group on the sulfur atom[25] shows, as is to be expected, a decreasing correlation in the 1400–900 cm.$^{-1}$ region with decreasing size of the aromatic substituent, this being because the introduction of an additional substitution on a single benzene ring modifies the vibrational modes of the substructure more than will one additional substitution on a polycyclic subgroup.

Several bands occur in approximately the same place in each of the halogenated phenylmercapturic acids as may be seen in Fig. 1. No assignments have yet been made for these persistent bands.

No bands were assigned to the carbon–halogen stretching vibration in the spectra of the halogenated phenylmercapturic acids. Nevertheless, it is interesting to speculate as to whether the 839 cm.$^{-1}$ band in *p*-fluorophenylmercapturic acid and the companion band at 838 cm.$^{-1}$ in *p*-fluorophenylcysteine might be due to the C–F stretching frequency. Likewise, it is possible that the 1295 cm.$^{-1}$ band in *p*-chlorophenylmercapturic acid and *p*-chlorophenylcysteine might be the first overtone of the C–Cl stretching frequency. These speculations are based on assignments made by Lecomte[24] for monohalogenated benzenes.

The 1225 Cm.$^{-1}$ Band in N-Acetylated Cysteines.—A striking difference between the spectra of the N-acetylated cysteines (which include the eight mercuric acids) and the spectra of the corresponding S-substituted non-acetylated cysteines is the presence of a strong band *ca.* 1225 cm.$^{-1}$ in the former only (see Fig. 1). This band is very constant in position. For the four halogenated mercapturic acids it is located at 1217 ± 3 cm.$^{-1}$; for the other mercapturic acids, at 1230 ± 3 cm.$^{-1}$.

A preliminary study[26] indicates that the 1225 cm.$^{-1}$ band, which is also present in amido acids, amino acid hydrochlorides and in dicarboxylic amino acids, may be assigned to some vibration of the C–O–H group. Various arguments may be put forward in support of an assignment either to the C–O stretching or bending vibration or to the O–H bending vibration, but without deuterium substitution experiments it is impossible to localize the assignment any more precisely.

The 860 Cm.$^{-1}$ Band in S-Substituted Non-acetylated Cysteines.—A rather prominent band at 860 cm.$^{-1}$ in the S-substituted cysteines is absent in the mercapturic acids. Among the possible explanations for this band would be that of a deformation vibration associated with the carboxylate ion which is reported to be found in the 930–870 cm.$^{-1}$ region.[17] A study similar to that made on the 1225 cm.$^{-1}$ band is not possible, the RFFD spectra not having been published below 1100 cm.$^{-1}$. Wright[16] gives spectra of a number of amino acids most of which have a band of medium intensity in this region, but no amino acid hydrochloride spectra are at present available for comparison purposes.

Acknowledgments.—We are particularly grateful to Dr. Harold D. West who made this study possible not only through suggesting the problem but also by his generosity in preparing all the unavailable compounds we needed.[27] We would like to express our thanks to Dr. E. Boyland, Dr. J. A. Stekol, and Dr. S. H. Zbarsky for supplying us with samples. We would also like to acknowledge the gift of several compounds from the late Dr. Werner E. Bachman. This investigation has been supported by a Frederick Gardner Cottrell Grant from the Research Corporation.

[25] Unpublished data recently obtained in this Laboratory.

[26] M. L. Josien and N. Fuson, *Compt. rend.*, **232**, 2016 (1951).

[27] Details of preparation are to be published elsewhere.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Visible and Ultraviolet Absorption Spectrum of the Tetrachloroferrate(III) Ion in Various Media[1]

BY HAROLD L. FRIEDMAN

A comparison is made of the ultraviolet and visible absorption spectra of the following systems: solutions of ferric chloride in concentrated aqueous hydrochloric acid, the ether extracts of these solutions, anhydrous ether solutions of $KFeCl_4$ and solid $KFeCl_4$. The similarity of the spectra provides evidence that the principal iron-containing species in each of these systems is the $FeCl_4^-$ ion with coördination number four for iron. This conclusion is supported by other spectral observations and is shown to be consistent with the known properties of these systems including the high solubility of $KFeCl_4$ in ether.

This paper presents the results of the beginning of an investigation of the properties of solutions of electrolytes in solvents of low dielectric constant. The electrolytes discussed in this paper all have the type formula $M'M'''Cl_4$, where M' is a monovalent element or group and M''' a trivalent metal.

It has been shown that trivalent iron is extracted from aqueous hydrochloric acid by various ethers[2,3,4,5] as the compound $HFeCl_4{\cdot}nH_2O$, with n equal to about 4.5. Similarly, trivalent gallium is extracted from aqueous hydrochloric acid by diisopropyl ether as the compound[6] $HGaCl_4$ with undetermined hydration. The following ob-

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[1] Presented in part before the 118th Meeting of the American Chemical Society, Chicago, Illinois, September 3-8, 1950.

