

Spectrophotometric Studies of Iron(III) Chloride in Nonaqueous Solvents

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Contribution from the William A. Noyes Laboratory, University of Illinois, Urbana, Illinois. Received December 4, 1964

By studying the ultraviolet spectra of mixtures of $FeS_6(CIO_4)_3$ (where S is the solvent) and $(C_2H_5)_4NCl$ at different mole ratios, we have been able to determine the principal species present when a small amount of iron(III) chloride is dissolved in methanol, *N*-methylacetamide, or dimethyl sulfoxide. Dichloro- and monochloroiron(III) complexes exist in methanol, monochloroiron(III) is the predominant species in dimethyl sulfoxide, and $Fe-(CH_3CONHCH_3)_6^{+3}$ is formed in *N*-methylacetamide. These results are interpreted in terms of the donor strength and solvating ability of the solvent. Means of estimating these properties are discussed.

Introduction

In previous studies of iron(III) chloride in phosphorus oxychloride, triethyl phosphate,² and *N,N*-dimethylacetamide³ (DMA), it was proposed that the species existing in solution could be accounted for by consideration of the solvent displacement of chloride ion from the coordination sphere of iron(III). In order to distinguish this approach to nonaqueous solvent chemistry in oxyhalide solvents from that of the solvent system concept, the term coordination model was proposed.

In order to gain some appreciation for the importance of the various solvent properties predicted to be of importance by the coordination model, the species which exist when iron(III) chloride is dissolved in a series of different solvents were studied and correlated with empirical measures of solvent donor and solvating abilities. The solvents dimethyl sulfoxide (DMSO), methanol (CH_3OH), and *N*-methylacetamide (NMA) were investigated in this study. The species present were determined by studying the ultraviolet spectra of the systems $FeS_6^{+3}-Cl^-$ (where S is the solvents) as a function of added chloride in the manner previously described for *N,N*-dimethylacetamide.³

Experimental

Apparatus. Ultraviolet absorption spectra were obtained on a Beckman Model DU spectrophotometer. Matched, quartz cells of 1.0-cm. path length were used. The solvent was placed in the reference cell.

Reagents and Solvents. Dimethyl sulfoxide was dried over Linde 4A Molecular Sieve and distilled under reduced pressure.

Methanol (reagent grade) was dried over Drierite and distilled from fresh Drierite. Precautions were taken to exclude atmospheric moisture during the distillation and subsequent handling.

(1) Abstracted in part from the Ph.D. Thesis of R. L. Carlson, University of Illinois, 1962.

(2) D. W. Meek and R. S. Drago, *J. Am. Chem. Soc.*, **83**, 4322 (1961).

(3) R. S. Drago, R. L. Carlson, and K. F. Purcell, *Inorg. Chem.*, **4**, 15 (1965).

N-Methylacetamide was dried over anhydrous calcium oxide and distilled under reduced pressure.

Reagent grade solvents were also used and yielded similar results.

Anhydrous iron(III) chloride was prepared as previously described.³

All solutions were prepared and the glass-stoppered quartz spectrophotometer cells were filled inside a drybox.

Tetraethylammonium tetrachloroferrate(III) was prepared by dissolving iron(III) chloride in a benzene-ethanol mixture. To the solution was added the stoichiometric quantity of tetraethylammonium chloride. Precipitation of green needles occurred immediately. These crystals were isolated by filtration, washed with anhydrous ether, and dried in a vacuum desiccator over phosphorus pentoxide. The yield was 98% of the theoretical.

Anal. Calcd. for $C_8H_{20}NFeCl_4$: C, 29.30; H, 6.15; N, 4.27. Found: C, 29.17; H, 6.11; N, 4.11.

Tetraethylammonium chloride (Eastman White Label) was recrystallized from acetone and dried at 100° in an Abderhalden drying tube.

