The authors wish to acknowledge their indebtedness to Mr. R. J. DeGray for assistance with the electrical hook-up and to Mr. Simon Deptula for translating Russian literature on heats of dilution.

Summary

1.   Heats of dilution of calcium nitrate solutions to infinite dilution have been measured.   The concentrations of the solutions studied range from 1.39 m to 19.55 m.

2.   The total heat of solution of calcium nitrate and the partial heats of solution of calcium nitrate and of water have been evaluated by means of the heat of dilution measurements.

3.   Values of the partial heat of solution of water calculated from calorimetric measurements have been compared with those calculated by means of Kirchhoff's equation from vapor pressure measurements.

Properties of Electrolytic Solutions.   VIII.   Conductance of Some Ternary Salts in Liquid Ammonia

BY CHARLES A. KRAUS AND PAUL B. BIEN[1]

I. Introduction

In the three preceding papers of this series,[2] results have been presented for the conductance of various types of binary salts in liquid ammonia with a view to determining the influence of ion constitution on the properties of electrolytes, particularly the dissociation constant.   It seemed of interest to extend the investigation to ternary salts.   Little is known regarding the behavior of ternary salts in non-aqueous solvents, particularly of ternary salts of divalent negative ions.   Usually, ternary salts are very difficultly soluble in liquid ammonia although there are a few salts, most of them of somewhat complex structure, which are readily soluble.

When benzophenone is treated with two atomic equivalents of sodium, the well-known disodium ketyl salt is formed.   With one equivalent of sodium,[3] a monosodium salt is formed which may be looked upon either as a binary salt derived from the anion $(C_6H_5)_2CO^-$ or as a disodium salt of the divalent benzpinacol ion.   It was hoped that conductance measurements might throw some light on this question.   The dialkyl and diaryl tin derivatives, when treated with two atomic equivalents of sodium, yield

(1) Metcalf Fellow in Chemistry at Brown University.
(2) Kraus and Hawes, THIS JOURNAL, **55**, 2776 (1933);   Kraus and Kahler, *ibid.*, **55**, 3537 (1933); Kraus and Johnson, *ibid.*, **55**, 3542 (1933).
(3) Wooster, *ibid.*, **50**, 1388 (1928).

compounds of the type Na_2SnR_2,[4] which are readily soluble in liquid ammonia and in which, presumably, there exists the divalent ion, $R_2Sn^=$. These salts are of particular interest because both charges are associated with the same atom, in place of two different atoms as is the case in the derivative of benzophenone. Unfortunately, disodium diphenylstannide undergoes reaction (presumably with the solvent) at concentrations below about 200 liters. It was found possible, however, to form a salt, Na_2-$[Sn(C_6H_5)_2]_2$, which may be looked upon as the disodium salt of tetraphenyl-distannane. Here again it is possible that the Sn–Sn bond breaks down in solution to yield the univalent ion R_2Sn^-. It was thought that conductance measurements might throw some light on the state of the electrolyte in solution. A similar type of salt is obtained on treating hydrazobenzene with sodium or potassium amide. Here, we have a salt corresponding to the formula $M_2[N(C_6H_5)]_2$ which may dissociate to give the simple ion $C_6H_5N^-$. It might be expected that, upon treating this salt with additional sodium, disodiumphenylamide, $Na_2NC_6H_5$, might be formed. However, no reaction occurs when disodium benzhydrazide is treated with additional atoms of sodium. For purposes of comparison with monosodium diphenylketyl, the conductance of sodium benzhydrolate was measured.

II. Apparatus and Procedure

The apparatus employed in the present investigation was substantially the same as that of Kraus and Hawes and need not be described here. Some minor changes were introduced, the most important of which was that the solution was stirred by boiling. A platinum tube, closed at the bottom, was sealed into the tube connecting the two chambers of the cell at the bottom (see Kraus and Hawes). A small heater was constructed consisting of a copper rod, the end of which projected into the platinum tube and the upper part of which was wound with resistance wire which was electrically insulated from the copper rod. Heat was transmitted from the copper rod through the platinum tube into the solution, which was thus boiled and stirred very conveniently. Three-way stopcocks were attached to the withdrawal tubes used for emptying the cell or for withdrawing solution. These stopcocks eliminated one additional stopcock in each case and permitted connecting the top of the capillaries with the interior of the cell when the process of withdrawal was completed.

The method of making up the solution and of carrying out the dilutions was the same as that of Kraus and Hawes. The cell was calibrated against a standardized reference cell and the electrical measuring apparatus was the same as that used in previous work. Before making up the solutions, the cell was washed until the conductance reached a value of approximately 1×10^{-7}. No corrections have been applied to the data for the conductance of the solvent. Monosodium and disodium diphenylketyl were made up by treating benzophenone with one and two atoms of metallic sodium. The monosodium ketyl was also prepared by treating benzpinacol with sodium amide. The conductance values were the same for the two methods of preparation.