[2] S. Kato and R. Ishii, *Sci. Papers Inst. Phys. Chem. Research, Tokyo*, **36**, 82 (1939).

[3] J. Axelrod and E. H. Swift, THIS JOURNAL, **62**, 33 (1940).

[4] N. H. Nachtrieb and J. G. Conway, *ibid.*, **70**, 3547 (1948).

[5] R. J. Myers, D. E. Metzler and E. H. Swift, *ibid.*, **72**, 3767 (1950).

[6] N. H. Nachtrieb and R. E. Fryxell, *ibid.*, **71**, 4035 (1949).

servations suggest a similarity of the constitution of these ether extracts and of the anhydrous ether solutions of $M'M'''Cl_4$ salts which are of primary interest in this investigation: (1) Just one molecule of HCl per molecule of $FeCl_3$ or $GaCl_3$ extracts from aqueous solution. Anhydrous diethyl ether solutions of $GaCl_3$ or $FeCl_3$ will dissolve exactly one mole of solid KCl or NH_4Cl per mole of trichloride.[7] (2) Under certain conditions of concentration, two liquid phases form in the isopropyl ether extracts.[6,8] Two liquid phases in equilibrium are observed in anhydrous ether solutions of suitable concentrations of $HFeCl_4$,[9] NH_4GaCl_4 and NH_4AlCl_4.[10] (3) The observed variation of extraction efficiency with metal ion concentration[5,6,11] requires that the apparent degree of polymerization of the $HM'''Cl_4$ in the ether extracts increases rapidly with increasing concentration. This is also indicated by measurements of vapor pressure lowering of solutions of $HFeCl_4 \cdot nH_2O$ in isopropyl ether.[12] The apparent degree of polymerization of NH_4GaCl_4 in anhydrous diethyl ether, calculated from the vapor pressure lowering of the solutions, also increases rapidly with increasing concentration.[10]

It is the purpose of the present paper to establish a fourth similarity between the ether extracts and the anhydrous solutions, similarity of spectra, and to examine some of the consequences of these observations.

Experimental

Materials.—All operations in the preparation of anhydrous solutions were performed either in a vacuum system or in a dry-box under a dried nitrogen atmosphere. Nitrogen: Commercial tank nitrogen was dried over calcium hydride. Chlorine: The commercial product was purified by condensing it on aluminum chloride. Diethyl ether: Reagent grade ether was refluxed over $LiAlH_4$. Ethylene bromide: A fraction boiling in the range 131.0–131.5° was taken. Potassium tetrachloroferrate (III): This was prepared by a modification of method 2[7] for the preparation of $M'M'''Cl_4$ compounds. The mixture of KCl and $FeCl_3$ was melted and stirred under two atmospheres pressure of Cl_2 before being heated *in vacuo*, then heating *in vacuo* was continued only until the product had refluxed for 2 min. Chlorine was condensed upon the cooled product to loosen it from the vessel. *Anal.* Found: Cl, 59.80, 59.80; Fe, 23.40, 23.40. Calcd. for $KFeCl_4$: Cl, 59.81; Fe, 23.61; m.p. 250–251° in sealed capillary. Ferric chloride: Anhydrous material was purified by repeated sublimation at 250° through sintered glass filters. Potassium tetrachloroaluminate: This was prepared by method 2,[7] m.p. 260° (lit.[13] 250°). Cesium tetrachloroaluminate: This was prepared by method 1,[7] m.p. 376°. Cesium tetrachloroferrate (III): This was prepared by method 1,[7] m.p. 382°. Lithium iodide: Lithium hydroxide was fused with excess ammonium iodide under nitrogen and was fused again in a vacuum to drive off residual ammonium iodide.

Analyses.—Chlorine was determined by Volhard titration using nitrobenzene. Iron was usually determined by titration with ceric sulfate between methylene blue and ferrous–orthophenanthroline end-points after reduction by titanous chloride. Solutions containing less than 0.001 *M* Fe were analyzed spectrophotometrically using the absorption maximum of ferric ion at 240 mμ. The molar extinction coefficient was found to be 4350 in 3.3 *M* $HClO_4$.