Preparation of Hexakis(dimethyl sulfoxide)iron(III) Perchlorate. To a solution of 0.25 g. of hexakis(*N,N*-dimethylacetamide)iron(III) perchlorate³ in 15 ml. of DMSO was added 75 ml. of anhydrous ether. An oily, white precipitate formed immediately. On standing overnight, a flocculent, white precipitate was obtained. The precipitate was filtered through a sintered glass funnel and washed with ether. The solid was dried under vacuum over phosphorus pentoxide.

Anal. Calcd. for $C_{12}H_{36}O_{18}S_6Cl_3Fe$: C, 17.51; H, 4.41. Found: C, 17.71; H, 4.39.

Preparation of Hexakis(*N*-methylacetamide)iron(III) Perchlorate. This compound was prepared by the reaction of anhydrous iron(III) chloride and anhydrous silver perchlorate in NMA. The procedure followed in the preparation of this compound is identical with that followed in the synthesis of hexakis(*N,N*-dimethylacetamide)iron(III) perchlorate.³ The yellow crystals were filtered, washed with anhydrous ether, and dried under vacuum over phosphorus pentoxide.

Anal. Calcd. for $C_{18}H_{42}N_6O_{18}Cl_3Fe$: C, 27.26; H, 5.34; N, 10.60; Fe, 7.04. Found: C, 26.94; H, 5.47; N, 10.24; Fe, 7.08.

Attempted Preparation of Hexakis(methanol)iron(III) Perchlorate. Two different methods of synthesis were used in attempts to prepare this compound. In the first, the reaction of iron(III) chloride and silver perchlorate in methanol was carried out. After removal of the precipitated silver chloride, addition of ether to the filtrate produced a red oil. No crystals

could be obtained from this oil. A displacement reaction using hexakis(N,N-dimethylacetamide)iron(III) perchlorate dissolved in methanol was also attempted. Addition of ether to this mixture gave a red oil from which no crystals could be obtained.

In order to obtain a methanol solution of the iron(III) cation free of chloride ion, either the filtrate containing iron(III) perchlorate (after removal of silver chloride) or a solution of hexakis(N,N-dimethylacetamide)iron(III) perchlorate in methanol was used. Both solutions gave identical spectra.

Results

The compound $[\text{Fe}(\text{DMSO})_6](\text{ClO}_4)_3$ was prepared for the purpose of studying the effect of added chloride ion upon its spectrum. The spectrum of $[\text{Fe}(\text{DMSO})_6](\text{ClO}_4)_3$ containing 0, 1, and 2 mole ratios of added chloride ion in DMSO is illustrated in Figure 1. It

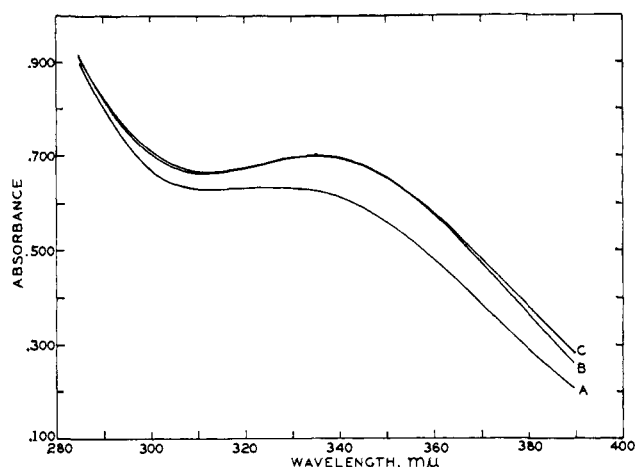


Figure 1. Ultraviolet spectra of $\text{Fe}[(\text{CH}_3)_2\text{SO}]_6(\text{ClO}_4)_3$ in the solvent $(\text{CH}_3)_2\text{SO}$ with and without added $(\text{C}_2\text{H}_5)_4\text{NCl}$. Iron(III) concentration of $1.52 \times 10^{-4} M$ for all curves: curve A, no added chloride; curve B, 1:1 mole ratio of chloride to iron(III); and curve C, 2:1.

