Solvation of Extracted Complex Metal Acids. I. The $HFeCl_4$–, $HFeBr_4$–, and $HInBr_4$–Nitrobenzene Systems[1]

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Abstract: The effects of nitrobenzene and metal and acid concentrations on the distribution of Fe(III) and In(III) between aqueous HCl or HBr and benzene solutions of nitrobenzene have been studied. The amount of water coextracting with the metal species was also determined. It was found that the extracted $H_9O_4^+ \cdot MX_4^-$ undergoes extensive ion-pair dissociation, even at relatively low nitrobenzene concentrations; the nitrobenzene solvation numbers for this species are 12 at high nitrobenzene concentrations and 6 at low concentrations. The results also demonstrate the dominant role played by a polar solvent in the ionization process and emphasize the relative unimportance of the bulk dielectric constant on the behavior of ions in the presence of a highly polar substance.

It is well known that many trivalent metals, *e.g.*, Fe(III), In(III), Ga(III), Au(III), etc., can be efficiently extracted from aqueous HCl or HBr solutions, even by such weakly basic organic solvents as the ethers and nitrobenzene; a notable exception is In(III) from HCl.[3–8] There is little doubt that the extracting species are, in all cases, the strong acids HMX_4 which are both hydrated and solvated in the organic phase. It is also generally accepted that there is no primary solvation or hydration of the metal anions which are tetrahedrally surrounded by halide ions[9,10] and assumed to be saturated.[4]

Diamond and co-workers,[11–14] in particular, have emphasized the idea that these extraction systems (which involve acids with very weakly basic, singly charged large anions) are best described in terms of a competition between water and the extractant for solvating the proton. They further point out that this picture applies not only to the complex metal acids but also to such strong acids as $HClO_4$ and $HReO_4$.

This comparison should be made with some caution, however. The distribution ratio for, *e.g.*, 10^{-4} *M* $HClO_4$ between 6 *M* HCl and nitrobenzene is less than that for Ga(III) under exactly the same conditions (*i.e.*, at an equilibrium aqueous metal concentration of 10^{-4} *M* in 6*M* HCl) by a factor of about $10^{-2.5}$; it is, in fact, almost the same as that for In(III) under identical circumstances.[15] In the case of In(III), the poor extraction is probably due to the lack of formation of the extractable anion $InCl_4^-$ in the aqueous phase;[3,4,10,16] this explanation will not, of course, suffice for the $HClO_4$ system. In this case it may be the result of a greater interaction of the smaller ClO_4^- ion with water (hydration numbers as large as 1.0 have been reported for this anion[17]), but the situation is not completely clear at the present time.

In any event, it appears desirable to group all dilute strong acid, water, basic extractant (less basic than H_2O) extraction systems together to be described by a single model. However, considerably more experimental evidence should be made available to justify this grouping. The purpose of this work is, then, to determine the composition of hydrated and solvated HMX_4 which has been extracted by a very weakly basic organic substance and to study the effects of such things as anion composition, aqueous phase acid concentration (or, rather, water activity), extractant molecular structure, "inert" diluent, and organic phase dissociation of the HMX_4 ion pairs on the solvation and hydration of the extracted acid.

In this paper, the extraction of $HFeCl_4$, $HFeBr_4$, and $HInBr_4$ from aqueous HCl or HBr by mixtures of nitrobenzene in benzene is described. The results not only provide interesting information concerning the high degree of solvation of these extracted acids by nitrobenzene, but also emphasize the necessity of determining whether or not the HMX_4 ion pairs are significantly dissociated in the organic phase before proceeding with the determination of solvation numbers using the dilution technique described by others.[18]

Experimental Section

Reagents. All chemicals were used as purchased without further purification with the following exceptions: Eastman White Label nitrobenzene was vacuum distilled and the middle fraction collected; reagent grade $FeCl_3$ was dissolved in reagent grade HCl, the

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(1) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant No. AF-AFOSR-65-63; presented in part as Paper 85, Division of Physical Chemistry, 149th National Meeting of the American Chemical Society, Detroit, Mich., 1965.

(2) (a) Taken from the thesis of R. L. Erickson, submitted in partial fulfillment of the requirements for the Ph.D. degree at North Dakota State University, Aug 1965; (b) to whom correspondence should be addressed.