Spectra.—A Beckman quartz model DU spectrophotometer having cell compartments controlled at 24.0–24.5° was used with absorption cell assemblies of various types. Each type A cell assembly consisted of a 1-cm. Corex cuvette sealed at right angles to the neck of a 10-ml. flask. The neck of the flask was extended to a ground glass joint. After the solution was introduced into the bulb of the flask by one of the methods described in the next section, the solution was cooled to −180° and the cell assembly was sealed off just below the ground joint. Each type B cell assembly consisted of a Pyrex absorption cell of 1 or 10 cm. length with demountable fused silica windows. This cell was connected to the neck of a flask of suitable volume to form a cell assembly which was then handled like the type A assemblies. Gaskets of 0.003-in. Teflon were placed between the optically flat cell faces and the silica windows which were clamped in place. Heating to 300° after assembly made the window seals vacuum tight.

Anhydrous Ether Solutions.—Solutions of trivalent iron compounds in ether are photosensitive and therefore such solutions were prepared and handled entirely by dim artificial light, which was found to be without effect. Several methods of preparation have been tried, none entirely satisfactory, and the positions of the maxima and minima of absorption of these solutions have been found to depend only on the nominal composition and not on the method of preparation nor even on the presence of moderate amounts of solid suspended impurities or dissolved stopcock grease. Results on such contaminated solutions have not been reported here. A suitable blank was used in the measurement of each spectrum. Concentrations were determined by chemical analysis of the solutions after the spectra were measured.

Four series of experiments were performed. In series I, $FeCl_3$ and a fragile sealed bulb containing dry KCl or NH_4Cl were introduced into the type A cell assemblies in the dry-box. Each cell assembly was then connected to the vacuum line and a suitable amount of ether distilled into it. After the spectrum of the resulting $FeCl_3$ solution had been measured, the bulb of KCl was broken by shaking, shaking was continued until equilibrium had been reached in the solution and the spectrum of the $KFeCl_4$ or NH_4FeCl_4 solution was observed.

In series II, a mixture of KCl and $KFeCl_4$ was extracted with ether. The resulting solution was diluted and introduced into the type A cell assemblies by a special apparatus designed to avoid contamination by air and stopcock grease.

In series III, a solution of pure $KFeCl_4$ in ether was handled by another special apparatus which enabled successive dilutions of the solution to be made and which introduced the diluted solutions into absorption cells of type B.

In series IV, pure $KFeCl_4$ was introduced into type A cell assemblies in the dry-box and ether was added after the cell assembly was connected to the vacuum line.

Ethylene Bromide Solutions.—The procedure was similar to that described as series IV above. The spectrum of a saturated solution did not change in a week at room temperature but changed irreversibly on warming to 60°. Ether solutions of $KFeCl_4$ are stable under the same conditions. The analysis of the solution was performed after the heating, therefore the extinction coefficients reported for this system may be somewhat in error.

Solid $KFeCl_4$.—Stoppered Corex spectrophotometer cells containing some solid $KFeCl_4$ were placed in a small electric furnace in an atmosphere of dry nitrogen, heated above the melting point of $KFeCl_4$, and then allowed to cool slowly. During this process each cell was oriented so that one of its windows became coated with as even a layer as possible of fused $KFeCl_4$. In several such expts. minima and maxima at the same wave lengths were observed in the light absorption of the fused layer. The intensity of the light absorption varied from one experiment to another in a manner which could be explained on the basis that the fissures in the fused solid scattered the spectrophotometer beam, producing a background of absorption whose intensity was independent of wave length in the visible region. Variation in the heat-treating procedure confirmed this: samples cooled more rapidly gave evidence of a much higher background absorption. It is believed that the observed spectrum cannot be attributed to an interaction of moisture with the $KFeCl_4$ because in all cases where this solid came in contact with moisture it was observed immediately to become coated with a layer of a red compound and no trace of this compound was observed in the samples used in these experiments. Furthermore, the absorption of one sample did not change when

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[7] H. L. Friedman and H. Taube, THIS JOURNAL, **72**, 2236 (1950).

[8] R. J. Myers and D. E. Metzler, *ibid.*, **72**, 3772 (1950).

[9] J. Houben and W. Fischer, *J. prakt. Chem.*, **123**, 89 (1929).

[10] H. L. Friedman and H. Taube, THIS JOURNAL, **72**, 3362 (1950).

[11] N. H. Nachtrieb and R. E. Fryxell, *ibid.*, **70**, 3352 (1948).

[12] D. E. Metzler and R. J. Myers, *ibid.*, **72**, 3776 (1950).

[13] J. Kendall, E. Crittenden and H. Miller, *ibid.*, **45**, 976 (1923).

