER VARIOUS SOLUTION CONDITIONS

(a) Aqueous Hydrohalic Acid

	δ		
X	1 *M* HX	3 *M* HX	5 *M* HX
Cl	0.990	0.985	0.973
Br	0.993	0.989	0.986
I	. . .	0.999	0.995[a]

(b) In the Presence of Added Nonaqueous Solvent

	% solvent	δ			
Acidity	(v/v)	Methanol	Ethanol	Propanol	Acetone
3 *M* HCl	5	0.986	0.988	0.987	0.990
	20	0.990	0.988	0.991	0.987
	40	0.992		0.993	0.986
	60	0.995	0.996		0.983
5 *M* HCl	5	0.972	0.982		0.988
	20	0.982	0.982		0.979
	40	0.990	0.984		0.979
	60	0.990	0.994		0.975
3 *M* HBr	5	0.989	0.991		0.991
	20	0.990	0.994		0.995
	40	0.994			0.988
	50	0.996	0.999		
5 *M* HBr	5	0.978			0.991
	10	0.986			0.995
	20	0.990			0.990
	30	0.988			0.988
4 *M* HI	5	0.996			0.995
	10	0.999			0.998
	20	0.999			0.992
	30	0.995			0.990

[a] 4 *M* HI.

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(9) D. G. Tuck, R. M. Walters, and E. J. Woodhouse, *Chem. Ind.* (*London*), 1352 (1963).

(10) Reference 4, p 509.

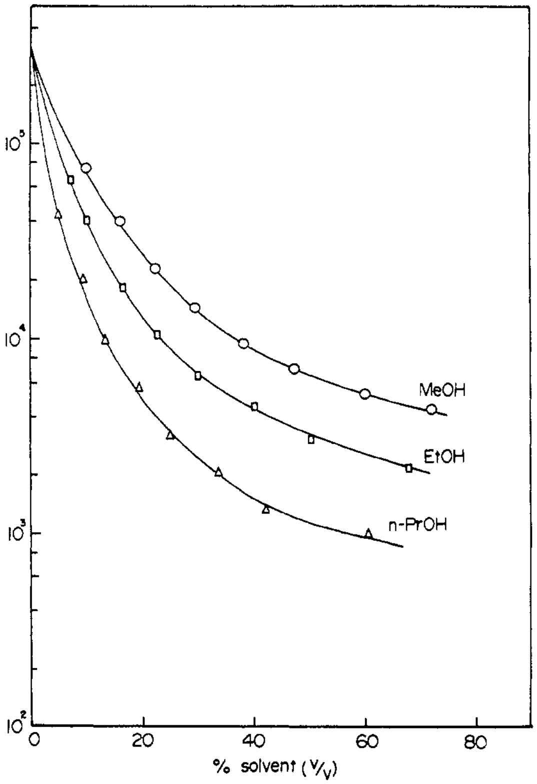

Figure 1.—Effect of added organic solvents on K_d for sorption of Au(III) on Amberlite IRA-400 from 4 *M* aqueous hydrochloric acid solution.

given alcohol and fixed acid concentration, δ increases with increasing alcohol concentration. The maximum correction to K_d resulting from resin swelling is for 5% methanol in 5 *M* hydrochloric acid, but even here δ is only 0.972. The necessary correction is very small compared with the observed changes in K_d (see below), and the values of K_d quoted in the remainder of this paper are therefore uncorrected for resin swelling.

Results and Discussion

General Comments.—Korkisch and Janauer[6] have listed the following factors which should be considered in discussing the effect of nonaqueous solvent on ion exchange: solvent uptake and resin swelling, dissociation of species in solution, solvation effects, complex formation, and ionic and molecular interactions. As these authors point out, these factors must be regarded as a system of mutually related variables.

We are concerned in this work with changes in the anion-exchange behavior of alcohols (and acetone). Since the experiments were all conducted under similar conditions of acidity, metal concentration, alcohol concentration, etc., it seems unlikely that the large changes in K_d observed can be explained in terms of effects in the resin phase alone. This conclusion has been reached in discussions of the effect of electrolytes on the anion exchange of zinc complexes with both resin and liquid ion exchangers, where the emphasis has been placed on effects in solution.[4] From the results in Table I, it was argued that resin swelling can be neglected in the discussion of the changes in K_d. Even ignoring the small changes in δ relative to the large changes in K_d, a comparison of the results for gold(III) and indium(III) shows that any explanation based on resin-swelling effects cannot apply in both these systems.

