depression curve, as compared to that of the corresponding strontium compound, is in accord with the hypothesis advanced above that the solute is at least partially in the form of aggregates of considerably larger than molecular dimensions.

Summary

1. The solubility of strontium acetate in pure acetic acid has been determined over a wide range of temperatures, and is found to be intermediate between those of the corresponding barium and calcium salts.

2. The solubility of nickel acetate in acetic acid at 30°, as well as the composition of the solid phase in equilibrium with the solution, is found to be variable. This anomalous behavior is attributed to the presence of colloidal constituents.

3. In the presence of high concentrations of ammonium acetate, the solubility of nickel acetate is found to decrease with increasing concentration of ammonium salt.

4. Two new compounds, $Sr(C_2H_3O_2)_2 \cdot HC_2H_3O_2$ and $Ni(C_2H_3O_2)_2 \cdot NH_4C_2H_3O_2 \cdot 2HC_2H_3O_2$, have been isolated and analyzed.

5. The freezing point depression curves of several acetates in acetic acid have been compared with the curve for an ideal solute, and their deviations therefrom have been discussed.

LAWRENCE, KANSAS

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Properties of Electrolytic Solutions. VI. Conductance of Sodium Triphenylstannide, Sodium Triphenylgermanide and Sodium Triphenylmethide in Liquid Ammonia[1]

BY CHARLES A. KRAUS AND W. HARLOW KAHLER[2]

I. Introduction

In the preceding paper of this series, values were given for the conductance of various salts in which nitrogen functioned as central element of the negative ion. The constitution of such ions may be modified by means of two substituent groups attached to the nitrogen atom. It seemed of interest to study corresponding ions of the elements of the fourth group, which form anions of the type R_3A^-, where R is an organic group or hydrogen. The salts of these ions are readily soluble in liquid ammonia and are appreciably soluble in ether and other similar solvents. Excepting the derivatives of tin and lead, the salts are stable in the pure state. Since

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[1] This and the preceding paper of this series formed the subject matter of the Edgar F. Smith Birthday Lecture delivered by the senior author at the University of Pennsylvania, May 23, 1930.

[2] Metcalf Fellow in Chemistry in Brown University.

an ion of this type has a very weak affinity for its charge electron, it is readily oxidized by more electronegative elements, including oxygen.

The salts may be looked upon as derivatives of extremely weak acids, R_3AH, and they, therefore, react readily with most protonic solvents. Fortunately, liquid ammonia is a very weak ammonolyzing agent and solutions of these salts are usually stable in this solvent. With the exception of silicon, salts of the type of sodium triphenylmethide are not ammonolyzed under ordinary conditions.

Sodium triphenylmethide is most conveniently prepared by the action of the sodium amide upon triphenylmethane. Reaction takes place according to the equation $(C_6H_5)_3CH + NaNH_2 = (C_6H_5)_3CNa + NH_3$. A similar reaction does not take place in the case of the corresponding derivatives of silicon, germanium or tin. The alkali metal salts of triphenylgermanium and triphenyltin may be prepared by the direct action of the metal upon the corresponding free groups in liquid ammonia.

Schlenk and Marcus[3] have shown that sodium triphenylmethide is a conductor in ethereal solution. Foster[4] carried out preliminary measurements of the conductance of sodium triphenylgermanide in liquid ammonia. Wooster[5] carried out similar measurements with sodium triphenylgermanide, triphenylmethide, and triphenylstannide. These measurements indicated that salts of this type are exceptionally good electrolytes.

We have measured the conductance of these salts in liquid ammonia in the hope of obtaining data that would be sufficiently accurate to enable us to calculate their dissociation constants. Unfortunately, solutions of these salts show signs of instability at low concentrations. Of the three salts, sodium triphenylstannide proved the most stable and sodium triphenylmethide the least. From our measurements we have been able to approximate the dissociation constant of sodium triphenylstannide.

II. Apparatus and Procedure

The general procedure was much the same as that of Kraus and Hawes.[6] The solutions were made up in the conductivity cell, the materials being sealed in fragile glass bulbs which were broken as needed. The ammonia introduced into the cell was measured in a pipet, and the amount of solution withdrawn from the cell was determined by weight after evaporation and absorption in water. The conductance cell differed from that of Kraus and Hawes and is described below.

The cell consisted of a cylindrical tube A (Fig. 1), which was closed at the top by means of a ground-glass stopper through which passed the stem B, carrying the electrode system C. The stem was movable through the slip-joint D. The platinum wire leads EE (Figs. 1a and 1b) were sealed through the end of the stem and were soldered to copper wire leads passing up through the stem B. In order to render the constant of the electrodes independent of their position in the cell, they were surrounded by a housing F, which was provided with small openings GG at top and bottom

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[3] Schlenk and Marcus, *Ber.*, **47**, 1678 (1914).

[4] Foster, Thesis, Brown University, 1926.

[5] Wooster, Thesis, Brown University, 1928.