is to be noted that the addition of one chloride ion to the iron(III) cation changes the spectrum in the 335- $m\mu$ region. The addition of the second chloride ion, however, has almost no effect upon the absorption spectrum. Also, the spectrum of iron(III) chloride dissolved in DMSO is qualitatively the same as that in which a 1:1 mole ratio of chloride ion to iron(III) is present. A single band, $\nu_{\text{max}} 335 \pm 3 m\mu$, is present. A similar spectrum is obtained from a solution of tetraethylammonium tetrachloroferrate(III) in DMSO. The instability of FeCl_4^- in this solvent is in agreement with a result published⁴ subsequent to the initiation of our studies from an investigation of the visible spectrum of this system. These authors report the absence of FeCl_4^- at $5 \times 10^{-4} M$ iron(III) concentrations at very large chloride to iron(III) mole ratios.

The spectrum of tetraethylammonium tetrachloroferrate(III) dissolved in methanol is shown in Figure 2. Two bands are present with maxima at 248 and 366–368 $m\mu$. A similar spectrum is obtained from a solution of iron(III) chloride in methanol. The spectrum

(4) V. Gutmann and G. Hampel, *Monatsh. Chem.*, **94**, 830 (1963).

of the iron(III) cation in methanol is presented in Figures 3 and 4. A broad band with maximum in the 356- $m\mu$ region and a second band with maximum in

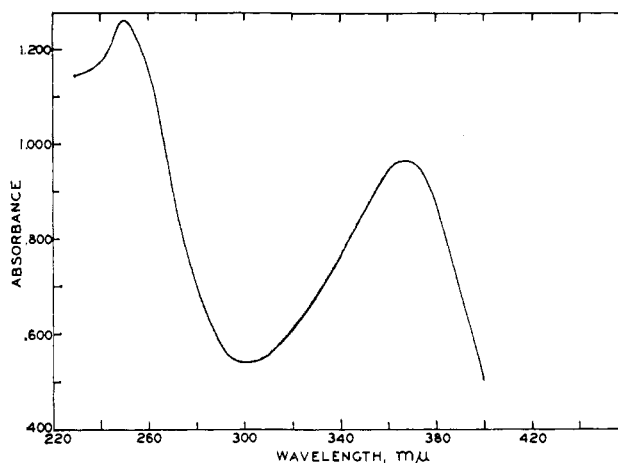


Figure 2. The spectrum of species resulting by dissolving $(\text{C}_2\text{H}_5)_4\text{NFeCl}_4$ in CH_3OH ; concentration of $(\text{C}_2\text{H}_5)_4\text{NFeCl}_4$ equals $2.9 \times 10^{-4} M$.

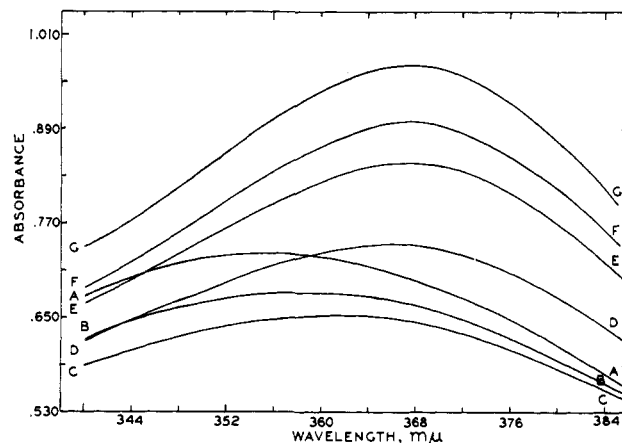


Figure 3. The spectra of $\text{Fe}(\text{DMA})_6(\text{ClO}_4)_3$ in the solvent CH_3OH with and without added chloride. For all curves the iron(III) concentration is $2.4 \times 10^{-4} M$. The following mole ratios of Cl^- to iron(III) correspond to the curves lettered A to G: A = 0 to 1; B = 0.27 to 1; C = 0.54 to 1; D = 1.07 to 1; E = 1.61 to 1; F = 2.14 to 1; and G = 3.22 to 1.