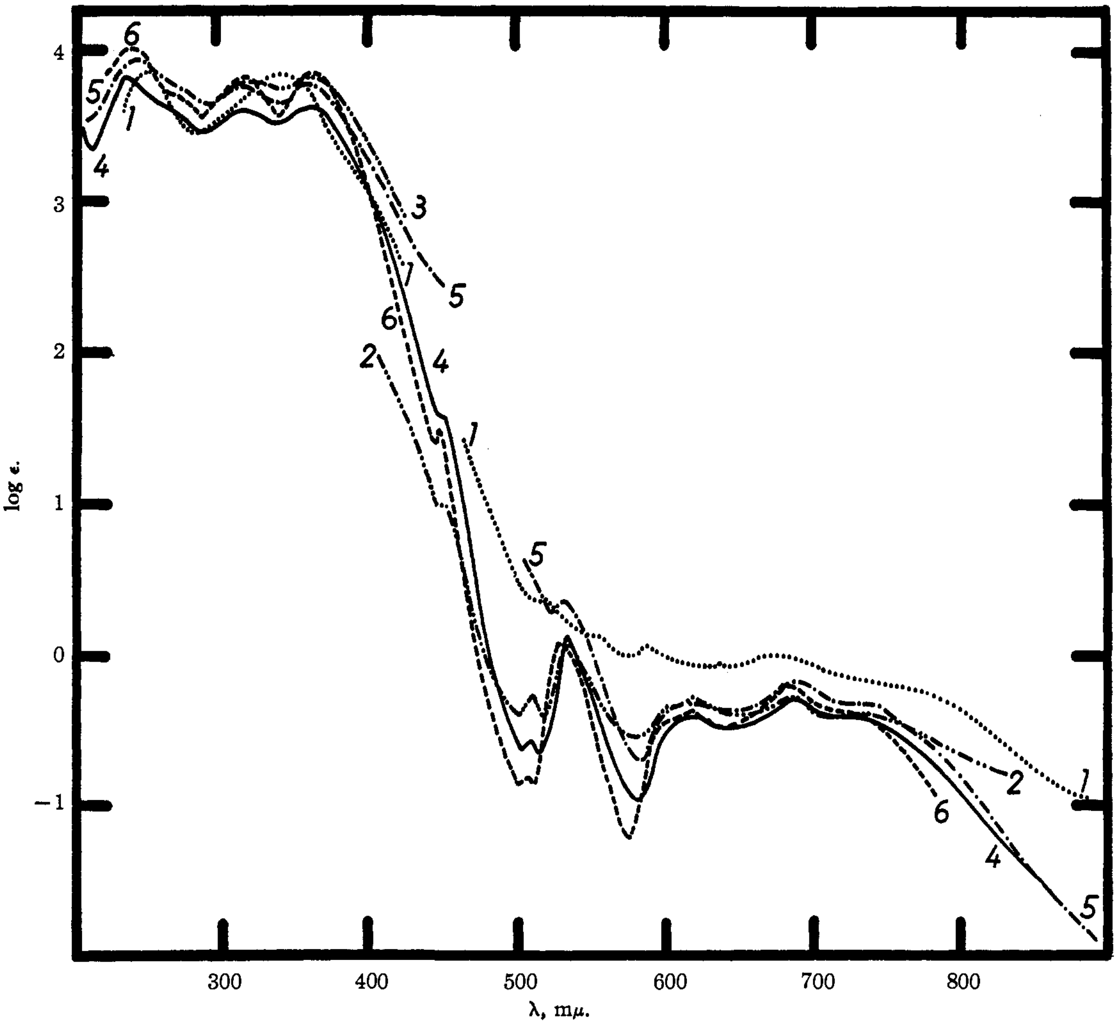

Fig. 1.—Ultraviolet and visible absorption spectra: curve 1, ultraviolet portion, $FeCl_3$ in diisopropyl ether,[14] visible portion, $FeCl_3$ in diethyl ether; curve 2, solid $KFeCl_4$; curve 3, $KFeCl_4$ in ethylene bromide; curve 4, $KFeCl_4$ in diethyl ether; curve 5, ultraviolet portion, $FeCl_3$ in 11.7 *M* aqueous hydrochloric acid[14]; visible portion, $FeCl_3$ in 16 *M* aqueous hydrochloric acid; curve 6, $HFeCl_4{\cdot}4.5H_2O$ in diisopropyl ether.[14] The ordinate of curve 2 is not the log of the molar extinction, but has been derived from the optical density measurements as described in the text.

it was stored for two months in the stoppered spectrophotometer cell.

