tions[18] which depend on the kinetics of the photosensitized autoxidation of 2-propanol gave even higher values. Wells attributes the large differences between these results and those in more concentrated acid solutions to differences in the acidity of the proton at various stages of hydration.

In conclusion, the following statements about the basicities of aliphatic alcohols can be made.

1. Several kinetic and equilibrium measurements have been reported previously which indicate a pK range of -2.2 to -3.8 in sulfuric acid, in agreement with the Raman work of Deno and Wisotsky.

2. Our results, in contrast to these, suggest a pK of almost -5, in agreement with kinetic results obtained by Gold and co-workers.

3. The earlier Raman results of Deno and Wisotsky can be reinterpreted to indicate that the extent of methanol protonation in all of their solutions was very small.

4. Contrary to optimistic statements by Arnett,[3] who describes the Raman method as producing "unequivocal" results, it seems quite clear that estimates of alcohol protonation obtained by this method differ significantly from several of those obtained by other methods. The Raman method, in principle a very direct one, may still reflect effects other than protonation, such as changes in hydrogen bonding.

The problem of hydrogen bonding, or more generally, of solvent–solute interaction, may well be the key to the lack of agreement between the various experimental measures of alcohol basicity. By their nature, these solutes will be strongly hydrogen-bonded to water molecules. In concentrated acid solutions, when the water concentration is low, there will be a competition between hydrogen bond formation (water–water and water–alcohol) and solvation (ion–water and ion–alcohol). Hence, one might anticipate complex medium effects which need not produce the same dependence on acid concentration for different methods of determining the alcohol basicity.

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Solvation of Extracted Complex Metal Acids. III. The $HFeCl_4$–Diethyl Ether System[1]

David A. Meyers and R. L. McDonald

Contribution from the Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822. *Received July 25, 1966*

Abstract: In an attempt to learn more about the solvation of extracted halometallic acids of the type HMX_4, the effects of acidity, Cl^- concentration, and ether concentration on the distribution of Fe(III) between aqueous HCl or acidified LiCl and diethyl ether–benzene mixtures were studied. The solvation number of the extracted ion pairs is near 4. A comparison of these results with nitrobenzene solvation studies has tempted us to suggest that with very weakly basic extractants one may not, on the basis of available data, definitely reject the possibility that anion (or dipole) solvation might play a significant role in the extraction of acids.

It is well known that many trivalent metals including Fe(III) are extracted from aqueous acid halide solutions by weakly basic solvents, *e.g.*, diethyl ether, as the halometallic acids, HMX_4.[2–7] It is also generally accepted that there is no primary solvation of the metal anion which is tetrahedrally surrounded by halides and assumed to be saturated.[3]

The common method of studying solvation in extraction systems is the so-called dilution technique. This essentially involves following the change in the distribution coefficient as the extractant is diluted with a second inert solvent, all other parameters being held effectively constant. Dilution studies involving strong acids and strongly basic extractants have generally been interpreted in terms of the concept that one may assign all of the observed (coordinately solvating) extractant molecules to the hydrated proton. This, of course, implies that any additional solvation of either ion which might occur is unobservable by the dilution technique. This concept has been used extensively by Diamond and co-workers[8–11] in the interpretation of their studies of strong acid extraction by the more basic (than the ethers) trialkylphosphine oxides and trialkyl phosphates. Recent work with the extremely weakly basic substance nitrobenzene,[12,13]

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however, has led us to postulate that, with nitrobenzene at least, some sort of (probably) noncoordinate, electrostatic interaction between the polar molecules and the ions is playing a significant role in the extraction process and, consequently, that these "electrostatically solvating" molecules are observable in dilution studies. This, we feel, emphasizes the need for the continuation of solvation studies involving extracted acids, particularly in view of the common practice of grouping all dilute strong acid, water, basic extractant extraction systems together to be described by a single model.