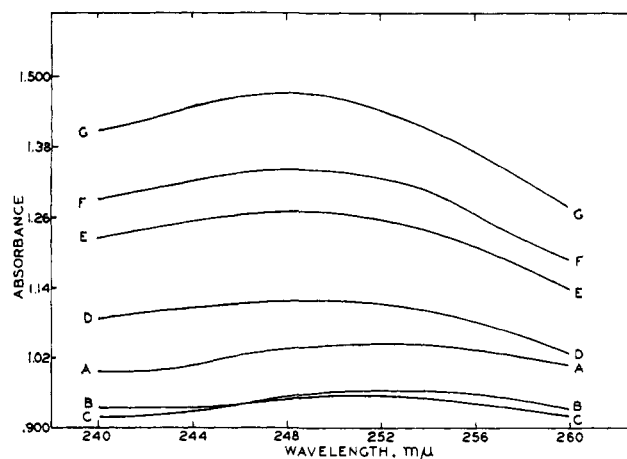


Figure 4. The spectra of $\text{Fe}(\text{DMA})_6(\text{ClO}_4)_3$ in the solvent CH_3OH with and without added chloride. The curves A to G correspond to the same solutions described in the caption of Figure 3.

the 253-m μ region are found. The effect of added chloride ion on the spectrum of the iron(III) cation is also shown in these figures. A pronounced shift in band positions occurs upon addition of chloride. The maxima at chloride to iron(III) mole ratios of one or greater are now identical with those found in methanol solutions of iron(III) chloride. Further addition of chloride ion up to a mole ratio of 5.8 chloride ions per iron(III) results in an increased intensity of both bands, but no further shift in band positions occurs. Although the spectral curves are not included, we have found that addition of chloride ion in the region 6:1 to 12:1 mole ratio of chloride ion to iron(III) causes no change in band positions and gives only slight intensity increases.

The spectrum of iron(III) chloride dissolved in NMA is presented in Figure 5. A single band, with $\lambda_{\max} \sim 344 \text{ m}\mu$ ($\epsilon \sim 2 \times 10^3$) is found. The spectra of

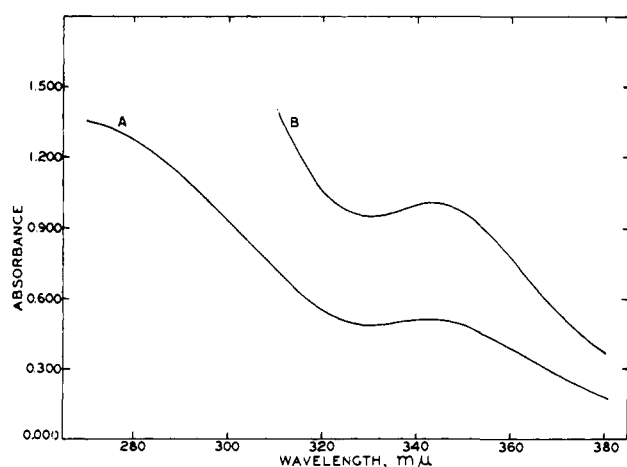


Figure 5. The spectra of iron(III) chloride in N-methylacetamide: A = $2.7 \times 10^{-4} M$; B = $5.4 \times 10^{-4} M$.

tetraethylammonium tetrachloroferrate(III) and of hexakis(N-methylacetamide)iron(III) perchlorate in NMA are the same both with regard to the position of the band maximum and the extinction coefficient.