The absorption curve from 500 to 900 mμ for solid $KFeCl_4$ in Fig. 1 was obtained in the following way. First 0.75 was subtracted from each of the observed optical densities of one sample to obtain optical densities corrected for the background absorption. The amount of this correction was chosen to give zero corrected optical density at 900 mμ, *i.e.*, where absorption is low in the other $FeCl_4^-$ spectra. The logarithm of the corrected optical density was then plotted on the same scale as the other curves of Fig. 1, and finally the scale of ordinates was moved vertically to cause this plot of the solid $KFeCl_4$ spectrum to coincide with the plot of the $KFeCl_4$-ether spectrum at 534 mμ. This adjustment was made to facilitate comparison with the other spectra and amounts to an assignment of the unknown product of molar concentration and path length in the solid $KFeCl_4$ sample. The absorption curve from 400 to 500 mμ for solid $KFeCl_4$ in Fig. 1 was obtained from the spectrum of a thinner sample of $KFeCl_4$ by plotting $a + \log (D + b)$, where D is the observed optical density of this sample, and a and b are constants independent of wave length and chosen to give good fit in the region of overlap, 470–500 mμ, of this spectrum and that of the thicker sample.

No maxima or minima were observed in suspensions of finely powdered $KFeCl_4$ in mixtures of nujol and vaseline or in the dry powder. A search was made for absorption bands not only in the visible and ultraviolet but also in the infrared to wave lengths as high as 20 μ. For the infrared work, a Perkin-Elmer infrared spectrophotometer was employed and the powdered samples were mounted between AgCl or KBr windows both with and without a nujol medium. No absorption maximum not characteristic of the suspension medium was found. However, the opacity of all of these samples was high, and it is possible that the failure to find absorption maxima in powdered samples in the visible as well as in the infrared is due to the high degree of scattering of the light beam by the powder.

Ferric chloride in 16 *M* HCl.—A magnetic stirrer and a solution of ferric chloride in hydrochloric acid were introduced into the flask of a type B cell assembly. Purified HCl at a pressure of 28 p.s.i.g. was next introduced and after the solution had been stirred until it was saturated, the assembly was sealed off.

Solubilities.—The solubilities of a number of compounds in ether and ethylene bromide at room temperature have been determined. These values are presented in Table I.

$CsFeCl_4$ very slowly reacts with ether according to the equation

$$3CsFeCl_4(c) = Cs_3Fe_2Cl_9(c) + FeCl_3(soln.).$$

A striking color change of the solid from yellow to red accompanies this reaction. The sharp color change progresses slowly from the top to the bottom of the layer of $CsFeCl_4$

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[14] These data are taken from the paper of Metzler and Myers, ref. 12.

TABLE I

Salt	Solvent	Solubility, moles/liter
$KFeCl_4$	Ether	2.7
NH_4FeCl_4[a]	Ether	2.2
$CsFeCl_4$	Ether	<0.003
$KFeCl_4$	Ethylene bromide	0.0001
LiI[a]	Ether	3.7
NaI	Ether	<0.001
LiI	Ethylene bromide	<0.001

[a] Solid phase analyzed, not a solvate.

being extracted by ether running downward through it, showing that this process is slow because of an unfavorable equilibrium. Two preparations of the red crystals were analyzed. Found: Cl, 38.8, 38.1; Fe, 13.4, 13.4. Calcd. for $Cs_3Fe_2Cl_9$: Cl, 38.50; Fe, 13.40.

Results and Interpretation

The results of the spectrophotometric measurements are presented in Fig. 1 and Table II.

TABLE II

DECADIC MOLAR EXTINCTION COEFFICIENTS AT ABSORPTION MAXIMA IN $FeCl_4^-$ VISIBLE SPECTRA

Solvent	Solute	Concentration, moles/liter	ϵ_{456}	ϵ_{509}	ϵ_{534}	ϵ_{619}	ϵ_{688}	ϵ_{725}
$(C_2H_5)_2O$	$KFeCl_4$	2.74[d]	..	0.30	1.1	0.43	0.58	0.42
		1.47[a]	..	.29	1.2	.42	.57	.42
		1.26[c]	..	.28	1.4	.46	.63	.45
		1.23[a]	..	.57	1.3	.41	.57	.42
		0.155[a]	..	.34	1.1	.39	.53	.38
		.084[a]	31	.57	1.3	.44	.59	.41
		.017[a]	32	..	1.3	..	..	..
		.0037[c]	36	..	..	..	..	..
		.0030[b]	30	..	..	..	..	..
$(C_2H_5)_2O$	NH_4FeCl_4	.168	..	..	1.4	.52	.72	..
		2.24	..	.39	1.3	.50	.60	.44
16 *M* aq. HCl	$FeCl_3$	0.68	..	..	2.3	.49	.67	.47
$(i\text{-}C_3H_7)_2O$ extract	$HFeCl_4$	.3–0.6[e]	32	.15	1.31	.41	.62	.46

[a] Series I. [b] Series II. [c] Series III. [d] Series IV. [e] Metzler and Myers, ref. 12.