Sodium benzhydrolate was prepared by treating benzhydrol with sodium amide. It might be expected that disodium diphenylketyl might be prepared by treating benzhydrol with two equivalents of sodium amide. This, however, was not the case. In liquid ammonia solution, neither sodium nor potassium amide acts upon the monoso-

(4) Kraus and Greer, THIS JOURNAL, **47**, 2568 (1925); Kraus and Brown, *ibid.*, **52**, 4031 (1930).

dium or potassium salt of benzhydrol. The solutions were in all cases colorless and the conductance corresponded to that of a mixture of the amide and the mono-salt of benzhydrol. When the solvent was evaporated and the mixture of benzhydrolate and amide heated to room, or higher, temperatures, reaction occurred as was indicated by the appearance of the red color characteristic of the dimetal ketyl. There is here an interesting case where a salt is stable in liquid ammonia solution without hydrolysis but which cannot be made by the action of a base on the corresponding acid.

Disodium benzhydrazide was prepared by the action of sodium amide on hydrazobenzene. Monosodium hydrazobenzene could not be prepared. If hydrazobenzene is treated with one equivalent of sodium amide, the disodium salt is formed and the additional hydrazobenzene is not acted upon. It was found impossible to split the N–N bond to form disodium phenylamide by treating disodium benzhydrazide with an equivalent amount of sodium. Neither was it possible to prepare the salt by the action of sodium amide upon monosodium phenylamide. An attempt to carry out measurements with the disodium salts of dihydroxybenzenes was unsuccessful because of the fact that none of these salts was appreciably soluble in liquid ammonia.

III. Results

Equivalent conductance values of the various salts are given in the following table. Although in a number of instances the conductance was measured below 10^{-4} N, the data are not presented since it was felt that they were not sufficiently reliable. The conductance of the solvent introduces uncertainties at lower concentrations, particularly in the case of salts that are poor conductors.

TABLE I
CONDUCTANCES OF SALTS IN LIQUID AMMONIA AT $-33°$

Disodium Tetraphenyldistannide, $Na_2[Sn(C_6H_5)_2]_2$				Dipotassium Diphenylhydrazide, $K_2(NC_6H_5)_2$			
V	Λ	V	Λ	V	Λ	V	Λ
79.17	82.79	1307	137.6	27.50	13.37	560.4	41.44
140.1	91.56	2274	156.2	42.63	15.83	930.3	49.56
245.2	101.2	3956	178.2	71.62	19.15	1544	59.01
429.2	111.6	6845	202.6	119.6	23.36	2563	68.43
746.7	122.7	...	...	199.8	28.42	4230	79.43
				331.6	34.32	...	...

Monosodium ketyl, $NaOC(C_6H_5)_2$				Sodium Benzhydrolate, $NaOCH(C_6H_5)_2$			
44.08	31.43	801.1	71.77	95.40	13.09	1029	41.14
66.81	34.78	1204	81.90	143.1	14.41	1718	51.52
101.4	38.96	1790	92.30	217.0	18.28	2870	65.23
153.8	43.71	2663	103.6	364.6	24.29	4763	82.97
233.1	49.14	4040	116.0	616.2	32.11	7953	106.7
353.8	55.60	6010	131.1				
528.6	62.82	9058	147.0				

Disodium ketyl, $Na_2OC(C_6H_5)_2$			
17.87	15.68	478.9	50.00
26.80	17.04	852.5	61.90
47.95	20.87	1517	75.45
83.95	26.26	2670	95.70
150.3	33.39	4673	120.0
269.0	40.98	8270	148.7

Only one series of measurements is given for each salt, although check determinations were made in the case of all salts with the exception of dipotassium diphenylhydrazide.

IV. Discussion

The conductance curves are shown graphically in the accompanying figure, where the logarithms of concentrations are plotted as abscissas and the conductance values as ordinates.   Inspection of the figure will show that practically all the salts are rather weak electrolytes.   For purposes of comparison, there are drawn curves for sodium triphenylstannide ($K = 130 \times 10^{-4}$) and sodium phenolate ($K = 3.82 \times 10^{-4}$).   It will be noted that, although sodium phenolate is quite a weak electrolyte in liquid ammonia, it is a better conductor than most of the salts measured in the present investigation.   The conductance curve for sodium phenolate rises much more steeply than does that of the salts which we have measured.
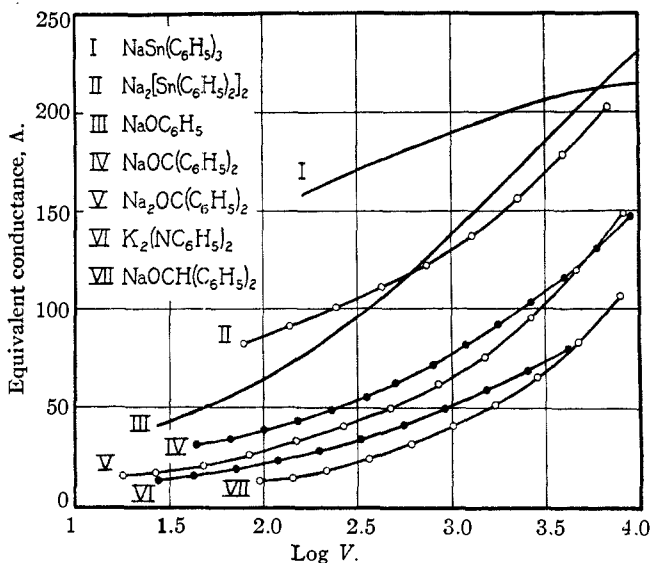