In this, the third paper in the series, the extraction of $HFeCl_4$ from aqueous HCl and acidified LiCl by mixtures of diethyl ether in benzene is described. The results provide interesting comparative data concerning the solvation of extracted acids and emphasize the fact that the observable solvation numbers of these acids may vary appreciably with different types of weakly basic extractants (*e.g.*, diethyl ether, nitrobenzene, etc.).

Experimental Section

Reagents. All chemicals were used as purchased without further purification. HCl solutions ranging from 4 to 12 *M* were prepared from reagent grade HCl (Du Pont) and analyzed for acid concentration by titration with standard base to the phenolphthalein end point. Solutions of diethyl ether in benzene were prepared by adding a known amount of Baker reagent grade diethyl ether to a volumetric flask and bringing it up to volume with Eastman Spectrograde benzene; literature values of the densities[14] were used to calculate the mole fractions of the ether in the mixtures. Acidified LiCl solutions were obtained by dissolving Baker reagent grade LiCl in 0.10 *M* HCl; the total chloride in these solutions was determined with standard $AgNO_3$ using K_2CrO_4 as indicator.

Procedure. The metal distribution studies were carried out in duplicate at 25 ± 0.5° as described elsewhere.[12] Except for a few experiments to test the effect of metal concentration on the distribution ratio, all experiments were done at trace metal concentration; *i.e.*, no iron was added except that present in the ^{59}Fe tracer solution purchased either from Oak Ridge National Laboratory or Nuclear Science and Engineering Corp. as Fe(III) in aqueous HCl. The shaking time was 1 hr or longer; an initial check showed the distribution coefficient to be constant after about 15 min.

Results and Discussion

Initial studies with 1.91 *M* diethyl ether in benzene showed the distribution coefficient, E (= ratio of total metal concentration in the organic phase to that in the aqueous phase), to be essentially independent of Fe(III) concentration in 8.14 *M* HCl over the equilibrium aqueous phase Fe(III) concentration range 5.2×10^{-7}–1.7×10^{-3} *M*. This is the expected behavior with low dielectric constant nonionizing organic media.

Results of studies of trace iron distribution between aqueous HCl and $(C_2H_5)_2O$–C_6H_6 mixtures are shown in Figure 1, where log E is plotted against log mole fraction of $(C_2H_5)_2O$ initially present in the organic phase. At the two lowest acid concentrations, the slopes of the straight (solid) line portions of the curves are *ca.* 4.3. The reason for the decrease in slope at low $(C_2H_5)_2O$ concentration is, presumably, that the contribution to E from C_6H_6 extraction becomes appreciable there. At the higher acid concentrations, the $(C_2H_5)_2O$ is extracted into the aqueous phase (as evidenced by appreciable volume changes for each phase), resulting in a decrease in both the organic phase ether and aqueous phase HCl concentrations. This leads to a decrease in slope as the HCl concentration is increased, and finally to an inverse relationship between E and $(C_2H_5)_2O$ concentration. (This is similar to the inverse relationship between E and HCl concentration that has been reported for pure $(C_2H_5)_2O$ extraction of Fe(III) from concentrated HCl.[2])

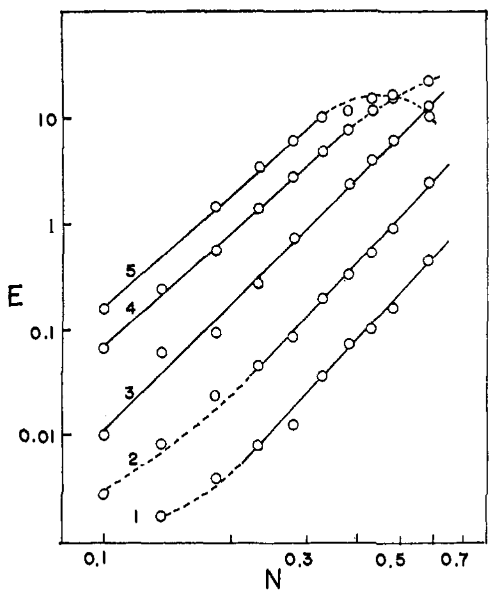

Figure 1. Log–log plot of distribution coefficient *vs.* initial mole fraction of ether for Fe(III) extraction from (1) 5.1 *M* HCl, (2) 6.1 *M* HCl, (3) 6.9 *M* HCl, (4) 8.1 *M* HCl, (5) 9.1 *M* HCl by diethyl ether–benzene mixtures.

