The Freezing-point Curve for Sulfur Trioxide.—The data of Hammett and Deyrup[7] and Brand[8] show that the molar freezing-point depression for sulfur trioxide in sulfuric acid is nearly constant; the slope of the line corresponds to about 1.3 moles of new substance for each mole of added sulfur trioxide. This slope is constant as far as the measurements were made—to about 0.5 *M*. If pyrosulfuric acid were formed but incompletely ionized, the curve should have a slope of nearly two in dilute solution and curve upwards, approaching a slope of one. The observed effect is not in accord with the ideas presented, and no explanation can as yet be offered.

Acknowledgment.—The author wishes to express his indebtedness to the later Professor W. C. Bray, under whose direction this research was begun, and to Professor W. M. Latimer, who undertook the direction of the work after Professor Bray's death in 1946.

Summary

1. The conductivities of fuming sulfuric acid have been redetermined and the results compared with those of previous authors.

2. The effect of added potassium bisulfate on the conductivities of solutions of water and sulfur trioxide in sulfuric acid has been studied. The evidence from water solutions substantiates prior evidence that water is highly ionized in this solvent. The studies in fuming sulfuric acid can be interpreted qualitatively as showing that pyrosulfuric acid is a weak acid in sulfuric acid, and that its neutralization by bisulfate ion does not proceed to completion except in the presence of an excess of one of the reactants.

3. The autoprotolysis constant for pure sulfuric acid has been estimated by several methods. The agreement between these methods is cited as evidence that the dissociation of pure sulfuric acid is due chiefly to the autoprotolysis reaction.

ITHACA, N. Y. RECEIVED DECEMBER 6, 1949

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Solutions of Ammonium Chlorogallate in Diethyl Ether

BY HAROLD L. FRIEDMAN[1] AND HENRY TAUBE

In a previous paper[2] the high solubility in ether of some compounds of the type $M'M'''Cl_4$ was noted. It was shown that NH_4GaCl_4, NH_4FeCl_4, and NH_4AlCl_4 distribute themselves between the solid phases and the saturated solutions in ether without change in composition. However, some other compounds of this type, including $LiGaCl_4$, change their composition when treated with ether. The saturated ether phase being enriched in $M'''Gl_3$ relative to $M'Cl$. The present investigation was undertaken in order to learn something of the constitution of the solute in these solutions. The general features of the behavior of electrolytes in solvents of low dielectric constant have been explored by C. A. Kraus, R. M. Fuoss and co-workers.[3] It seemed of interest to make comparisons between the present systems and those studied by Kraus[4] because of the relatively small size and simple character of the cations and the relatively complex nature of the anions in the present systems. The results would appear to have a direct bearing also on the extraction of iron and gallium by ether from aqueous hydrochloric acid solutions of Ga(III) and Fe(III). These elements are taken up into the ether phase as $HFeCl_4$[5] and $HGaCl_4$[6] (with a rather large number of water molecules) and presumably exist in ether as the etheronium or hydronium compounds. In composition they therefore resemble NH_4GaCl_4, and their behavior in ether solutions can be expected to show resemblances to that of NH_4GaCl_4.

Results

Two-Phase Liquid Region.—When the concentration of the solute NH_4GaCl_4[7] in ether is increased at constant temperature, a composition is reached at which a new liquid phase appears. Further increase in concentration causes the solute-rich phase to grow at the expense of the other; finally, only the solute-rich phase is left, which then increases in concentration until it is saturated with solute. Analyses were made of the two co-existing liquid phases with the results as reported in Table I.

TABLE I

	Upper phase	Lower phase	
Density, g./ml.	0.75	0.82	±0.02
Atoms Cl/atoms N	3.99	4.00	± .01
Concn., molality	0.45	0.88	± .05

---

[1] Department of Chemistry, University of Southern California, Los Angeles 7, California.

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

[3] *Cf.* review by C. A. Kraus, *J. Franklin Inst.*, **225**, 687 (1938).

[4] Kraus, *et al.*, studied as solutes salts of the type tetraalkylammonium or trialkylammonium halide, nitrate, perchlorate, thiocyanate, or picrate. Solutions of silver perchlorate in benzene were also studied but there is evidence for a stable complex between silver ion and benzene: A. E. Hill, THIS JOURNAL, **44**, 1163 (1922); L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949).

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

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

[7] The preparation, purification, and precautions in handling of the materials were described in the previous paper.

These data show that the solute maintains the composition NH_4GaCl_4 in each of the liquid phases. The composition of each of the phases can therefore be expressed in terms of two components and the system with the two liquid phases and the vapor in equilibrium is monovariant. An interesting feature to note for the system is that the immiscible phases are both rather dilute, the more concentrated being only 0.9 molal in solute, or 6 mole per cent. solute.