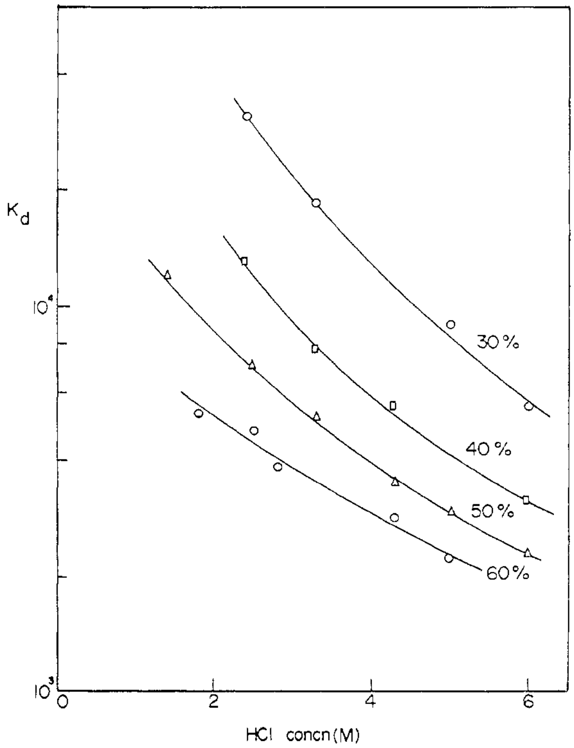

Figure 2.—K_d for sorption of Au(III) from aqueous hydrochloric acid for various ethanol concentrations (Amberlite 400).

For all three elements studied in the present work, five different hydrophilic organic solvents produce changes in the anion-exchange equilibrium which are qualitatively but not quantitatively independent of the solvent added. It is believed that in the case of gold(III), effects in both resin and solution phases are important, but that in the case of indium and gallium, changes in the nature of the species in the solution phase predominate.

Results for Gold(III) Systems.—Anionic gold(III) halide complexes of the type AuX_4^- are known to be formed with all four halides; the stability constants are high (*e.g.*, β_4 = 26 for $AuCl_4^-$, ~32 for $AuBr_4^-$ [11]) and the structure is square planar both in the solid state[12] and in aqueous solution.[13] The dependence of K_d for anion exchange on hydrochloric acid concentration shows a smooth decrease[2] from ~10^6 at 3 *M* HCl to ~10^4 at 10 *M* acid. Figure 1 shows the changes in K_d brought about by adding methyl, ethyl, and *n*-propyl alcohols to 4 *M* hydrochloric acid solutions of gold(III); the decrease in K_d is clearly qualitatively independent of the alcohol used. Similarly, Figure 2 demonstrates that the results with ethanol are generally independent of the acid concentration, and it seems reasonable to assume that, as in the indium case discussed below, similar results would hold for the other alcohols.

Resin swelling was shown above to be negligibly

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[11] Reference 7, pp 288, 324.

[12] A. Sabatini, L. Sacconi, and V. Schettino, *Inorg. Chem.*, **3**, 1775 (1964).

[13] H. Stammreich and R. Forneris, *Spectrochim. Acta*, **16**, 363 (1960).

altered by the addition of alcohols, and in view of the high stability of AuX_4^- anions, dissociation into neutral or cationic species on adding alcohol cannot easily explain the decrease in K_d. The formation of AuX_5^{2-} and AuX_6^{3-} complexes in nonaqueous solution has been reported,[14] and the presence of significant amounts of such species in solution would lead to a decrease in K_d, all other things being equal, since these highly charged anions would be more strongly hydrated than AuX_4^-. We have therefore investigated the nature of the species sorbed onto the resin from 2 M aqueous hydrochloric acid ($K_d \approx 10^6$) and from 2 M HCl in 58% aqueous ethanol ($K_d = 9 \times 10^3$), using Raman spectroscopy.[15] The spectra of the two resin samples were identical within experimental error and show only emissions of the square-planar $AuCl_4^-$ ion. Similar results were obtained with Au(III)–HBr. The sorption of species other than MX_4^- onto the resin can therefore be eliminated from the argument for Au(III) exchange.

The association of ions and similar effects caused by the addition of an alcohol to an electrolyte solution are in part the result of the lowering of the dielectric constant of the liquid phase. This may be an important factor in the present work. A second effect, peculiar to ion exchange, can be discussed in terms of the Born equation

$$\Delta G_t = \frac{Z^2e^2}{2r}\left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2}\right)$$

where ΔG_t is the free energy of transfer of an ion of charge Z and radius r from a solvent of dielectric constant ϵ_1 to a solvent of dielectric ϵ_2. For the transfer from aqueous solution (ϵ ~80) to a resin (ϵ ~40),[16] ΔG_t must be positive, but any decrease in ϵ_{aq} will lower ΔG_t and hence also reduce K_d. Both this effect and effects such as ion association depend in some way on the dielectric constant of the solution phase. Figure 3 shows the results for Au(III)–HCl–ROH as a plot of log K_d against $1/\epsilon$. The bulk dielectric constants for 4 M HCl–H_2O–ROH mixtures have not been measured, so that we have been forced to use the results for H_2O–ROH systems.[17] The errors introduced by this procedure are unknown, but the results in Figure 3 suggest that they are systematic, since the points for a given alcohol lie on a smooth plot, and there are only small differences between the effects of different alcohols.