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solution neutralized with NH_4OH, and the resulting Fe_2O_3 was dried and used to prepare the Fe(III) stock solutions; reagent grade aqueous HBr was shaken with nitrobenzene to remove any Fe(III) impurity (and, incidently, the yellow-brown color present in the HBr before the treatment with nitrobenzene). When the bromide systems were studied, the ^{59}Fe and ^{114}In tracers, purchased from Oak Ridge National Laboratory as the trivalent chlorides in HCl solution, were converted to the bromides by neutralization with NH_4OH, evaporation to dryness, heating to remove the NH_4Cl, and addition of aqueous HBr to the trace amount of oxides so produced. Approximately 0.15 *M* stock solutions of Fe(III) in either HCl or HBr were prepared by dissolving the Fe_2O_3 in the appropriate concentrated acid. The solutions were analyzed for Fe by the Zimmerman–Reinhard method modified for the bromide systems,[19] and for total acid by titration with standard base to the phenolphthalein endpoint. An approximately 0.15 *M* stock solution of In(III) was prepared by dissolving 10 g of 99.999% pure In metal (A. D. Mackay, Inc.) in hot concentrated HBr. The solution was filtered and analyzed for In(III) gravimetrically and for total acid by titration as before. Series of dilutions of these stock solutions were made to cover the concentration ranges studied. Solutions of nitrobenzene in benzene were prepared by adding a known amount of nitrobenzene to a volumetric flask and bringing it up to volume with Eastman Spectrograde benzene.

Procedure. **(1) Metal Distribution Studies.** All experiments were done at least in duplicate, often in larger numbers. For each measurement, 10 ml of each phase containing the desired concentrations of nitrobenzene, HCl or HBr, metal ion, and metal tracer was placed in a polypropylene centrifuge tube with a snap-cap cover, and the tubes were shaken on a wrist action shaker for at least 1 hr; the bottom ends of the tubes extended into a thermostated water bath at 25.0 ± 0.2°. (It was found that the distribution ratio remained constant after 15 min for all systems studied.) After shaking, phase separation was facilitated by centrifugation and 4-ml aliquots were withdrawn from each phase with a pipet. The γ activity of each sample was determined by counting with a well-type NaI (Tl) scintillation crystal and a single-channel analyzer. The distribution ratio (= ratio of total metal concentration in the organic phase to that in the aqueous phase) was taken as the ratio of the counts per minute in the organic phase to those in the aqueous phase after correction for background radiation. The reproducibility among duplicates was generally better than 10%.

(2) Organic Phase Water Determination. This was done by titration with Karl Fischer reagent. The end point, detected with a Beckman Zeromatic pH meter equipped with a polarizing jumper, was taken as the point where the addition of 1 drop of Karl Fischer reagent caused a change of approximately 200 mv.[20] The procedure employed to determine the water/metal ratio was equilibration of equal volumes of each phase in a separatory funnel at room temperature, followed by centrifugation to assure complete phase separation, and then titration of an aliquot of the organic phase with Mallinckrodt Karl Fischer reagent which had been standardized by titration of samples of ethanol with known water content. For those systems where metal ion was present, sufficient radioactive tracer was also added so that the distribution ratio (and thus the metal concentration in the organic phase) could be simultaneously determined by γ counting as before. The water extracted with metal present minus the amount extracted under identical conditions, except without metal present, was taken as the water associated with the extracted metal complex.

Results

The solvation number, *i.e.*, the number of extractant molecules in the extracted metal complex, is commonly determined by studying the change in the distribution ratio, *E*, upon dilution of the extractant with a second, "inert" solvent while holding the aqueous phase constant.[3,11–14,18,21] The fact that the aqueous phase is not truly constant is usually ignored. That is, the equilibrium aqueous phase metal concentration, C_M, will vary from experiment to experiment depending on *E* as well as on the total amount of metal present. If C_M is sufficiently small, *E* will be independent of C_M even with the higher dielectric constant solvents where the extracted ion pairs undergo extensive dissociation.[6–8] Thus this practice is often, but (as will be shown here) not always, justifiable.

Of course the inertness of the solvent must also be verified. Participation by the solvent in the extracted complex generally results in a distribution ratio larger (or smaller) than that found for either solvent alone[4] (this effect is called synergism). In the nitrobenzene–benzene system here under discussion, *E* for trace metal was studied as a function of nitrobenzene mole fraction over the entire range, 0.1–1.0, at 4, 5, and 6 *M* HCl. *E* increased with increasing nitrobenzene concentration, reaching a maximum for pure nitrobenzene. This indicates synergism to be absent.