Discussion

It is the purpose of this study to investigate the species formed when a small amount of iron(III) chloride is dissolved in various nonaqueous solvents. This solute was selected since there are a number of species that can be formed under different conditions, and these are found to have different electronic absorption spectra. Since our main interest is in the effect of solvent on the species present in solution, the concentration of iron and chloride was held constant in these studies, *i.e.*, either $\sim 10^{-4} M$ in FeCl_3 or FeCl_4^- , in effect using these materials as indicators of the solvent properties. Those studies necessary to identify the species in solution in the various solvents were carried out. Consequently, we are not generalizing on the iron-chloro species which are capable of existence in these various solvents over a wide range of iron(III) and chloride ion concentrations.

From consideration of the spectra of iron(III) chloride in the solvents DMSO, CH_3OH , and NMA,

it can be concluded that the tetrachloroferrate(III) is not formed in appreciable amounts in any of these solvents under the conditions employed. This conclusion follows from the absence of absorption bands with λ_{\max} in the 315- and 365-m μ regions. These bands have been shown to be characteristic of FeCl_4^- in a variety of solvents such as triethyl phosphate,² DMA,³ aqueous HCl ,⁵ $(\text{C}_2\text{H}_5)_2\text{O}$,⁶ $\text{C}_2\text{H}_5\text{Br}$,⁶ dioxane,⁶ POCl_3 ,⁷ and $\text{C}_6\text{H}_5\text{POCl}_2$.⁸

The spectrum of $[\text{Fe}(\text{DMSO})_6](\text{ClO}_4)_3$ as a function of added chloride ion is given in Figure 1. A change in absorbance occurs when the amount of chloride in the system changes from zero to a mole ratio of chloride to iron(III) of 1:1. As additional chloride is added to give a mole ratio of 2:1, there is essentially no change in the spectrum except for a slight increase in absorbance at all wave lengths in the 280–400-m μ region. Making the reasonable assumption that the molar absorptivity and band shape for the dichloro iron(III) species are not identical with those of the monochloro iron(III) complex in this whole region, this result indicates that the monochloro iron(III) cation $[\text{Fe}(\text{DMSO})_5\text{Cl}]^{2+}$ (we are assuming a coordination number of 6 for iron cations) is the stable species in DMSO for this iron(III) concentration in this range of $\text{Cl}^-:\text{Fe}(\text{III})$ ratios. Further, the similarity in spectra between this cation in DMSO solution and that of iron(III) chloride in DMSO indicates that this cation, $[\text{Fe}(\text{DMSO})_5\text{Cl}]^{2+}$, is the primary species formed in dilute solutions of iron(III) chloride in DMSO. It should be noted that coordination compounds containing the cation $[\text{Fe}(\text{DMSO})_5\text{Cl}]^{2+}$ have been reported^{9,10} from syntheses in DMSO in which iron(III) chloride served as the starting material. This is consistent with the spectral evidence that in dilute DMSO solutions of iron(III) chloride the main cationic species is $[\text{Fe}(\text{DMSO})_5\text{Cl}]^{2+}$ and not $[\text{Fe}(\text{DMSO})_6]^{3+}$.

The fact that the spectra of iron(III) chloride, tetraethylammonium tetrachloroferrate(III), and $[\text{Fe}(\text{NMA})_6](\text{ClO}_4)_3$ in NMA are virtually identical can be reasonably interpreted by postulating that the stable species present in this solvent are the cation $[\text{Fe}(\text{NMA})_5\text{Cl}]^{2+}$ and chloride ion.

The interpretation of the methanol studies is more difficult. It seems clear, from the initial decrease and subsequent increase in intensity of the iron(III) cation absorption (as a function of added chloride ion) that more than one equilibrium is involved. A possible interpretation of these results follows. At mole ratios of chloride ion to iron(III) cation less than one, the monochloro species is formed. The extinction coefficient of this species is less than that of the solvated iron(III) cation; therefore, a decrease in absorption is noted. As the chloride ion to iron(III) ratio is increased, the dichloro species is formed with an extinction coefficient greater than that of the chloro-free iron(III) cation. Thus, the absorbance increases. Further increases in chloride ion concentration shift the equilibrium toward the dichloro side. In order

(5) G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.*, 1435 (1953).