If meaningful solvation numbers are to be obtained, it is desirable to find a system where the volume change is negligible for both phases during the extraction. A check showed that this could be achieved by replacing most of the H^+ in the preceding systems with Li^+. For example, there is little or no volume change of either phase when 10 *M* LiCl is shaken with an equal volume of $(C_2H_5)_2O$. In addition, since alkali metal cations have a negligible distribution coefficient compared to H^+,[15] no correction for Li^+ extraction is necessary.

Figure 2 shows plots of log E *vs.* log mole fraction of $(C_2H_5)_2O$ for trace iron extraction from acidified LiCl solution by $(C_2H_5)_2O$–C_6H_6 mixtures. The slopes of the straight (solid) line portions, obtained by a least-squares analysis of the data giving each point equal weight, are 4.26, 4.27, 4.31, 4.36, and 3.90 for curves 1–5 in that order. As has been pointed out elsewhere,[8–12] the slope of these lines may be taken as the number of ether molecules associated with each $HFeCl_4$, provided that there is no gross nonlinearity of the ether activity (with concentration) over the concentration span studied. For $(C_2H_5)_2O$–C_6H_6 mixtures, since both components adhere closely to Raoult's law over the entire composition range,[16] the activity of the ether is proportional to its mole fraction in solution. Further, the volume change during extrac-

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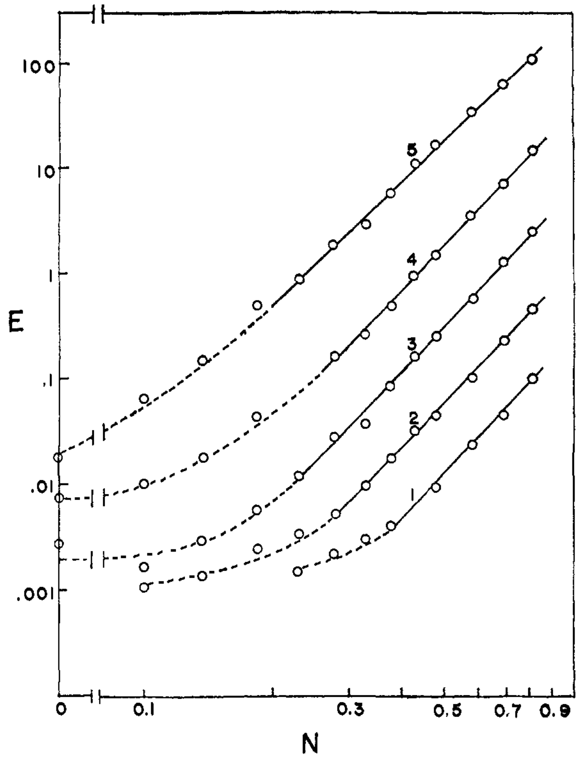

Figure 2. Log–log plot of distribution coefficient *vs.* initial mole fraction of ether for Fe(III) extraction from acidified (1) 5 *M* LiCl, (2) 6 *M* LiCl, (3) 7 *M* LiCl, (4) 8 *M* LiCl, (5) 9.4 *M* LiCl by diethyl ether–benzene mixtures.

tion is very small; thus one may reasonably assume that the wet, trace metal containing organic phase behaves as essentially a solution of $(C_2H_5)_2O$ in C_6H_6 and, therefore, that the numbers reported above are meaningful.