For the strongly complexing gold(III)–chloride system then, K_d is strongly dependent on the dielectric constant of the solution phase. Other interactions, including those arising from structural changes in the solution[18] or changes in the dielectric constant of the resin,[16] either are unimportant in the gold(III) exchange system or are subsumed in the general dielectric argument. It is worth pointing out that since the addition of electrolytes to water also lowers the dielectric constant,[19] the decrease in K_d with increasing hydrochloric acid concentration[2] may also be explained in such terms.

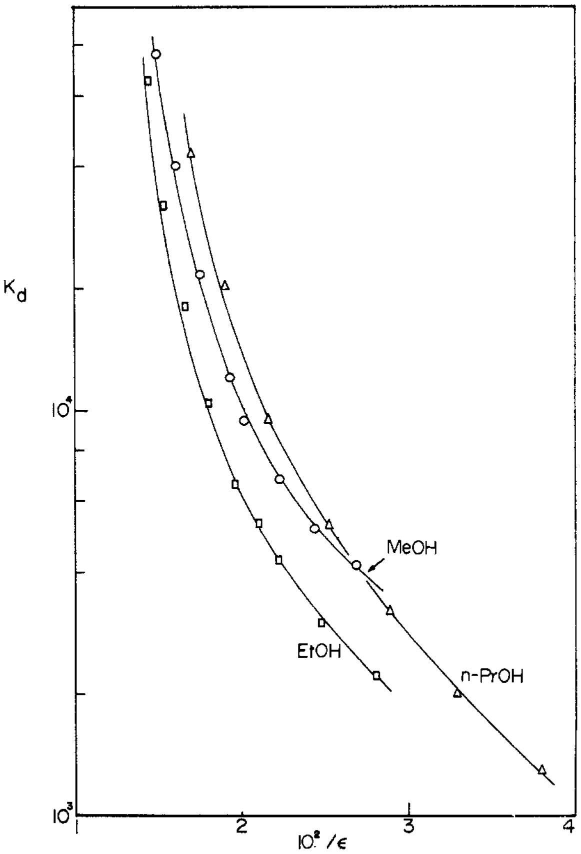

Figure 3.—Data from Figure 1 replotted as a function of the reciprocal of the (estimated) dielectric constant.

Indium(III) Systems.—Experiments with indium(III) were carried out in aqueous hydrochloric, hydrobromic, and hydriodic acid systems and with methanol, ethanol, 1-propanol, 1-butanol, or acetone as the added organic solvent.

The results are shown in Figure 4 in terms of the acid dependence of K_d for the three hydrohalic acids. The curve for hydrochloric acid is in good agreement with that given by Kraus and Nelson[2] for Dowex 1. The increase in K_d in the order I > Br > Cl is that found for the amine extraction of anionic indium complexes[8] and for extraction into basic oxygenated solvents,[20] which has been explained on the basis of the size of the anionic complex, and effect of this on the structure of the aqueous phase.[19,21]

The effect of adding organic solvent to the aqueous phase is shown in Figures 5–7 for hydrochloric acid, in Figures 8–10 for hydrobromic acid, and in Figures 11–13 for hydriodic acid. The common features of these curves follow.

(a) Addition of organic solvent causes an initial increase in K_d in all cases except 4.0 M hydriodic acid

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(14) C. M. Harris and I. H. Reece, *Nature (London)*, **182**, 1665 (1958).

(15) P. Dobud, D. Sutton, and D. G. Tuck, *Can. J. Chem.* in press.

(16) Reference 5, p 296.

(17) "Landolt-Bornstein Tabellen," Vol. 2, Part 6, Springer-Verlag, Berlin, 1969, p 751.

(18) F. Franks and D. J. G. Ives, *Quart. Rev. Chem. Soc.*, **20**, 1 (1966).

(19) J. B. Hasted, D. M. Riston, and C. H. Collie, *J. Chem. Phys.*, **16**, 1 (1948); G. H. Haggis, J. B. Hasted, and T. J. Buchanan, *ibid.*, **20**, 1452 (1952).

(20) H. M. Irving and F. J. C. Rossotti, *J. Chem. Soc.*, 1946 (1955).

(21) R. M. Diamond and D. G. Tuck, *Progr. Inorg. Chem.*, **2**, 109 (1960)