Two liquid phases have been observed to coexist also for solution in ether of each of the solutes: NH_4FeCl_4, NH_4AlCl_4 and $LiGaCl_4$. Some other examples of this behavior for polar solutes in solvents of low dielectric constant have been reported in the literature.[8]

Association of NH_4GaCl_4 in Ether.—The fact that NH_4GaCl_4 distributes itself between two liquid phases without change in composition is strong evidence that it does not dissociate appreciably into neutral molecules. Further information about the state of aggregation of the solute in ether solutions has been gained from studies of the vapor pressure of the solvent using the isopiestic method for making the measurements.

Experimental

A solution containing a known weight of NH_4GaCl_4 was allowed to come to vapor-pressure equilibrium at constant temperature with a solution containing a known amount of benzil. The apparatus was a modification of that described by Signer.[9] The approach to equilibrium could be followed by observing the changes in volume of the solutions, and the attainment of equilibrium verified by distilling a small amount of solvent from one side to the other, so as to observe the approach to equilibrium from the opposite direction. Figure 1 presents the kinetic data for one particular composition for the system. At lower concentrations of solute, longer times are required for attainment of equilibrium. Thus in an experiment at concentration about half of that of the most dilute solution represented in Fig. 2, equilibrium was not attained even after many weeks. In all cases the solutions were stirred by rocking the cell. The weight concentrations of the solutions at equilibrium were calculated from their volumes and densities, the weights of solute in each being known. Published values of the densities of solutions of benzil in ether were used,[10] and densities were measured at a few concentrations for NH_4GaCl_4 in ether. In a number of cases, the concentrations were checked by direct analysis and agreed with those derived from the volume measurements to within 1%. In no case was there transfer of chloride to the benzil side of the cell.

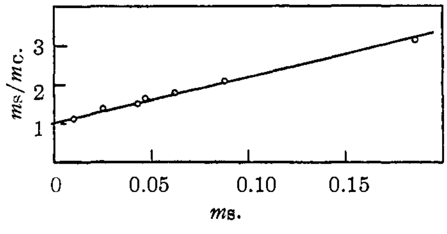

Fig. 1.—Association of ammonium chlorogallate in ether solution as a function of concentration.

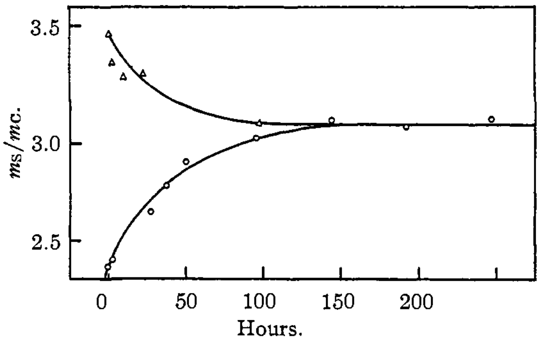

Fig. 2.—Approach to equilibrium.

If the solutions of benzil in ether may be regarded as ideal, the ratio m_s/m_c (where m_s is the stoichiometric molality of the NH_4GaCl_4 solution and m_c the molality of the benzil solution in equilibrium with it) is a measure of the state of aggregation of the solute NH_4GaCl_4. The assumption that the benzil solutions are ideal over the concentration range covered by our measurements is supported by data obtained by Beckmann[11] on the boiling point elevations produced in ether by benzil at various concentrations. The accuracy of Beckmann's data is of the order of 10% in $\Delta T/m$, judging by the internal consistency of these data, and they agree with Raoult's law within this rather large margin. A calculation[12] using Hildebrand's equation[13] relating departures from ideal behavior to differences in molal volume and internal pressures of the two components also supports the assumption that the benzil solutions are nearly ideal (within 6%) over the concentration range in which they were used.

The data obtained at 25° for m_s/m_c for NH_4GaCl_4 in ether are presented in Fig. 2. Evidently marked departures from ideality are observed even in fairly dilute solution, the apparent degree of association of the solute being about 3 at a concentration of 0.15 molal. This behavior is similar to that observed in a number of systems studied by Kraus and co-workers.[14]

The Electrical Conductivity of Solutions of NH_4GaCl_4 in Ether.—Fuoss and Kraus[3] have explored the electrolytic behavior of highly polar substances in a number of solvents of low dielectric constant. It seemed of interest to obtain data also for the solvent ether with NH_4GaCl_4 as the electrolyte, and the conductances of such solutions were measured at a number of concentrations.

Experimental.—Specific conductances were measured in special cells which could be attached to a vacuum system for filling with solvent. The data of curve II in Fig. 3 were obtained with an improved model of the first cell and are probably more reliable. In the second series of experiments, all concentrations were determined by weighing, and the density of the solution was assumed equal to that of pure ether. No correction was made for the specific conductance of the solvent, which was a thousandth that of the most dilute solution. Solvent conductance was measured by a d. c. arrangement; the other conductances were measured on a modified Jones bridge at 500 c. p. s.

---

[8] $AgClO_4$ in benzene, A. E. Hill, THIS JOURNAL, **44**, 1163 (1922); Na in ammonia, C. A. Kraus and W. W. Lucasse, *ibid.*, **44**, 1949 (1922).