Figures 1, 2, and 3 show typical plots of log *E vs.* log C_M for Fe(III) extraction from aqueous HCl, and Fe(III) and In(III) extraction from aqueous HBr into several different nitrobenzene in benzene solutions. In all cases, *E* shows the C_M dependence expected[3,6,22] for solvents of sufficiently high dielectric constant to permit acidic dissociation of the complex metal acid.

Table I summarizes the results of the water extraction studies. Column 4 is the mole ratio of water (in excess of that found when no metal was present) to metal (or H^+) in the organic phase. To obtain this quantity in the Fe(III) systems, a correction, established by Myers, *et al.*,[23] of one-half the number of formula weights of iron present must be added to the apparent number of formula weights of water "found" in order to obtain the correct amount of water present in the system. This correction is presumably due to Fe(III) oxidation of the iodide produced when the Karl Fischer reagent reacts with water.

Table I. Organic Phase Water/HMX_4 Ratios

Metal	Acid, *M*	(Nitrobenzene), *M*	$(H_2O)/(HMX_4)$
Fe(III)	8.00 (HCl)	5.06	3.85
		4.28	4.65
		3.51	4.34
		2.73	3.93
	6.84 (HBr)	5.06	3.98
		4.28	3.94
		3.51	3.92
		2.73	3.66
		1.94	3.42
	6.02 (HBr)	5.06	3.99
		4.28	3.87
In(III)	7.51 (HBr)	5.06	4.11
		4.28	3.69
		3.51	3.47
	6.02 (HBr)	5.06	4.12
		4.28	3.89

Two experiments were performed to ascertain whether or not a similar situation might exist for In(III). Dry $InCl_3$ and a small, known amount of water were titrated in absolute ethanol with Karl Fischer reagent. The water "found" was less than that added by an amount

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(20) (a) J. Mitchell, Jr., and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948; (b) Beckman Application Data Sheet pH-80-MI, Beckman Instruments, Inc., Fullerton, Calif.

(21) A. T. Casey and A. G. Maddock, *Trans. Faraday Soc.*, **58**, 918 (1962).

(22) A. G. Maddock, W. Smulek, and A. J. Tench, *ibid.*, **58**, 923 (1962).

(23) R. J. Meyers, D. E. Metzler, and E. H. Swift, *J. Am. Chem. Soc.*, **72**, 3767 (1950).

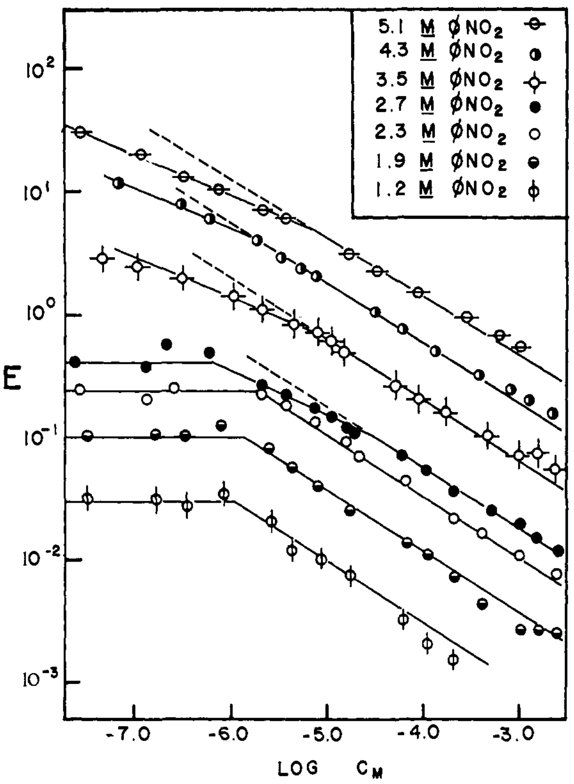

Figure 1. Log–log plot of distribution coefficient *vs.* equilibrium aqueous metal concentration for Fe(III) extraction from 8.00 *M* HCl by nitrobenzene–benzene mixtures.

very nearly equal to the amount of In(III) present (within 6% in each case). For this reason, the numbers in column 4 of Table I for In(III) contain a correction similar to that for Fe(III), except that here the correction is equal to the number of formula weights of In(III) present. Using this correction, the water/H$^+$ ratios agree nicely with those found in the Fe(III) systems and, in addition, are satisfying close to the value of 4.0 which might be expected in these systems where water is the strongest base present.[13] Experimental information concerning the underlying causes of this correction is not known to us; additional work along this line is indicated.