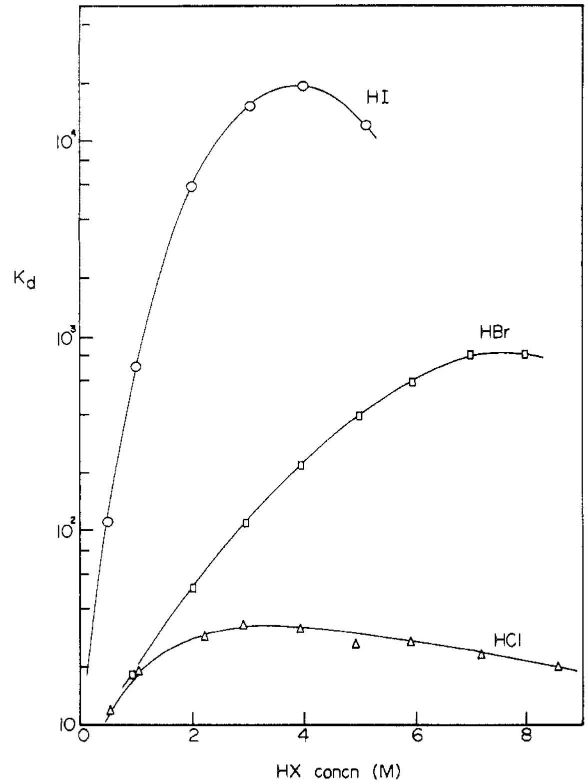

Figure 4.—Effect of acid concentration on K_d for sorption of indium(III) on Dowex 1-X8 from aqueous hydrohalic acid solution.

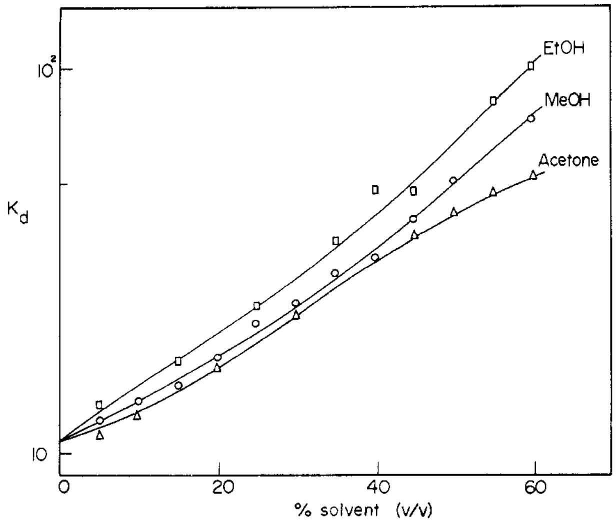

Figure 5.—Effect of added nonaqueous solvents on K_d for sorption of In(III) on Dowex 1-X8 from 1 *M* hydrochloric acid solution. The results for n-C_3H_7OH lie between those for CH_3OH and C_2H_5OH and have been omitted for clarity.

(Figure 13), for which the results are not unlike those for the Au(III)–HCl system.

(b) For hydrobromic and hydriodic acid systems, again with the exception of 4.0 *M* HI, K_d goes through a maximum with increasing nonaqueous solvent concentration. This maximum is not seen in the hydrochloric acid–alcohol systems but does appear when acetone is the added solvent. For a given solvent, and similar acid concentrations, the maximum appears in the order HCl < HBr < HI. For a given acid and a given solvent, the maximum appears at lower solvent concentrations as the acid concentration is increased.

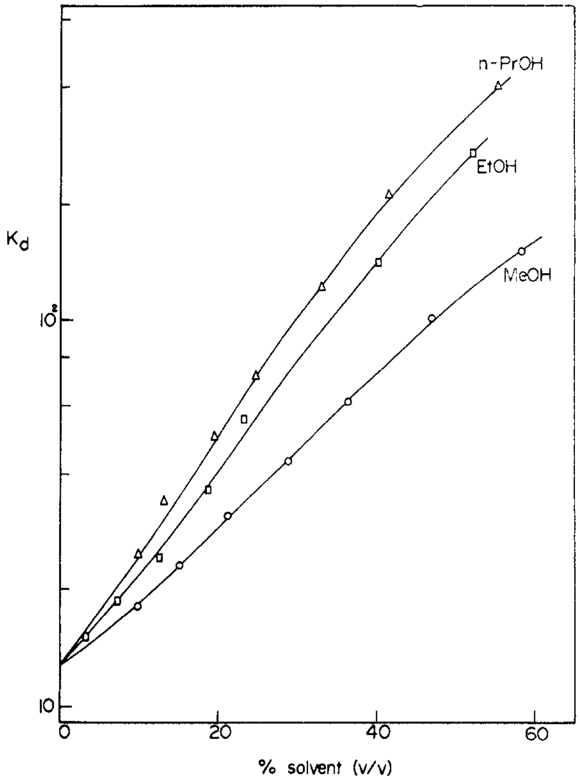

Figure 6—Effect of added nonaqueous solvents on K_d for sorption of In(III) on Amberlite IRA-400 from 3.5 *M* hydrochloric acid solution.