(6) H. L. Friedman, *J. Am. Chem. Soc.*, **74**, 5 (1952).

(7) M. Baaz, V. Gutman, and L. Hubner, *Monatsh. Chem.*, **91**, 537 (1960).

(8) M. Baaz, V. Gutman, and L. Hubner, *ibid.*, **92**, 135 (1961).

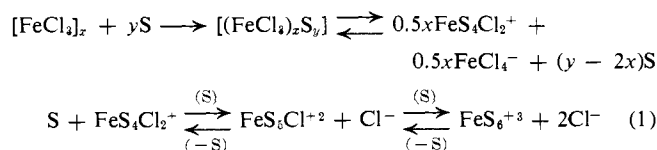
(9) D. W. Meek, R. S. Drago, and D. K. Straub, *J. Am. Chem. Soc.*, **82**, 6013 (1960).

(10) F. A. Cotton and R. Francis, *ibid.*, **82**, 2986 (1960).

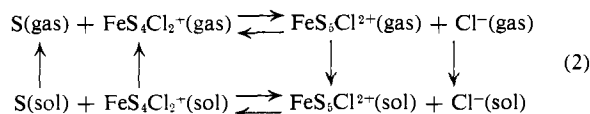
to account for the fact that the shift in band position is complete at a lower chloride ion to iron(III) cation ratio than is the increase in band intensity, it must be assumed that the location of the band maxima for the mono- and dichloro species are quite similar but the molar absorptivities are not in all regions. According to this interpretation the primary species present in dilute iron(III) chloride solutions in CH₃OH are the mono- and dichloro iron(III) cations and chloride ion. It is possible that this system is further complicated by the possibility that solvolysis reactions can occur. The species would then not be as simple as those represented above for DMSO. It is reasonable to assume that chloride ion coordination is causing the observed spectral changes.

In addition to the systems studied here, it has previously been reported that FeS₄Cl₂⁺ and FeCl₄⁻ are the principal species in CH₃C(O)N(CH₃)₂,³ OPCL₃,⁷ OP(OC₂H₅)₃,² OP(OCH₃)₃,⁴ and C₆H₅POCl₂.

According to the coordination model the following equilibria represent different extents to which chloride ion dissociation can occur when iron(III) chloride is dissolved in a nonaqueous solvent, S.



For simplicity, we shall consider the energetics of one of these steps by constructing an energy cycle.



The enthalpy of the gas phase reaction depends upon the relative donor strength of solvent and chloride. The position of equilibrium in solution will depend upon entropy effects and the difference in solvation of the products and reactants. The direct measurement of all these terms is not possible at present. The following statements can be made.

(1) Strong donor solvents will result in more extensive chloride ion dissociation than weak ones, other things being equal.

(2) The more polar, strongly solvating solvents will tend to shift the equilibrium in solution (eq. 2) to the right. The polar solvent will interact more strongly with the more highly charged ions in the product than with those in the reactants which are not as highly charged.

(3) Charge separation will be facilitated by a solvent with a high dielectric constant and inhibited by one with a low dielectric constant.

A simple extension of these considerations to eq. 1 indicates that the stronger donor, better solvating solvents will cause more extensive chloride ion dissociation than solvents which do not have these properties. With the exception of dielectric constant, these solvent properties cannot be directly measured. Qualitative estimates for various solvents will be made from the best data that are available for this purpose. These properties will then be compared with the species which are formed when iron(III) chloride is dissolved in the solvent.

In order to obtain an estimate of the solvating properties of a solvent, the association constant, K_{as} , for tetraalkylammonium halides in these solvents can be compared. Since the alkylammonium cations are not Lewis acids, the donor properties of the solvent should not affect these data. It is also of interest to compare the Z values¹¹ of the solvents which are measures of the effect solvation has on the energy of the charge-transfer transition of an N-substituted pyridinium iodide.