[9] R. Signer, *Ann.*, **478**, 246 (1930).

[10] D. Tyrer, *J. Chem. Soc.*, **97**, 2630 (1910).

[11] E. Beckmann, *Z. physik. Chem.*, **63**, 197 (1908).

[12] H. L. Friedman, Ph.D. Dissertation, University of Chicago, 1949.

[13] J. H. Hildebrand, *Chem. Rev.*, **44**, 37 (1949).

[14] D. A. Rothrock, Jr., and C. A. Kraus, THIS JOURNAL, **59**, 1699 (1937).

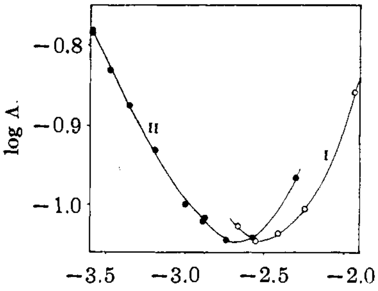

Fig. 3.—Equivalent conductance of solutions of ammonium chlorogallate in ether.

The results obtained are shown in Fig. 3. The minimum in the equivalent conductance as a function of concentration is also found in the systems studied by Fuoss and Kraus. Their theory of this phenomenon makes it possible to calculate the ionic dissociation constant of the solute from the location of the minimum and the limiting equivalent conductance of the ions carrying the current. Assuming that the limiting equivalent conductance of the electrolytes is 100, the equilibrium constant k for its dissociation into ions can be calculated as 10^{-9}. The value of the product $(-\log k)D$ (where D, the dielectric constant, is 4.7) for the present system is about 42. It appears from the work of Fuoss and Kraus that for a large number of electrolytes in solvents of D less than 10, this product has values between 39 and 46.

Further discussion of these results in terms of the theory of Fuoss is possible, but not justified because of the uncertainties in the data and in the nature of the ions which carry the current.

General Discussion

The experiments have shown that the general behavior of NH_4GaCl_4 with respect to association and electrolytic dissociation resembles that of other highly polar substances in solvents of low dielectric constant. The information gained is important in understanding the properties of such solutions. Its usefulness in formulating a detailed picture of the solute in the solvent is, however, limited. Answers are sought to such questions as: Is the solute converted to solvated ions which then associate in pairs, etc., or is there direct ion–ion contact in the associated forms? What is the nature of the solute–solvent interaction in the first sphere? The conductivity is rather insensitive to the energy and mode of interaction in the first sphere, presumably because the particles involved in the phenomenon remain largely solvated. The importance of the specific solute–solvent interactions (which will be most important in the first sphere) is demonstrated by considering the solubility of a particular polar substance in a variety of solvents. Enormous differences in solubility are observed using solvents of appreciably the same dielectric constant, but different molecular properties.

Acknowledgment.—This research was supported by funds from the Office of Naval Research under Contract No. N6ori, Task Order No. XVI.

Summary

The behavior of ammonium chlorogallate in ether has been investigated. In a certain range of compositions, two liquid phases co-exist in the system. Association of the solute was studied by the isopiestic method, and electrolytic dissociation by measurements of conductance.

LOS ANGELES, CALIFORNIA RECEIVED JANUARY 20, 1950

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

X-Ray Diffraction and Melting Point–Composition Studies on the 9,10-Epoxy- and Dihydroxystearic Acids and 9,10-Epoxyoctadecanols[2]

BY LEE P. WITNAUER AND DANIEL SWERN

This paper reports the results of X-ray diffraction and melting point–composition studies on the isomeric 9,10-epoxy- and dihydroxystearic acids, and the isomeric 9,10-epoxyoctadecanols. The need for such an investigation arose from two independent lines of work being pursued in our laboratory. First, it was desired to use X-ray diffraction methods to obtain direct proof of the validity of certain conclusions regarding the stereochemistry of some of these long-chain compounds.[3] Second, a means of analyzing mixtures of isomeric pairs would be of value in studies of the mechanism of the reaction of oleic acid, methyl oleate, and oleyl alcohol (and their *trans* isomers) with oxygen,[4] since mixtures of isomeric 9,10-epoxy compounds and 9,10-dihydroxy compounds are obtained which can be positively identified at present only after numerous fractional crystallizations, and isolation of the individual products. Naturally, in such a purification procedure, loss of product occurs, much time is consumed, and the product most readily isolated is the less soluble of a given isomeric pair, the other isomer usually being isolated in poor yield, if at all.

As is well known, melting point–composition diagrams have been used to determine the composition of binary mixtures. The technique is simple and convenient, and in many cases the

---

[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

[2] This paper is number XI in the series, Chemistry of Epoxy Compounds. For paper X, see THIS JOURNAL, **71**, 3849 (1949). This paper was presented at the 117th Meeting of the American Chemical Society, Philadelphia, Pa., April 9-13, 1950.

[3] Swern, *ibid.*, **70**, 1235 (1948).

[4] Knight and Swern, *J. Am. Oil Chem. Soc.*, **26**, 366 (1949).