Comparison of curves 4 and 6 of Fig. 1 indicates that $FeCl_4^-$ is the light absorbing species in both of these systems. This conclusion is supported by the Beer's law studies on the isopropyl ether extracts[4,12] and on the anhydrous solutions (Table II). It is also supported by the fact that iron-containing solutions which by virtue of their composition are not expected to contain $FeCl_4^-$ ions have very different spectra, *e.g.*, curve 1 of Fig. 1, and the spectrum of the Fe^{+++} aq. ion in strong perchloric acid.[15] Conversely then, curve 4 or 6 is typical of the $FeCl_4^-$ ion and not of Fe(III) compounds in general.

Curve 2 resembles the visible part of the $FeCl_4^-$ spectrum very much and this implies that solid $KFeCl_4$ contains $FeCl_4^-$ ions. The most probable alternative is that the coördination number of Fe in $KFeCl_4$ is six and the solid consists of layers of $FeCl_6$ octahedra sharing corners, and the K^+ ions are between the negative layers (*e.g.*, the $TlAlF_4$ structure[16]). Now in order for $KFeCl_4$ to have the same spectrum in the solid and in ether solutions, either (1) in both phases the iron is disposed in discrete $FeCl_4^-$ ions and has coördination number four, (2) in both phases the iron has coördination number six, toward six chlorine atoms in the solid and toward four chlorine atoms plus two oxygen atoms of the solvent in solution, or (3) the spectrum is not sensitive to the coördination number of the iron. It is believed that the close similarity of the spectra makes the second alternative far less likely than the first and that the third alternative is less likely still. This conclusion would be more definite if the ultraviolet spectrum of the solid were known as well. This could not be obtained, so as an alternative, the ultraviolet spectrum of $KFeCl_4$ in ethylene bromide solution was studied. In order to have coördination number six in this solution, the iron atom must coördinate two bromine atoms from the solvent in addition to the four chlorine atoms of the $FeCl_4^-$ ion. Again the spectrum (curve 3) is similar to curve 4.

It is not to be expected that substitution of halogen for oxygen would leave the spectrum entirely unchanged and the wide range of wave lengths and large number of absorption bands compared leave little possibility that the spectral region studied just happens to be insensitive to these changes. This possibility is also diminished by the fact that the absorption maximum at 588 mμ for $FeCl_3$ in diethyl ether reported here does not appear in the spectrum of $FeCl_3$ in isopropyl ether.[4] Therefore, the best interpretation of Fig. 1 is that curves 2, 3, 4 and 6 are characteristic of systems containing discrete $FeCl_4^-$ ions, not solvated in the first coördination sphere.

Kato and Ishii[2] and Metzler and Myers[12] noted the great resemblance of the spectra of the ether extracts and the spectrum of Fe(III) in concentrated aqueous HCl. Curve 5 of Fig. 1 is a composite of the ultraviolet spectrum of Fe(III) in 12 *M* aqueous HCl, and the visible spectrum of Fe(III) in 16 *M* aqueous HCl. The agreement with curve 4 and 6 is good except between 400 and 520 mμ. In the visible spectrum of 11.5 *M* aqueous HCl[15] the onset of the intense absorption leading into the ultraviolet appears at 580 mμ and obscures the 532 mμ peak but the visible spectrum is otherwise identical with curve 5. This confirms the interpretation of Metzler and Myers that small amounts of $FeCl_3$·aq. in equilibrium with the $FeCl_4^-$ in 12 *M* aqueous HCl solution absorb light

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(15) A. Kiss, J. Abraham and I. Hegedus, *Z. anorg. allgem. Chem.*, **244**, 98 (1940).

(16) C. Brosset, *ibid.*, **235**, 139 (1937).

strongly enough in the region 400–580 mμ to obliterate the low intensity $FeCl_4^-$ spectrum in this region. Increase from 12 *M* HCl to 16 *M* HCl shifts the equilibrium

$$FeCl_3 + Cl^- \rightleftarrows FeCl_4^-$$

just far enough to the right to reveal the 532 mμ peak of the $FeCl_4^-$ in the spectrum. This requires a threefold increase in the HCl activity (from 1 to 3 atmospheres) so it will not be easy to reduce the $FeCl_3$ concentration far enough to reveal the smaller 510 and 450 mμ peaks in aqueous solution as well. However, it seems certain that in concentrated aqueous HCl the principal trivalent iron species is $FeCl_4^-$ with coördination number four for iron.

Measurements of the magnetic susceptibility of the isopropyl ether extracts of $HFeCl_4$[12] and of solid $CsFeCl_4$[17] show that iron in these compounds has 5 unpaired electrons. Therefore, the $FeCl_4^-$ ion is probably tetrahedral (sp^3 or association complex). Only three unpaired electrons are expected for a square planar (dsp^2) $FeCl_4^-$ion.