The donor strength of the solvent toward the cation is also difficult to measure directly. We can make estimates of the relative donor strengths of solvents by comparing enthalpy data obtained in the gas phase or in poorly solvating solvents. It is well known that orders of donor strength change when the acid is varied.¹² Consequently, data toward different types of acids should be considered in ascertaining a solvent donor order. For a series of similar ligands, the spectrochemical parameter Dq can be used¹³ to indicate the magnitude of the metal ion-ligand interaction. Data pertaining to the above-mentioned criteria for the solvents of interest here are contained in Table I.

The order of donor strengths predicted for these solvents toward iron(III) is CH₃OH > (CH₃)₂SO ~ CH₃C(O)N(CH₃)₂ > CH₃C(O)NHCH₃. The order of solvating ability is given by CH₃C(O)NHCH₃ > (CH₃)₂SO > CH₃OH > CH₃C(O)N(CH₃)₂ > OP(OC₂H₅)₃.

It is interesting that even though the data in Table I indicate that DMA is a stronger donor than NMA, considerably more dissociation of chloride ion from iron(III) occurs in the latter because it is a much better solvating solvent. The donor strengths of DMSO and DMA are very similar toward phenol, iodine, and nickel(II). Once again, the more extensive chloride ion dissociation that is observed in DMSO compared to that in DMA can be attributed to the greater solvating properties of the former. Little data are available on the donor strength of triethyl phosphate. However, the lack of extensive chloride ion dissociation and the stability of FeCl₄⁻ in this solvent correlate with the poor solvating characteristics of this material.

Methanol is a complex solvent material. It is capable of undergoing extensive hydrogen bonding interactions with certain anions. In the case of iron(III) chloride it is felt that hydrogen bonding to chloride ion results in extensive dissociation of chloride ion from iron(III) in this solvent. For a solute in which this type interaction is not large, the large K_{as} and low dielectric constant (Table I) predict that methanol will be a poor ionizing solvent. It should also be remembered that methanol is extensively associated *via* self-hydrogen bonding and this will lead to poor solvent properties when specific interactions of the Lewis acid-base type do not occur with the solute cations and anions.

For the solvents considered in this study, the range of donor strengths is not very large and the extent of chloride ion dissociation from iron(III) parallels the

(11) E. M. Kosower, *et al.*, *J. Am. Chem. Soc.*, **78**, 5700, 5838 (1956); *ibid.*, **80**, 3253, 3261, 3267 (1958).

(12) See, for example, R. J. Niedzielski, R. S. Drago, and R. L. Midaugh, *ibid.*, **86**, 1694 (1964).

(13) R. S. Drago, *et al.*, *Inorg. Chem.*, **2**, 124 (1963).

Table I. Donor and Solvating Tendencies of Some Solvents

Solvent	K_{as} (salt)	Z^a	Dielectric constant, ϵ	$-\Delta H$, kcal. mole ⁻¹ C ₆ H ₅ OH ^g	I_2	Dq , ^b cm. ⁻¹
CH ₃ OH	26 (Bu ₄ NBr) ^{c,h}	83.6 ^e	33.5 (25°)	...	1.9 ^p	850 ^h
(CH ₃) ₂ SO	0 (Bu ₄ NBr) ^l	71.1 ^e	48.9 (25°)	6.5	4.4 ^q	773 ⁱ
CH ₃ C(O)NHCH ₃	0 (Et ₄ NBr) ^{c,m}	77.9 ^f	175.7 (40°)	4.7 ^d	...	752 ^j
CH ₃ C(O)N(CH ₃) ₂	20 (Et ₄ NBr) ⁿ	66.9 ^f	38 (25°)	6.4	4.0 ^r	769 ^j
OP(OC ₂ H ₅) ₃	1600 (Et ₄ N picrate) ^o	...	13 (25°)	6.2