It appears, then that the average solvation number of $HFeCl_4$ (by$(C_2H_5)_2O$) is near 4. Whether the nonintegral values are due to mixtures of solvates or to experimental errors and/or small deviations from Raoult's law because of the presence of water and HCl is a difficult question to answer. What we feel is more important is the fact that the solvation number is without doubt greater than 3. This latter value has been most commonly found for strong acid solvation by a variety of basic solvents,[8–11,17,18] nitrobenzene being the major exception.[12] The lack of sensitivity of the solvation number to anion composition led Diamond to postulate that three solvent molecules are associated with the hydrated proton, and he has proposed the following structure for this solvated cation: $H_3O^+ \cdot 3(\text{extractant}) \cdot yH_2O$, where y varies from 0 to 3 depending upon the basic strength of the extractant relative to water.[8–11]

The amount of water coextracting with $HFeCl_4$ into ethers has been the subject of several studies. With bis(2-chloroethyl) ether, 4.5 molecules of water per metal was found,[19] and, with diisopropyl ether, the value 5 was reported[20] although Fomin and Morgunov[21] have claimed smaller values (3–4) for ethyl, butyl, and isoamyl ethers. In any event, it appears likely that y is near 3 in ether systems. This is to be expected. y has been found to decrease with increasing extractant basicity from 3 with nitrobenzene[12] and Dibutyl Cellosolve[22] to 0 with trioctylphosphine oxide;[11] this parallels the increasing ability of the extractant to displace water molecules from $H_3O^+(H_2O)_3$. Since the ethers are very weak bases indeed, it is not surprising that they do not succeed in the competition for the H_3O^+.

It seems probable then, that the extracted species is $H_3O^+(H_2O)_3 \cdot FeCl_4^-$, further solvated by ether and perhaps, water) molecules. The question now arises as to how to assign the ether molecules to the ions. It is not impossible that they are all attached to the cation. However, in recent work with nitrobenzene we have found: (1) nitrobenzene solvation numbers as high as 12 for the dissociated ions $H_9O_4^+$, $FeCl_4^-$; $H_9O_4^+$, $FeBr_4^-$ and $H_9O_4^+$, $InBr_4^-$;[12] (2) the ion pair $R_3NHFeCl_4$ (R = tri-*n*-octyl) is solvated by four more molecules of nitrobenzene than is R_3NHCl in benzene–nitrobenzene mixtures.[13] While neither of these observations conclusively proves observable anion solvation, they make us unwilling to categorically reject any possibility of it. For this reason, we hesitate to assign all of the extractant molecules to the cation as is usually done. A meaningful discussion of the structures of these solvates, if indeed definite structures do exist, must await further work.

The fact that E is independent of metal concentration indicates that the hydrated, solvated $HFeCl_4$ exists principally as an ion pair[2,12] in ether–benzene mixtures. This is in contrast to the situation in nitrobenzene–benzene mixtures where essentially complete dissociation (at metal concentrations below *ca.* 10^{-3} *M*) was observed,[12] even down to nitrobenzene concentrations where the bulk dielectric constant of the organic phase was comparable to that of diethyl ether. This immediately raises the question of the effect of ion-pair dissociation on the solvation number. Since the process of ionization must necessarily involve solvation of the ions, it is not improbable that ion-pair formation–dissociation may directly affect the observable solvation number. However, there is very little information in the literature, at present, which might be used to help support or reject this suggestion. While the few experiments of Morgunov and Fomin[23] suggest that dissociation may not affect the degree of solvation, these authors themselves point out that this requires further investigation. Continuing work in our laboratories with higher dielectric constant ethers may provide additional useful information concerning this point.

Finally a comparison of our results with other ether solvation studies is in order. Fomin, *et al.*,[21] reported that $HFeCl_4$, extracted from HCl, formed a trisolvate with dibutyl ether in benzene solution. However, Morgunov and Fomin[23] stated in a later paper that (apparently) the same data could be in-

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terpreted in terms of a mixture of di- and trisolvates; the reasons for this discrepancy are not clear to us. These latter authors have also, on the basis on rather limited data, suggested that $HFeCl_4$ forms a tetrasolvate with diisopropyl ether and perhaps a mixture of di- and trisolvates with diisoamyl ether (at least, the slope of the log *E vs.* log ether concentration plot was 2.5).[24] This suggests that the solvation number decreases as the length of the hydrocarbon chains on the ether increase, but more data should be made available before any real attempt is made to correlate these two factors.