Discussion

Consider the following reaction which defines, thermodynamically, the extraction process.

$$HX + MX_3 + mH_2O + n(C_6H_5NO_2)_o \longrightarrow (H^+ + MX_4^-)_o \cdot m(H_2O)_o \cdot n(C_6H_5NO_2)_o \quad (1)$$

The subscript o refers to the organic phase (no subscript to the aqueous phase), and $C_6H_5NO_2$ represents nitrobenzene, X the halogen, and M the metal. The right-hand side of eq 1 has been written to indicate that the extracted HMX_4 "ion pairs" undergo appreciable acidic dissociation in the organic phase and, further, that an *a priori* assumption of only proton solvation may be misleading here. Under the conditions of constant aqueous phase ionic strength, one may write an equilibrium constant for eq 1

$$K = \frac{(H^+)_o(MX_4^-)_o g_\pm^{\,2}}{C_M[C_6H_5NO_2]_o^{\,n}} \quad (2)$$

where ( ) represents concentration, [ ] represents activity, and $g_\pm$ is the mean ionic activity coefficient in the organic phase. The concentrations of the hydrated and/or solvated organic phase ions are represented by $(H^+)_o$ and $(MX_4^-)_o$ for brevity. The distribution coefficient, *E*, is defined as the ratio of the total metal in the organic phase to that in the aqueous phase, *i.e.*

$$E = \frac{(C_M)_o}{C_M} = \frac{(MX_4^-)_o + (HMX_4)_o}{C_M} \quad (3)$$

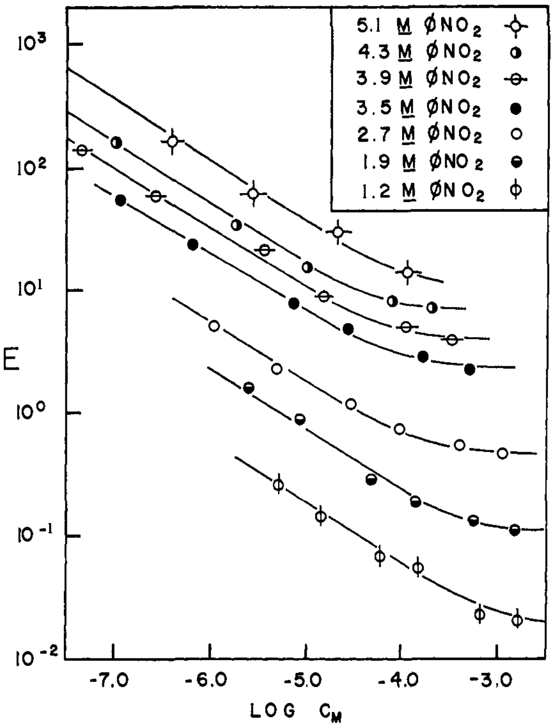

Figure 2. Log–log plot of distribution coefficient *vs.* equilibrium aqueous metal concentration for Fe(III) extraction from 7.97 *M* HBr by nitrobenzene–benzene mixtures.

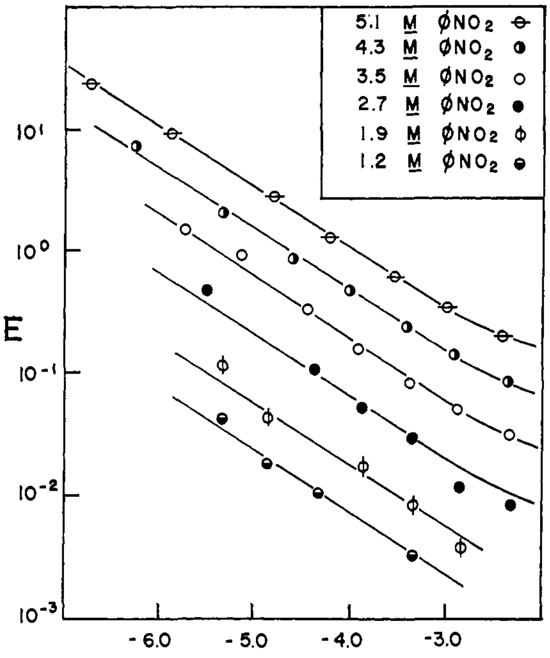

Figure 3. Log–log plot of distribution coefficient *vs.* equilibrium aqueous metal concentration for In(III) extraction from 6.07 *M* HBr by nitrobenzene–benzene mixtures.