Discussion

In this section it will be shown that the conclusions regarding the existence of $FeCl_4^-$ ions in the systems studied are consistent with other observations upon these systems.

(1) It has been suggested[7] on the basis of the constancy of melting points in the series NH_4AlCl_4, NH_4FeCl_4, NH_4GaCl_4 (m.p. 300 ± 5°), that the coördination number of the M''' atom is four in each of these substances. The argument was that $FeCl_3$ has the almost same structure[18] as $AlCl_3$[19] with coördination number six for the metal atom, but these compounds have widely different melting points (300° and 190°, resp.). Much smaller differences are expected in the series above only if the solids have similar structures, if the coördination number of the metal atom is four so that the metal–chlorine bonds need not be broken in the melting process, and if the complex anions have similar dimensions. The data on the molar volumes of the $NH_4M'''Cl_4$ salts indicate that this last condition is fulfilled. In the same way the observations that $KAlCl_4$, $KFeCl_4$ and $KGaCl_4$ melt at 255 ± 5° and $CsAlCl_4$, $CsFeCl_4$ and $CsGaCl_4$ melt at 380 ± 5° indicate that each of these solids is composed of M'^+ ions and $M'''Cl_4^-$ ions.

Furthermore, $KFeCl_4$, $CsFeCl_4$, NH_4FeCl_4, $HFeCl_4 \cdot 2Et_2O$[9] and $HFeCl_4 \cdot 2H_2O$[20] are all yellow or yellow-green while $FeCl_3$, in which iron has coordination number six to chlorine is red[21] and Cs_3FeCl_6,[22] and $Cs_3Fe_2Cl_9$, in which iron probably has coördination number 6 to chlorine are bright red. There thus seems to be good correlation between the coördination number of the iron and the color of the salt.

(2) The retention by the iron atom in the chloroferrate ion of coördination number four in solution as well as in the crystals of chloroferrate implies that "chemical" forces or "covalent" bonds are not operative between this ion and the solvent. Since covalent bond formation between potassium ion or ammonium ion and the solvent is not expected either, it should be possible to explain the high solubility of $KFeCl_4$ and NH_4FeCl_4 in ether in terms of the electrostatic forces operative between the ions in the crystals and between the ions and solvent in solution. Calculations of the sort required here have been made only for the alkali halides and aqueous solution[23] and cannot at present be made for the systems of primary interest here because of lack of data. Therefore, the solubilities of the chloroferrates will be compared with those of some of the alkali halides for which at least the lattice energies are known. The solubility data are presented in Table I. It is clear that in both series of compounds ether solubility falls off sharply with increasing ionic dimensions and that solubility is much smaller in ethylene bromide than in ether, although both solvents have the same dielectric constant (4.5) and molecular dipole moment (about 1.3 debye). Some idea as to the origins of these effects may be obtained by considering the free energy of solution as the difference between the free energy of formation of the crystal from the gaseous ions and the free energy of solvation of the gaseous ions at the same concentration.

The free energies of solution in water of all of the alkali halides have been successfully correlated on an electrostatic basis,[23] indicating that for all of these ions the contribution of covalent bond formation with the solvent water to the solvation energy is small. There is no reason to believe that solvation in ether will be much different in this respect even with lithium ion. First of all, substitution of ethyl groups for hydrogen is not expected to increase the polarizability of oxygen or otherwise increase its ability to form a covalent bond with a metal ion, and, secondly, even the *fraction* of the solvation energy of metal ions which is due to covalent contributions will not be much larger for ether than for water because the electrostatic part of the solvation energy, given by the Born equation,[24] $\Delta F = -Z^2(1 - 1/D)/2r_e$,[24] is about 80% as great for ether as for water.

The difference between the free energy of formation of the crystal lattice from the (hypothetical) 1 *M* gaseous ions at 298° and ΔH for this same process ($-\Delta H$ = lattice energy) is the same (12 ± 1 kcal.) for all of the alkali halides so lattice energy may be considered instead of free energy of formation of the lattice from the ions in seeking the factors which govern solubility. As the ratio of the radii of cation to anion of an alkali halide decreases below unity at constant radius sum, the lattice energy first remains about constant and then

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[17] Unpublished work in this Laboratory.

[18] N. W. Gregory, THIS JOURNAL, **73**, 472 (1951).

[19] J. A. A. Ketelaar, C. H. MacGillavry and P. A. Renes, *Rec. trav. chim.*, **66**, 501 (1947).

[20] M. Engel, *Compt. rend.*, **104**, 1708 (1887).