^a The Z value is the transition energy in kcal. at 25°, 1 atm. pressure, for the charge-transfer transition of 1-ethyl-4-carbomethoxypyridinium iodide. The larger values correspond to better solvating solvents. ^b The Dq value for the octahedral nickel(II) complex of this ligand. For comparison, the Dq value for chloride ion is 720. ^c Bu stands for *n*-butyl and Et for ethyl. ^d This value was obtained from the phenol frequency shift, see footnote *g* below, and represents the enthalpy for unassociated amide complexing to phenol. ^e See ref. 11. ^f This work. ^g See M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962). ^h V. Imhof and R. S. Drago, *Inorg. Chem.*, **4**, 427 (1965). ⁱ D. W. Meek, R. S. Drago, and T. S. Piper, *ibid.*, **1**, 285 (1962). ^j See ref. 13. ^k H. Sodek and R. M. Fuoss, *J. Am. Chem. Soc.*, **72**, 301 (1950). ^l P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956). ^m C. M. French and K. H. Glover, *Trans. Faraday Soc.*, **51**, 1418 (1955). ⁿ G. R. Lester, T. A. Glover, and P. G. Sears, *J. Phys. Chem.*, **60**, 1076 (1956). ^o C. M. French, P. B. Hart, and D. F. Muggleton, *J. Chem. Soc.*, 3582 (1959). ^p H. Tsubomura and R. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961). ^q R. S. Drago, B. Wayland, and R. L. Carlson, *ibid.*, **85**, 3125 (1963). ^r R. S. Drago, *et al.*, *ibid.*, **83**, 3572 (1961).

solvating ability of the solvent. In the best solvating solvent, NMA, the principal species are FeS₆³⁺ and chloride ion (see eq. 1). In DMSO the principal species are FeS₅Cl²⁺ and chloride ion. Even though methanol is estimated to be the best donor solvent of those studied, both FeS₅Cl²⁺ and FeS₄Cl₂⁺ exist. This result correlates with the low dielectric constant of methanol and extensive ion pairing of Bu₄NBr in this solvent. In the poorer solvating solvents, DMA, (CH₃O)₃PO ($\epsilon = 20.60$ at 20°),⁴ (C₂H₅O)₃PO, POCl₃ ($\epsilon = 14$ at 22°), C₆H₅POCl₂, and possibly in many other oxyhalide solvents, the principal species are FeS₄Cl₂⁺ and FeCl₄⁻.

It is interesting that the above interpretation has been so simple. This is probably due to the fact that we have selected systems where the difference in solvation energies is large enough to overcome any entropy differences that exist between the systems studied. When very similar systems are compared or when there are very large entropy differences between the systems compared, which counteract the enthalpy, such an interpretation may not be possible.

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Infrared Spectra of Complexes of L-Cysteine and Related Compounds with Zinc(II), Cadmium(II), Mercury(II), and Lead(II)¹

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Complexes of L-cysteine, S-methyl-L-cysteine, methyl-L-cysteinate, and 3-mercaptopropionic acid with Zn²⁺, Cd²⁺, Pb²⁺, and Hg²⁺ have been prepared under solution conditions of varying acidity. Infrared spectra of solid compounds have been employed to assist in determining which groups are coordinated to the metal. Among the new solid species formed are a number of complexes which are believed to be trinuclear, of the form [M₃L₃]²⁺-MCl₄²⁻. The infrared spectra in D₂O solution of complexes of the form Na₂[ML₂], where L is (SCH₂CHNH₂-

CO₂)₂⁻ or (SCH₂CH₂CO₂)₂⁻, and [ML₂], where L is (SCH₂CHNH₂CO₂CH₃), have been obtained. From the shifts in the carboxylate or carbonyl frequencies as a function of M, it appears that the order of strength of coordination to either oxygen or the amino group is in the order Zn > Cd > Hg > Pb. The over-all driving force for complex formation is in the reverse order because metal-sulfur bonding is of overriding importance.

Cysteine, which figures prominently in discussions of metal ion binding to protein, has three possible coordination sites, namely sulfhydryl, amino, and carboxylate groups. This provides three possible combinations for forming a chelate ring with a divalent

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(2) Alfred P. Sloan Research Fellow; to whom inquiries should be addressed.