or, introducing the degree of dissociation of the HMX_4 ion pairs in the organic phase, α, and substituting in eq 2

$$E = \frac{K[C_6H_5NO_2]_o^n}{g_\pm^2\alpha(H^+)_o} \tag{4}$$

Now, following the general procedure outlined by Saldick[24] and elaborated by Diamond[3] and Poskanzer,[6] we introduce the requirement of electrical neutrality in the organic phase

$$(H^+)_o = (MX_4^-)_o + (X^-)_o \tag{5}$$

and the ion-pair dissociation constant for the organic phase HX

$$(K_{HX})_o = \frac{(H^+)_o(X^-)_o g_\pm^2}{(HX)_o} \tag{6}$$

Solving eq 6 for $(X^-)_o$ and eq 2 for $(MX_4^-)_o$, one may rewrite eq 5 as

$$(H^+)_o = \frac{1}{g_\pm}[KC_M[C_6H_5NO_2]_o^n + K_{HX}(HX)_o]^{1/2} \tag{5'}$$

Finally, α may be eliminated by introducing the ion-pair dissociation constant of $(HMX_4)_o$, $(K_M)_o$

$$(K_M)_o = \frac{\alpha(H^+)_o g_\pm^2}{1 - \alpha} \tag{7}$$

and substituting the equivalent expressions for α and $(H^+)_o$ from eq 7 and 5′ into eq 4 to obtain

$$E = \frac{K[C_6H_5NO_2]_o^n}{(K_M)_o} + \frac{K[C_6H_5NO_2]_o^n}{g_\pm[KC_M[C_6H_5NO_2]_o^n + (K_{HX})_o(HX)_o]^{1/2}} \tag{8}$$

This rather formidable expression of the relationship between E and $[C_6H_5NO_2]$ may be simplified considerably if one operates in the region $10^{-6}\ M < C_M < 10^{-3}\ M$ where, as can be seen from Figures 1–3, $(\partial \log E)/(\partial \log C_M) = -0.5$. In this region, C_M is small enough (and $(K_M)_o$ is large enough in all of the system studied) that the first term in the right-hand side of eq 8 is negligible compared to the second term. Further, since HX is extracted only poorly and is very weakly ionized in nitrobenzene,[7] the term $(K_{HX})_o(C_{HX})_o$ is negligible with respect to $C_MK(C_6H_5NO_2]_o^n$. The solvation number, n, can thus be conveniently determined in this region since here[25]

$$\frac{\partial \log E}{\partial \log [C_6H_5NO_2]} = \frac{n}{2} \tag{9}$$

It can be argued with equal validity that at "trace" metal concentration the term $C_MK[C_6H_5NO_2]_o^n$ should become negligible compared to $(K_{HX})_o(C_{HX})_o$; thus the more familiar relationship

$$\frac{\partial \log E}{\partial \log [C_6H_5NO_2]} = n \tag{10}$$

should prevail at very low metal concentrations. It appears, however, that this situation was never realized in our work. While it is true that Figure 1 shows E becoming independent of C_M when $C_M < 10^{-6}\ M$, the fact that this behavior was found to be limited to those nitrobenzene concentrations, where a significant fraction of the metal present initially remained in the aqueous phase at equilibrium, leads one to suspect that in no case was the initial metal concentration less than *ca.* $10^{-6}\ M$. That is, C_M was calculated on the basis of the amount of $FeCl_3$ added initially to the aqueous phase and no correction was made for either the presence of Fe(III) impurity in the reagent grade HCl or for the amount of Fe(III) carrier in the tracer solution. Both of these contributions can be estimated from analyses furnished by the manufacturers; the HCl made the principal contribution and this was of the order of $10^{-6}\ M$ Fe. Furthermore, if one corrects C_M accordingly, then not only do the flat portions of the curves under discussion disappear, but also those curves in Figure 1 which show regions of "intermediate" slope (between 0 and -0.5) in the vicinity of C_M *ca.* 10^{-5}–$10^{-6}\ M$ become well behaved, and the points follow the dashed lines of slope -0.5 shown.