To summarize, our work emphasizes the fact that observable solvation of strong acids by weakly basic organic substances does not necessarily involve three molecules of the base. We further suggest that, while solvation of the hydrated proton is undoubtedly important to the extraction process, the possibility of observable solvation of the anion (or, perhaps, solvation of the dipole (ion pair) as an entity) cannot be definitely rejected, at least with the very weakly basic extractants.

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The Electrical Double Layer in Dimethyl Sulfoxide Solutions

Richard Payne

Contribution from the Air Force Cambridge Research Laboratories, L. G. Hanscom Field, Bedford, Massachusetts. *Received October 4, 1966*

Abstract: Electrocapillary curves and double-layer capacities have been measured for a number of solutions of inorganic electrolytes in dimethyl sulfoxide (DMSO) and mixtures of DMSO with water. There is a strong resemblance between the behavior of DMSO and aqueous solutions. Thus anions are specifically adsorbed from DMSO solutions in the order $I^- > Br^- > Cl^- > NO_3^- > ClO_4^- > PF_6^-$, whereas cations are not significantly adsorbed. The electrocapillary maximum (ecm) is shifted in the positive direction in DMSO as compared with water, and a large hump appears close to the limit of anodic polarization in solutions where the anion is not strongly adsorbed. The influence of the diffuse layer capacity is more marked in DMSO solutions as expected in view of the lower dielectric constant. The effect of the diffuse layer capacity at the ecm vanishes for 0.1 *M* KPF_6 in DMSO–water mixtures containing ~30 mole % of DMSO. The interfacial tension at the ecm is lower by ~60 dynes/cm in DMSO than in water. These results are discussed critically in terms of current theories of the double-layer structure.

The importance of dimethyl sulfoxide (DMSO) as an ionizing solvent has been recognized for some time although few results of electrochemical measurements have been reported. The study of this solvent system has recently received considerable stimulus in the United States as a result of intensive efforts to develop novel types of batteries employing couples of high specific energy density in DMSO and similar high dielectric constant aprotic solvents.[1] The need for basic thermodynamic and electrochemical data in these solvent systems is therefore firmly established. Furthermore, such data are of considerable theoretical interest. This is especially true in the area of the electrode-solution double layer. In this paper, therefore, an attempt is made to give a broad description of the electrocapillary properties of the mercury–DMSO interface. No attempt is made at a detailed analysis of the data, which indeed is not possible in the absence of thermodynamic data. Nevertheless, certain generalizations can be made which have a direct bearing on double-layer theory and the more general area of electrode reactions in DMSO solutions.

Experimental Section

The double-layer capacity at a growing mercury drop was measured with a precision of 0.1% using an ac bridge technique similar to that described previously.[2] General Radio components were used as the bridge elements. A 4-decade capacitor (Type 1423A) giving a range of 100 pf to 1.111 μf ± 0.05% was used as the capacitance standard. The resistance was measured by a 6-decade resistor (Type 1432-X) giving increments of 0.1 ohm. Variable ratio arms were constructed from two pairs of single-decade resistors (Types 510D and E) mounted in a shielding aluminum box. The oscillator (GR Type 1304B) and the detector circuits were isolated from the bridge by screened transformers (Type 578A). All connections were made with coaxial cable with the braiding connected at both ends to the component shields. The performance of the bridge at low signal levels was improved by the use of a tuned amplifier (GR Type 1232A) in the output circuit. The output was displayed on a Hewlett-Packard oscilloscope (Type 130C). Timing of the drop growth was achieved by use of a Hewlett-Packard preset decade counter (Type 5214L) giving a timed interval of up to 100 sec in 100-μsec increments with an accuracy of 0.001%. The electrode potential was measured with a precision of 0.1 mv using a Honeywell potentiometer (Type 2781), galvanometer (Type 3134), and constant current power supply (Type 2798-1). Measurements were carried out in a water thermostat controlled to 0.01°. The signal frequency in all the measurements reported was 1 kc.

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