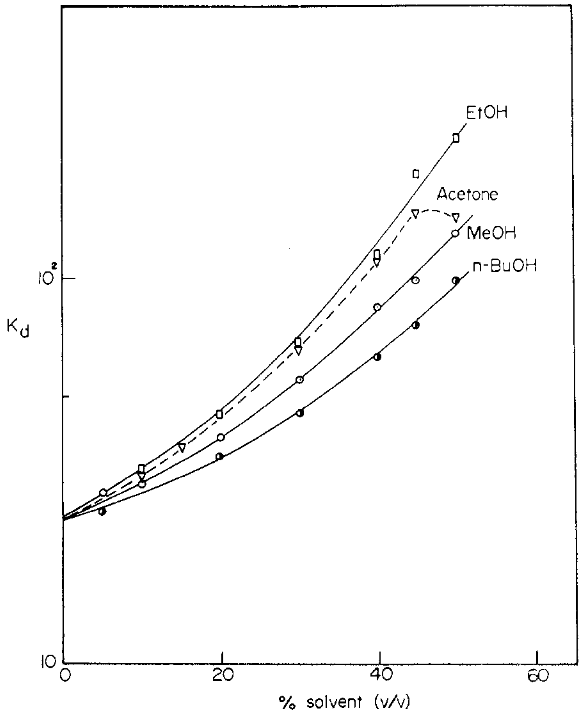

Figure 7.—Effect of added nonaqueous solvents on K_d for sorption of In(III) on Dowex 1-X8 hydrochloric acid solution. The results for n-C_3H_7OH lie between those for CH_3OH and C_2H_5OH and have been omitted for clarity.

(c) For a given nonaqueous solvent, the order HI >

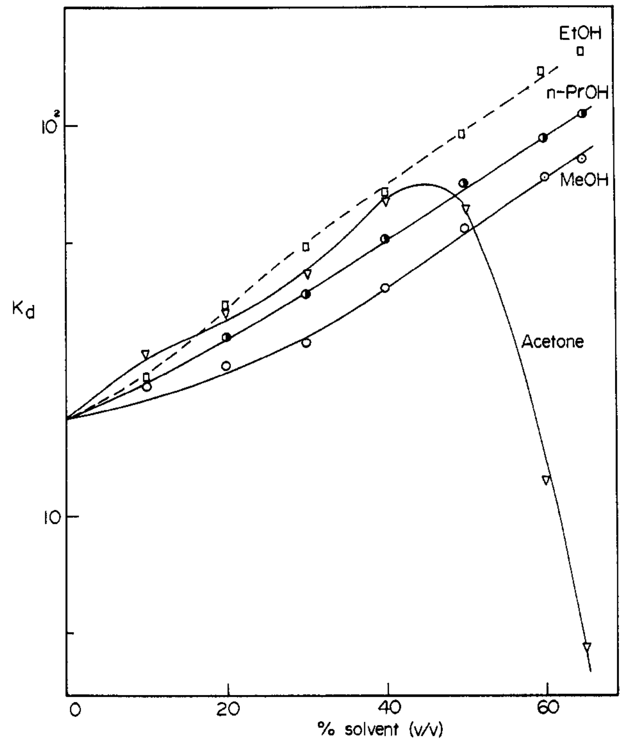

Figure 8.—Effect of added nonaqueous solvents on K_d for sorption of In(III) on Dowex 1-X8 from 1 *M* hydrobromic acid solution.

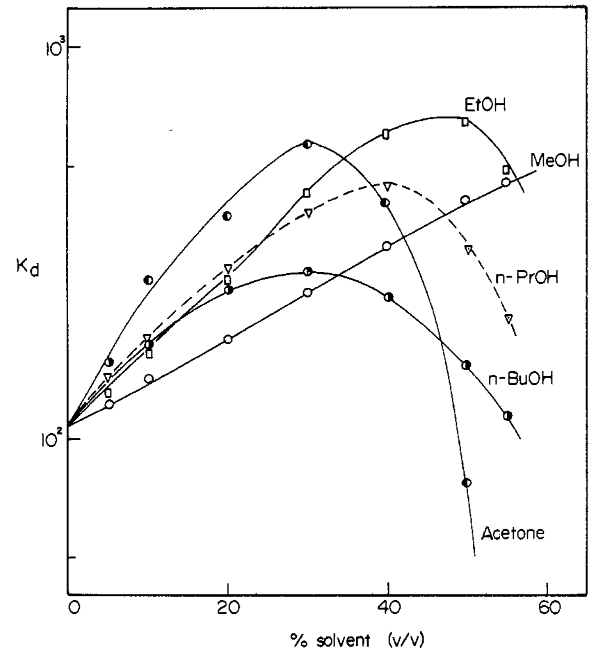

Figure 9.—Effect of added nonaqueous solvents on K_d for sorption of In(III) on Dowex 1-X8 from 3 *M* hydrobromic acid solution.

HBr > HCl for K_d persists in the regions of increasing K_d.

(d) For a given acid, and acid concentration, the maximum appears in the concentration order n-$C_4H_9OH < C_2H_5OH < CH_3OH$. Acetone is roughly equivalent to propanol in this respect.