[6] Kraus and Hawes, THIS JOURNAL, **55**, 2776 (1933).

to allow free flow of the solution past the electrodes. The cell was emptied by withdrawing the solution through the capillary tube H. This tube also served as stirring tube, ammonia vapor being passed through it by means of a modified Toepler pump I, similar to that used by Kraus and Hawes. Solution was withdrawn through the capillary J, which left a determinable quantity of solution in the cell. The solution passed through a special stopcock K into the receiver as described by Kraus and Hawes. Stopcocks L and M were used to equalize the pressure between the withdrawing tube and the interior of the cell.

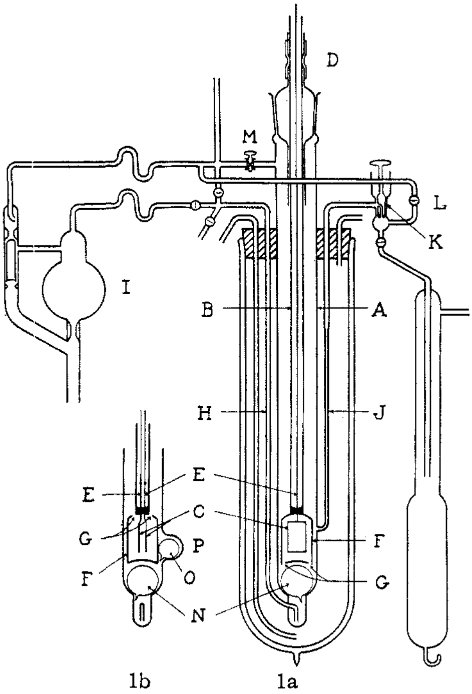

Fig. 1.—Conductance cell.

The materials used in preparing the salts were sealed in weighed glass bulbs N and O. One of these, containing the metal, was placed immediately under the electrode housing, while the other was placed in the pocket P. The housing at the bottom was made sufficiently heavy so that the bulbs could be crushed by bearing down on the stem of the electrode system, which was movable in the slip-joint D.

After washing the cell repeatedly with liquid ammonia until the desired specific conductance was obtained, a measured quantity of ammonia was condensed in the cell, the bulbs were crushed under the liquid, and the contents of the cell were stirred. Only a few minutes were required to complete the reaction. In the case of sodium triphenylmethide, the sodium bulb was first crushed and the metal converted to amide, the reaction being accelerated by a bit of iron oxide.

The cell constant was determined by intercomparison with a standardized cell. Three different sets of electrodes were used whose constants were approximately 0.36, 0.13 and 0.06. The electrical measuring apparatus was the same as that used by Kraus and Hawes. Triphenyltin and triphenylgermanium were products that had been prepared in this Laboratory, and were purified by recrystallization from benzene. Triphenylmethane was purified by recrystallization. Sodium was introduced into weighed bulbs as described by Kraus and Hawes. Ammonia was purified as usual by means of metallic sodium. A correction of 2×10^{-7} has been applied for the conductance of the solvent.

III. Experimental Results

Conductance values of sodium triphenylstannide, sodium triphenylgermanide and sodium triphenylmethide are given in the following table. In the case of all three salts, measurements were made at concentrations much lower than the lowest given in the table. The values, however, were manifestly unreliable, since the conductance changed with time and the conductance curve showed a marked change in curvature. The difficulty was overcome to some extent by carrying the measurements out very rapidly. In the case of tin, fairly satisfactory results were obtained down to relatively low concentrations. In the case of germanium and carbon, however, satisfactory results could not be obtained at low concentrations. With sodium triphenylstannide, the conductance curve tended to rise abruptly at low concentrations, while, in the case of the triphenylmethide, the conductance curve fell consistently at concentrations below 0.001 *N*. The germanium salt exhibited an intermediate behavior. In some respects, sodium triphenylmethide behaved as though it were undergoing ammonolysis. In this connection it may be noted that, according to Kraus and Kawamura,[7] sodium triphenylmethide is completely ammonolyzed when an ammonia solution of this salt is evaporated at −33°.

TABLE I

CONDUCTANCE OF SALTS IN LIQUID AMMONIA AT −33°

V	Λ	V	Λ	V	Λ
Sodium Triphenylstannide		Sodium Triphenylgermanide		Sodium Triphenylmethide	
160.9	158.4	230.9	159.3	59.21	125.1
370.5	173.2	512.0	172.4	83.41	137.5
1146	191.3	1133	182.8	176.0	148.7
2515	202.6	2512	190.4	372.7	157.0
5520	210.7	5564	195.3	782.6	161.0
12120	214.8				
26580	218.3				
58350	219.4				

IV. Discussion

The conductance curves of the three salts are shown graphically in Fig. 2, values of the equivalent conductance being plotted as ordinates and logarithms of concentrations as abscissas. Inspection of the figure will show that all three salts are very strong electrolytes in liquid ammonia. Although the mobilities of the negative ions are relatively low because of their large size, at higher concentrations these salts are, nevertheless, much better conductors than are the ordinary salts. For the purpose of comparison, the conductance curve for sodium bromate, which is one of the stronger inorganic salts, is likewise plotted in Fig. 2. It will be noted that, although the limiting conductance of sodium bromate (278) is much higher than that of the three salts which we have measured, it is a markedly poorer conductor at concentrations above 0.01 *N*. The conductance curves for the three salts are very nearly parallel at higher concentrations, the conductance of the tin salt being highest and that of the carbon salt lowest. It was found that, toward lower concentrations, the curve for sodium triphenylmethide falls off rapidly and that of sodium triphenylgermanide less rapidly. The solutions are evidently unstable at lower concentrations. The curve for sodium triphenylstannide appears to be normal and resembles

[7] Kraus and Kawamura, THIS JOURNAL, **45**, 2756 (1923).

that of sodium triphenylboron ammide.[8] It is of interest to note that the triphenylstannide and the triphenylboron ammide ions are of about the same size and have much the same symmetry.