Finally, if one goes to high metal concentrations, the entire second part of the right-hand side of eq 8 should eventually become negligible, E should become independent of C_M, and eq 10 should also apply. Many of the curves appear to show at least the beginning of such behavior; it is most pronounced in the iron(III) bromide systems. However, in general at high metal concentrations the contribution of the metal to both the aqueous and organic phase ionic strengths is no longer negligible; thus the activity coefficients heretofore neglected become important. For this reason, the remainder of the discussion will be limited to data in the range where E was definitely found to be dependent on $(C_M)^{-1/2}$.

Figures 4 and 5 show plots of log E *vs.* log nitrobenzene vapor pressure[26] for Fe(III) and In(III) extraction at constant C_M. The slopes of the lines are 6.0 at high $(C_6H_5NO_2)$ and 3.0 at low $(C_6H_5NO_2)$ corresponding to values of n, calculated from eq 9, of 12 and 6, respectively. The exact position where the slope begins to decrease is doubtful as is the question of whether or not this point is acid dependent. That is, the magnitude of the experimental errors is such that it is virtually impossible to answer these questions from the data presented here.

It should be pointed out that it is highly unlikely that this decrease in slope is due to extraction by benzene although it was not possible to check this point experimentally. The extraction of metal by pure benzene can be measured and was measured for the iron(III) chloride system over the range from trace metal concentration up to $C_M = 10^{-4}\ M$. E was found to be independent of metal concentration as expected in this low dielectric constant, nonionizing medium and was about 10^{-1} as

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[24] J. Saldick, *J. Phys. Chem.*, **60**, 500 (1956).

[25] The fact that the slopes of the log E *vs.* log C_M curves are all -0.5 within experimental error suggests that $g_\pm$ is essentially independent of the organic phase metal concentration in this concentration range; presumably it is near unity. To estimate $g_\pm$ using the Debye–Hückel or Bjerrum theories would require a knowledge of the dielectric constant in the vicinity of the ions. As will be discussed later, this quantity is probably very different from the bulk dielectric constant of the solvent mixture and remains unknown.

[26] A. R. Martin and C. M. George, *J. Chem. Soc.*, 1413 (1933), served as the source of nitrobenzene vapor pressures above benzene solutions at 70°. Since there is no significant volume change in either phase during the extraction process and since the free nitrobenzene exceeded that involved in the extracted metal complex by a factor of more than 10^3 for all experiments, the wet, trace metal and acid-containing organic phase can be treated to a good approximation as a benzene solution of nitrobenzene only. In addition, it was assumed that the temperature correction to 25° is independent of nitrobenzene concentration, *i.e.*, the data at 70° were used in constructing these plots.

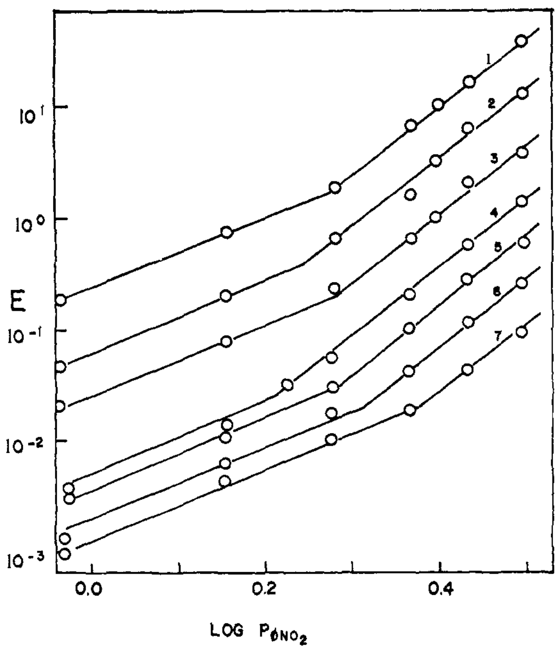

Figure 4. Log–log plot of distribution coefficient *vs.* vapor pressure of nitrobenzene in benzene for Fe(III) extraction from (1) 7.97 M HBr, (2) 6.87 M HBr, (3) 5.99 M HBr, (4) 8.00 M HCl, (5) 6.94 M HCl, (6) 6.04 M HCl, and (7) 4.98 M HCl by nitrobenzene–benzene mixtures. $C_M = 10^{-5}$ M for (1), (2), and (3) and $C_M = 10^{-4}$ M for (4), (5), (6), and (7).