The first conclusion which can be drawn is that, whatever the species sorbed onto the resin, the order

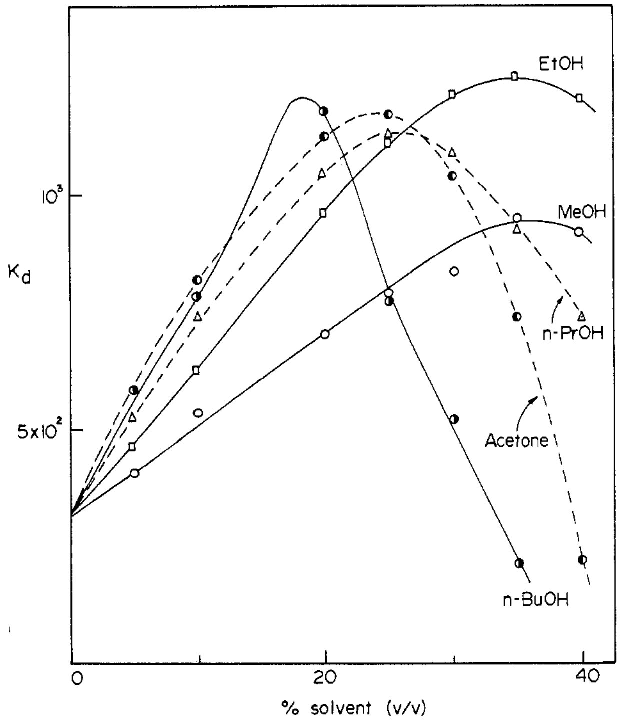

Figure 10. Effect of added nonqaueous solvents on K_d for sorption of In(III) on Dowex 1-X8 from 5 *M* hydrobromic acid solution.

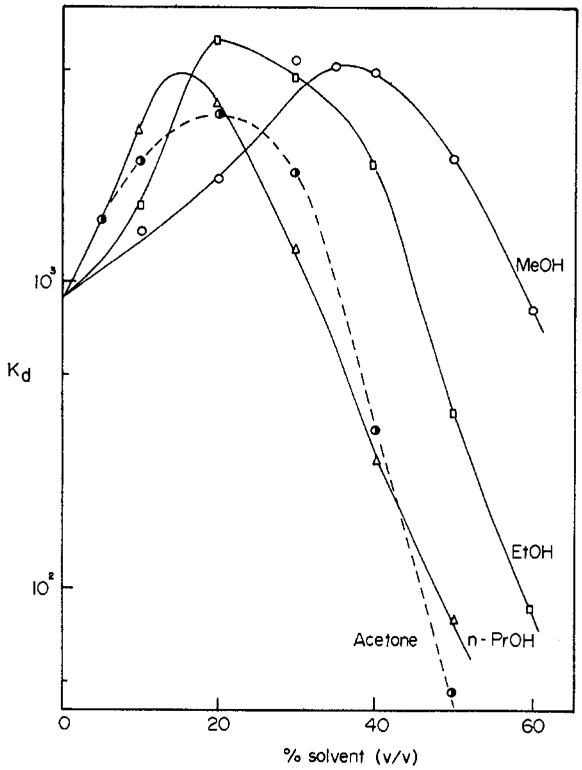

Figure 11.—Effect of added nonaqueous solvents on K_d for sorption of In(III) on Dowex 1-X8 from 1.10 *M* hydriodic acid solution.

I > Br > Cl applies to all acidities and is independent of the added solvent. It therefore seems reasonable to assume that the species sorbed on the resin phase is not changed by the addition of organic solvent to the solution phase. This has been confirmed by Raman studies.

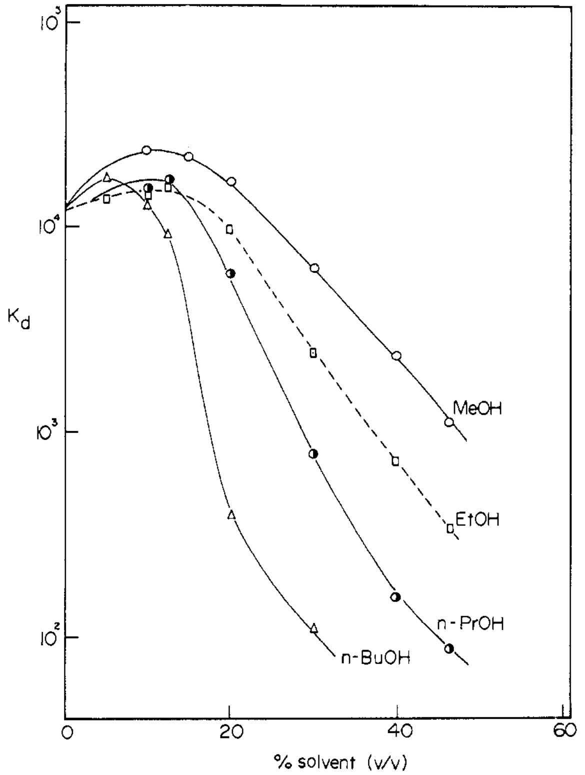

Figure 12.—Effect of added nonaqueous solvents on K_d for sorption of In(III) on Dowex 1-X8 from 3 *M* hydriodic acid solution. The results for acetone are close to those for n-C_3H_7OH and have been omitted for clarity.