The determination of precise values of Λ_0 and of K is not possible, even in the case of sodium triphenylstannide. Indeed, this salt is so highly ionized that a satisfactory evaluation of K cannot be made except with highly precise data. Nevertheless, Λ_0 and K could be approximated fairly closely. The values found are: $\Lambda_0 = 226$ and $K = 0.013$. Sodium triphenylstannide is a salt having about the same strength as sodium triphenylboron ammide, and its limiting conductance has nearly the same value.

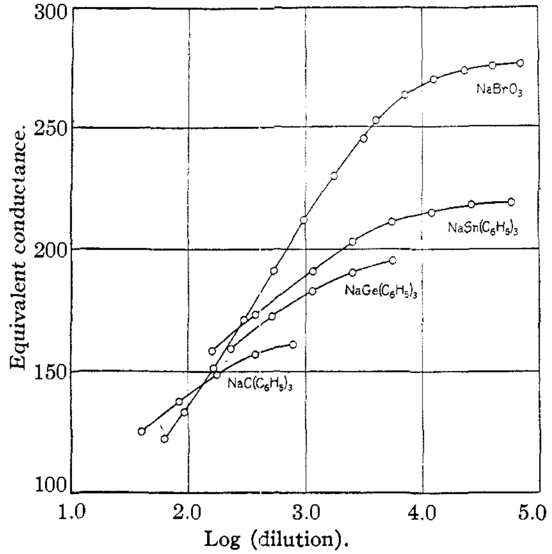

Fig. 2.—Conductance of salts in liquid ammonia.

It may be of interest to point out that familiar inorganic salts, which are usually considered to be typical electrolytes, are, in fact, much weaker electrolytes than the compounds here investigated. Thus, the dissociation constant of sodium bromate is 35×10^{-4}, while that of sodium triphenylstannide is about four times as great. The dissociation of a salt is primarily determined by the size of its ions, or, in other words, by the work necessary to separate a pair of ions from their position of minimum energy. When the ions are small, the energy of separation is large and the dissociation constant is correspondingly small.[9] It is also evident that the affinity of the negative ion for its electron has no influence on the dissociation of its salts. Thus, the affinity of an ion such as triphenylmethide or triphenylstannide for its electron is exceedingly small in comparison with that of the

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(8) Kraus and Hawes, THIS JOURNAL, **55**, 2776 (1933).

(9) Fuoss and Kraus, *ibid.*, **55**, 1019 (1933).

chloride or the bromate ion. While it is true that, in the case of the acids, ionization is the greater the more electronegative the ion, this is not true generally for salts in solvents of lower dielectric constant, where ion association is appreciable.

V. Summary

The conductances of solutions of the sodium salts of triphenyltin, triphenylgermanium and triphenylmethyl in liquid ammonia have been measured.

All three salts are very strong electrolytes. The dissociation constant of sodium triphenylstannide is approximately four times that of sodium bromate.

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Properties of Electrolytic Solutions. VII. Conductance of Sodium Trimethylstannide and of the Sodium Salts of Certain Phenols and Thiols in Liquid Ammonia

BY CHARLES A. KRAUS AND EDMUND G. JOHNSON

I. Introduction

In the two preceding papers of this series, conductance values were given for electrolytes in which the charge of the negative ion was localized on nitrogen,[1] tin, germanium or carbon,[2] the remaining valences of these elements being satisfied by organic groups. The purpose of these investigations has been to study the influence of ion size and constitution on the properties of the electrolyte, particularly its dissociation constant. The results already presented lend support to the view that the dissociation of an electrolyte is primarily determined by the size of its ions and, to a lesser degree, by their configuration. Electrolytes with large ions, which cannot approach each other very closely, have a lower energy of dissociation and, consequently, a higher dissociation constant. Where the ions are unsymmetrical, constitutional factors have a marked influence and it may be expected that the salts of such ions will be the more highly ionized the more the charge is screened by neutral atoms of the ion complex.

It seemed of interest to determine the dissociation constants of salts of simple oxygen and sulfur acids of the type RAH, which give ions of the type RA^-. The salts of the ordinary alcohols are not sufficiently soluble in liquid ammonia to permit of conductance measurements, but the salts of the aromatic alcohols are readily soluble and are well suited to the purpose

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(1) Kraus and Hawes, THIS JOURNAL, **55**, 2776 (1933).

(2) Kraus and Kahler, *ibid.*, **55**, 3537 (1933).