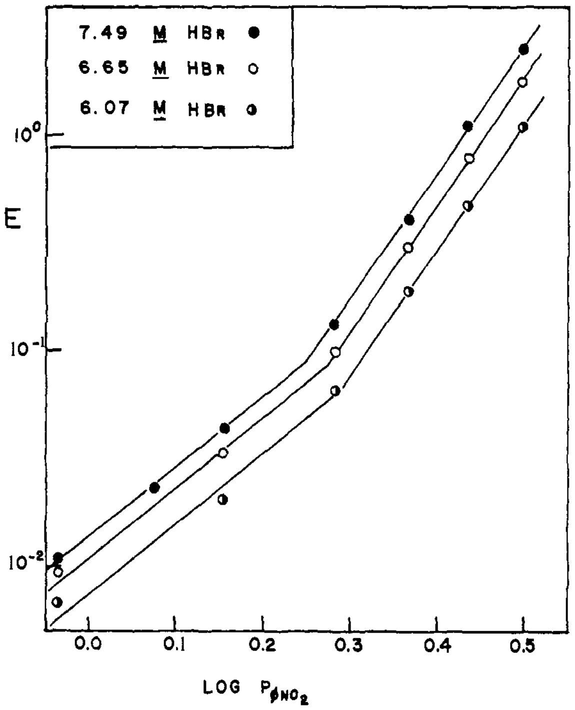

Figure 5. Log–log plot of distribution coefficient *vs.* vapor pressure of nitrobenzene in benzene for In(III) extraction from aqueous HBr by nitrobenzene–benzene mixtures ($C_M = 10^{-4}$ M).

great as E for trace metal extraction into 1.17 M nitrobenzene (the most dilute nitrobenzene solution studied) from the same aqueous HCl concentration (8.0 M). While it is true that the E values in Figures 4 and 5 were obtained at higher metal concentrations (where E is considerably less than the trace metal value), the relationship $(\partial \log E)/(\partial \log C_M) = -0.5$ applies to any system where ion-pair dissociation of the HMX_4 is extensive; that is, the contribution to the total E from benzene extraction will become metal dependent once the ionizing agent nitrobenzene is added to the system. (This was observed experimentally in that E for some of the dilute nitrobenzene–benzene systems at the higher metal concentrations was actually significantly less than that found for the solvent benzene alone.) Thus it may be reasonably assumed that benzene makes a contribution of 10% or less to the total distribution ratios reported for dilute nitrobenzene solutions even at higher values of C_M; this is insufficient to produce the observed slope decrease.

It remains to examine the possibility that K, defined by eq 2, might be affected by changes in the dielectric constant. Although the bulk dielectric constant of our nitrobenzene–benzene extraction mixture must change appreciably over the nitrobenzene concentration range studied, we have ignored any effect of this on K. The justification for this rests on the fact that the dielectric constant in the immediate vicinity of the ions is apparently much greater than in the bulk of the liquid (and hopefully does not vary much with nitrobenzene concentration). This is evidenced both by our observation of essentially complete ion-pair dissociation for $C_M <$ *ca.* 10^{-3} M even in 1 M $C_6H_5NO_2$ solutions where the bulk dielectric constant is only about 4.5[27] and the observations of Maddock and co-workers,[22] who report that the addition of a very small amount of nitrobenzene to a benzene solution of extracted $HFeCl_4$ or $HAuCl_4$, insufficient to alter the bulk dielectric constant of the medium appreciably, results in a considerable increase in the concentration of ionic species. (This is understandable when viewed in the light of work by Gilkerson and Ezell,[28] who emphasize the specific role played by a polar solvent in the ion-pair dissociation process and the relative unimportance of the bulk dielectric constant of the medium.) It seems likely then that any variation in bulk dielectric constant has little effect on K; thus the values of n calculated here do indeed imply that twelve or six nitrobenzene molecules are associated with each HMX_4 at high or low nitrobenzene concentrations, respectively.

The water extraction data in Table I provide evidence that $H_9O_4^+$ is the extracting cation as expected in a system where water is the strongest base present.[13] The small decrease in H_2O/HMX_4 values observed as the molarity of nitrobenzene was decreased remains troublesome; however, the reasons for it are not obvious to us. The fact that there is essentially no tendency for nitrobenzene to displace the four water molecules from the proton is in agreement with other evidence indicating that nitrobenzene possesses only very little, if any, proton-attracting ability.[29]

In the ether systems, where the maximum solvation number reported is three,[30,31] it is generally accepted that only the cation of the ion pair (probably $H_9O_4^+$) receives primary, coordinate solvation[3,4] and that any

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[27] Landolt-Börnstein, "Zahlenwerte und Funktionen," Vol. II, 6th ed, Part 6, Springer-Verlag, Berlin, 1959, p 841.