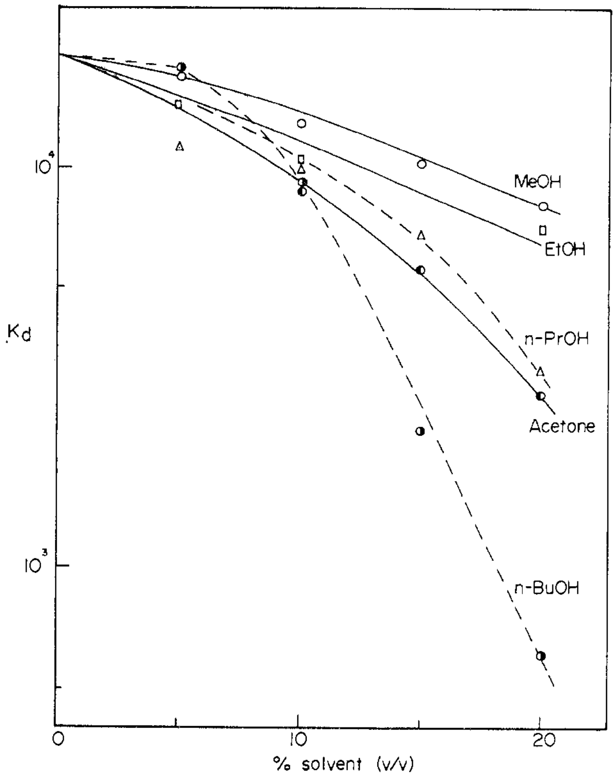

Figure 13.—Effect of added nonaqueous solvents on K_d for sorption of In(III) on Dowex 1-X8 from 4 *M* hydriodic acid solution.

No spectra could be recorded in the In(III)–HCl case, because of the background emission from the resin,[15] but with both bromide and iodide, the characteristic spectrum of the tetrahedral InX_4^- species was observed. The presence of added ethanol in the system during equilibration did not cause significant changes in the Raman spectrum of the resin in the In(III)–HI case. The effects of adding organic solvents are therefore not due to any detectable change in the composition of the sorbed species.

The results for gold(III) show a decrease in K_d on adding organic solvent, related to changes in dielectric constant, but this explanation will clearly not suffice for indium(III). Indeed, it seems that the observed changes in K_d must override those decreases in K_d due to changes in dielectric constant.

We believe that the present results are explicable in terms of the equilibria proposed from earlier solvent extraction work[19]

$$\begin{tikzcd}
\mathrm{InX_4(H_2O)_2^-} \arrow[r, shift left] \arrow[d, shift left] & \mathrm{InX_4^-} + 2\mathrm{H_2O} \arrow[l, shift left] & (1) \\
\mathrm{InX_5(H_2O)^{2-}} \arrow[u, shift left, "\mathrm{X^-}"] \arrow[r, shift left] \arrow[d, shift left] & \mathrm{InX_5^{2-}} + \mathrm{H_2O} \arrow[l, shift left] & (2) \\
\mathrm{InX_6^{3-}} \arrow[u, shift left, "\mathrm{X^-}"] & &
\end{tikzcd}$$

The order of electrostatic hydration energies for the various anionic halo complexes will be $InX_4^- < InX_5^{2-} < InX_6^{3-}$. The aquo complexes will be solvated by virtue of both the electrostatic hydration and the hydrogen bonding of water molecules to the ligand water. The species preferentially sorbed onto the resin should therefore be InX_4^-, as is found spectroscopically. The addition of hydrophilic organic solvents to aqueous solutions reduces the water activity,[22] so that equilibria such as (1) will move to the right, generating InX_4^- species and hence increasing K_d. Activity coefficient data for water in solutions studied are not available, but for water–alcohol mixtures, a_w at a given H_2O:ROH ratio increases in the order $CH_3OH < C_2H_5OH < C_3H_7OH$.[23]

Raman studies of solutions of indium(III) in aqueous hydrohalic acids confirm the reality of these changes. Woodward and his coworkers[24] have shown that $InCl_4^-$ cannot be detected in aqueous hydrochloric acid solutions of In(III), even when the solution is saturated with gaseous hydrochloric acid.[24c] For the bromide case, $InBr_4^-$ is not present in appreciable concentrations up to 6 *M* acid.[24a] In 4 *M* hydriodic acid, InI_4^- is the predominant indium(III) species.[24b] In all three systems, the only species found in the extract organic phase (ether or ketone) is InX_4^-. Hanson and Plane[25] have recently reexamined the indium(III) chloride and bromide systems in more detail. No $InBr_4^-$ was detected, up to 0.86 *M* Br^- (Br:In ratio 7.00). With indium and chloride, an anionic complex with In:Cl 1:4 is observed, but this species is not

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(22) J. R. V. Butler, D. W. Thompson, and W. H. Maclennan, *J. Chem. Soc.*, 674 (1933).