[21] O. Hönigschmidt, L. Birckenbach and R. Zeiss, *Ber.*, **56**, 1473 (1923).

[22] P. T. Walden, *Z. anorg. u. allgem. Chem.*, **7**, 331 (1894).

[23] W. M. Latimer, K. S. Pitzer and C. M. Slansky, *J. Chem. Phys.*, **7**, 109 (1939).

[24] ΔF, free energy of solvation of gaseous ion; Z, charge on ion; D, dielectric constant of solvent; r_e, radius of cavity made by ion in the solvent.

decreases quite sharply,[25] but the sum of the magnitudes of the solvation energies of the gaseous ions increases steadily (application of the Born equation). Thus a salt tends to be more soluble the more its radius ratio differs from unity. On the other hand, at constant radius ratio the difference between the lattice energy and sum of ionic solvation energies of an alkali halide is independent of the sum of the ionic crystal radii if $0 = r_e - r_c$ (r_c = crystal radius of ion). However, $r_e - r_c$ may be interpreted[23] as the distance from the surface of a solvated ion to the center of charge of the nearest solvent molecule and is therefore greater than zero. This causes the solubility of an alkali halide to tend to become larger with increasing radius sum but the solubility is much less sensitive to radius sum than to radius ratio for any reasonable choice of parameters for ether solutions.

These considerations indicate that the high ether solubility of lithium iodide is a result of the small value of its radius ratio (0.28) compared to that of sodium iodide (0.44). The relatively small solubility of lithium iodide in ethylene bromide is due to a considerably larger value of $r_e - r_c$ for this solvent compared to ether, a difference which is reasonable in view of the large size of a bromine atom compared to an oxygen atom. The estimated radius ratio of $KFeCl_4$ is 0.33 and that of $CsFeCl_4$ is 0.42, but it is not clear how well the equation for the crystal energy of an alkali halide may be expected to apply to a crystal containing complex ions. A similar trend in ether solubility observed in the series $KGaCl_4$,[7] $RbGaCl_4$,[17] $CsGaCl_4$[7] confirms the interpretation presented here but more extensive data on the solubilities of the alkali halides in various solvents and on the deviations from ideality of the resulting solutions are needed to test this theory.

(3) The similarity in properties of the $HM'''Cl_4$ ether extracts and the anhydrous $M'M'''Cl_4$ solutions suggests that the solute in the ether extracts is disposed in ion pairs and clusters as it is in anhydrous solution.[10] This is in accord with the apparent polymerization of the solute as its concentration increases,[6,8] but offers no clue to the separation of some of the extracts into two ether phases. The similarity of the spectra of the two ether phases of the isopropyl ether extracts[7] and the similarity of the spectra of the two liquid phases in anhydrous NH_4FeCl_4 solutions indicate that the phase separations do not correspond to structural changes in the solute.

If the extracted species, say $H_3O^+FeCl_4^-$, exists as ion pairs in the extract and as free ions in the aqueous phase, the efficiency of extraction may be expected to be determined by, (1) those properties of the extracting medium which make it a good solvent for anhydrous salts, *i.e.*, large dielectric constant, nearness of centers of electric charge to surface of molecule, and large molecular dipole moments, and (2) the immiscibility of the solvent with concentrated aqueous HCl. At any rate, it does not seem that ability to extract efficiently $HFeCl_4$ or $HGaCl_4$ ought to be a property peculiar to ethers if the constitution of the extracts here proposed is correct.

In a series of preliminary experiments it has been found that Fe(III) extracts from 12 *M* aqueous hydrochloric acid into benzene, ethylene chloride, benzonitrile, nitrobenzene, thiophene and nitromethane and that in each case the accessible portion of the spectrum is identical with the corresponding portion of the $FeCl_4^-$ spectrum of Fig. 1. At equilibrium the ratio of molarity of iron in the organic phase to that in the aqueous phase varies from the order of 10^{-5} for benzene to 10 for nitromethane. It would be of interest to analyze these extracts for water to see how important a role the coextracted water plays in determining the efficiency of extraction.

(4) The evidence presented in this paper for the existence of $FeCl_4^-$ ions with coördination number four for iron in aqueous solution poses a problem regarding the coördination number of other labile ferric complexes. In ferric alums, Fe^{+3} has six coördinated water molecules, but there is at present no evidence as to where in the following series of ferric complexes the coördination number of the iron changes from six to four: $Fe(H_2O)_6^{+3}$ (in alum), Fe^{+3} (aq.), $FeCl^{+2}$ (aq.), $FeCl_2^+$ (aq.), $FeCl_3$ (aq.), $FeCl_4^-$ (aq.).

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(25) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940; equations 43-5 and 45-4.