[28] W. R. Gilkerson and J. B. Ezell, *J. Am. Chem. Soc.*, **87**, 3812 (1965).

[29] W. Gordy, *J. Chem. Phys.*, 7, 93 (1939).

[30] V. V. Fomin, D. L. Zagorets, A. F. Morgunov, and I. I. Tertishnik, *Russ. J. Inorg. Chem.*, 4, 1038 (1959).

[31] A. F. Morgunov and V. V. Fomin, *ibid.*, **8**, 263 (1963).

additional, secondary, electrostatic solvation which may occur is not observable from equilibrium measurements of the type reported here. Nitrobenzene is considerably less basic than the ethers.[29] Thus it is questionable whether it is capable of coordination at all; if so, it undoubtedly does so only with the $H_9O_4^+$. Since this cannot reasonably account for the large values of n in the nitrobenzene systems, it seems likely that here we are observing a more general electrostatic interaction between the polar molecules and the ions as well as (perhaps) coordinate solvation. These two types of binding are presumably indistinguishable (by our techniques) for nitrobenzene. Whether the differences between nitrobenzene and ethers are due to the considerably larger dipole moment or lesser basicity of nitrobenzene, geometry effects, dissociated ions *vs.* ion pairs, anion solvation, or a combination of these, or other effects, is not known at present; further speculation would seem fruitless in view of the lack of structural information for these solvates.

The Effect of Pressure on the Rate of Solvolysis of Benzyl Chloride in Aqueous Ethanol

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Abstract: The high-pressure apparatus and associated conductometric technique for following rates of solvolysis of alkyl halides in ethanol–water mixtures as a function of pressure are described. Results of the redetermination of ΔV_0^* for *t*-butyl chloride in 80% aqueous ethanol are presented to establish the precision and accuracy of the method. The dependence of ΔV_0^* on the composition of the ethanol–water medium for solvolysis of benzyl chloride is reported. ΔV_0^* for this system passes through an extremum at approximately 0.3 mole fraction of ethanol.

The influence of solvent on the kinetics of reactions in solution has been the subject of intensive study for the past 4 decades. Over this period the progressive refinement of the arguments and rationalizations of observed effects has left little doubt that the major impediment to a detailed understanding of the phenomenon is the lack of a definitive description of the liquid state of the solvent system. As a result of these limitations the explanations offered for solvent effects on rate processes have been largely of the empirical type. Relationships between rate and expressions involving bulk dielectric constant[1–6] have been most commonly employed together with linear free energy relationships of the *mY* type as proposed by Winstein, *et al.*[7] The principal objection to the use of these parameters has been that they reflect the bulk properties of the solvent medium, but neglect any specific type of substrate–solvent interaction that may be of more than passing significance in determining solvent effects on the rate process. Recently, spectroscopically determined solvent parameters of the type proposed by Kosower[8] (*Z* values) appear to take better account of such specific interactions, but even in these cases the rate relationships with such parameters are essentially empirical in form.

Notwithstanding the apparent lack of understanding of the specific nature of the substrate–solvent interaction in single component solvent systems, there has recently been a considerable revival of interest in the effect of varying the composition of binary solvent media on the various kinetically measurable rate parameters, ΔH^*, ΔS^*, and ΔC_p^*.[9–13] These pseudo-thermodynamic parameters exhibit an extremum behavior as a function of solvent composition that is not manifest in the directly measurable $\log k$ or ΔF^*. Compensatory effects of ΔH^* and ΔS^* ($\Delta F^* = \Delta H^* - T\Delta S^*$) are generally accepted as the reason for this phenomenon.

The observed extremum behavior of these kinetic parameters in binary solvent systems has been ascribed to a specific interaction between the reacting substrate and the binary solvent environment. Until recently, however, there was no experimental evidence to indicate whether the initial or transition state, or both, of the reacting substrate is primarily influenced by these specific solvent effects since the various Δ parameters measure the *difference* between the initial and transition states. This difference could vary as a result of changes in either the initial or transition state or changes in both. Recently, however, Arnett and co-workers[14,15] have measured "instantaneous" heats of solution of reacting

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