(23) C. W. Davies and J. J. Thomas, *ibid.*, 160 (1952).

(24) (a) L. A Woodward and P. T. Bill, *ibid.*, 1699 (1955); (b) L. A. Woodward and G. H. Singer, *ibid.*, 716 (1958); (c) L. A. Woodward and M. J. Taylor, *ibid.*, 4473 (1960).

(25) M. P. Hanson and R. A. Plane, *Inorg. Chem.*, **8**, 746 (1969).

tetrahedral $InCl_4^-$. On adding methanol to the solution, however, the spectrum of $InCl_4^-$ appears, in agreement with the discussion of eq 1 above. The addition of perchloric acid has the same effect, and presumably this is also due to a lowering of a_w.

This evidence supports the view that adding a hydrophilic organic solvent in anion-exchange systems increases the concentration of InX_4^- by dehydration of $InX_4(H_2O)_2^-$ and hence increases K_d. This explains the initial increase in K_d seen in Figures 5–12. A competing effect must be the lowering of the solution-phase dielectric constant (*cf.* the results for Au(III)), and the presence of maxima in Figures 8–12 suggests that at high solvent concentrations the decrease in ϵ becomes predominant; possibly the indium is effectively all present as InX_4^- in these regions. The experiments at 4 *M* hydriodic acid show only a decrease in K_d with added solvent (Figure 13); since InI_4^- is already the main indium species in such solutions, addition of solvent can only affect the dielectric constant, causing K_d to fall. [We are grateful to a referee for pointing out that decreases in K_d at high solvent concentrations may also be due to the formation of $InX_4(ROH)_2^-$ species, which could be strongly solvated in the solution phase.] Conversely, in hydrochloric acid solutions (Figures 5–7), alcohols apparently do not cause complete formation of $InCl_4^-$ at any of the concentrations studied, and no maximum appears. The anion-exchange results therefore confirm earlier views on the indium(III) species present in aqueous hydrohalic acid solutions.

It should also be noted that for similar HX concentrations and with a given solvent, the concentration of exchangeable InX_4^- species is increased in the order HI > HBr > HCl. This is in keeping with previous arguments[8] that process 1 occurs in this order, which has been explained in terms of easier formation of four-coordinate indium(III) species with "soft" ligands. The stability of $InCl_4(H_2O)_2^-$, with six "hard" ligands, toward dehydration is consistent with this view.[26]

Gallium(III) Chloride Studies.—We have studied the effect of methanol and ethanol on the anion exchange of gallium(III) from aqueous hydrochloric acid. The results for these two alcohols are very similar (Figure 14), and as with indium(III), K_d increases with increasing alcohol concentration over the whole range studied; the rise in K_d is more pronounced than in the comparable indium(III) situation (Figure 6).

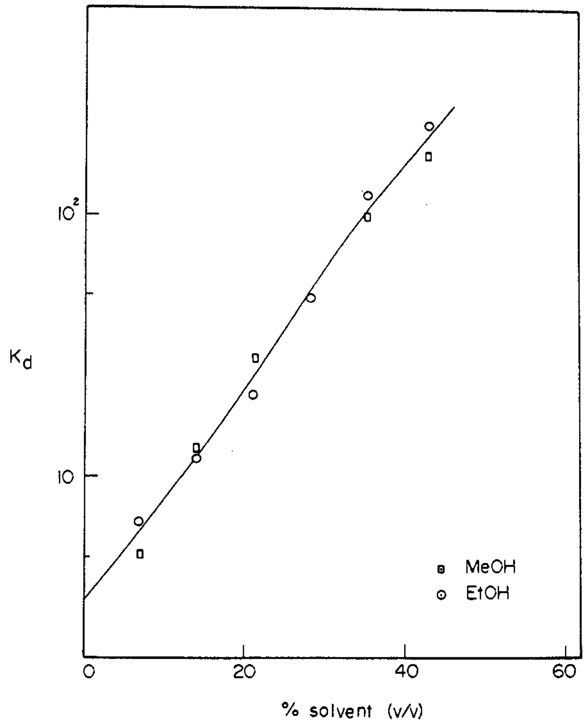

Figure 14.—Effect of added ethanol on K_d for sorption of gallium(III) on Amberlite IRA-400 from 3 *M* hydrochloric acid solution.

Raman studies show that in 6.3 *M* aqueous hydrochloric acid, the anion $GaCl_4^-$ is present.[27] The formation of this ion has also been confirmed by nmr studies.[28] The addition of acetone causes an increase in the concentration of $GaCl_4^-$. There is insufficient experimental information from the present studies to justify a detailed discussion, but it is clear that here again the addition of alcohols causes an increase in K_d by enhancing the solution-phase concentration of the exchangeable $GaCl_4^-$ anion.

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