Fig. 1.—Conductance of salts in liquid ammonia.

According to the Debye–Hückel theory, we should expect the conductance of ternary salts to be much lower than that of corresponding binary salts. If a mass action effect occurs, as in the case of binary electrolytes, the constitution of the ions should have a marked influence on conductance.

The conductance curve for disodium ketyl lies slightly below that of the monosodium salt at higher concentrations but very nearly coincides with it at low concentrations.   This indicates that the ionization of the two salts is approximately the same.   Analysis of the curve for monosodium ketyl

according to the method of Fuoss and Kraus[5] indicates that we are not dealing here with a simple binary equilibrium. It is impossible, however, to state definitely that the equilibrium is a purely ternary one. It is possible that a combination of binary and ternary equilibria exists and it is also conceivable that the charge on the monoketyl ion oscillates between oxygen and carbon. It is a remarkable fact that monosodium ketyl is a much better conductor than sodium benzhydrolate. The only difference between the two salts is that a hydrogen atom is associated with the aliphatic carbon atom in the one case and not in the other. It seems evident that constitutional factors play a large part in the dissociation phenomenon in the case of these salts.

Disodium benzhydrazide is a much weaker electrolyte than disodium ketyl. The low conductance value of this electrolyte indicates that we are here dealing with a ternary equilibrium. If the N–N bond were broken, the conductance of the resulting binary electrolyte should correspond approximately to that of sodium or potassium phenylamide. The conductance of potassium phenylamide has been measured by Kraus and Hawes and is enormously greater than that of the benzhydrazide here measured.

Disodium tetraphenyldistannide is a relatively good electrolyte. At low concentrations the conductance approximates that of sodium triphenylstannide but at higher concentrations the conductance is much below that of the binary salt, as may be seen from the figure. Evidently, we have to deal, here, with a ternary salt, but there is a possibility that an equilibrium exists between the univalent ions $(C_6H_5)_2Sn^-$ and the divalent ion $[(C_6H_5)_2 Sn]_2^-$. It is known that the Sn–Sn bond is weak and it is quite conceivable that it is broken down under the action of electrostatic repulsion.

Although the data admit of only a qualitative interpretation, they seem to show that the ternary salts of divalent negative ions are much less highly ionized than are corresponding binary salts, and that, as in the case of salts of simpler ions, the dissociation as indicated by the conductance is the greater the larger the negative ion. It is hoped that at a later date more exact data may be presented. For this purpose, the experimental technique is being perfected.

Summary

Conductance values are presented for a number of salts of ternary type in liquid ammonia. In several of these salts the charges on the anion are associated with different atoms and there exists the possibility of dissociation of the anion complex into simple ions.

The results are discussed. Dipotassium diphenylhydrazide seems to behave like a ternary salt. In the case of disodium tetraphenyldistannide, there is evidence of dissociation of the anion complex. The conductance

(5) Fuoss and Kraus, THIS JOURNAL, **55**, 470 (1933).

curve for monosodium diphenylketyl does not correspond to that of a simple binary electrolyte.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. IX. Conductance of Some Salts in Benzene

BY RAYMOND M. FUOSS AND CHARLES A. KRAUS

I. Introduction

In the first paper of this series,[1] the conductances of tetraisoamylammonium thiocyanate and of tri-isoamylammonium picrate in benzene were reported. With the apparatus then available, it was impossible to investigate the conductance at concentrations below the minimum; in fact, it was only possible to argue by inference from the behavior in mixed solvents that the conductance in a strictly non-polar solvent such as benzene would show a minimum. The appearance of inflection points in the conductance curves in the neighborhood of 0.001 N for some salts and not for others also made further experimental work desirable. It seemed especially important to determine, experimentally at least, how the complexity of the curve depended upon the ions of the electrolyte.

By constructing cells with constants as low as 0.003 and by improving the electrical measuring system, it has been possible to measure conductances at concentrations below 10^{-6} N with an accuracy of several per cent. We report herewith the conductance of tetraisoamylammonium thiocyanate, picrate, iodide, bromide, chloride and fluoride in benzene at 25°.

Actual minima in conductance, followed by slopes approximating that required by the law of mass action, were found in the case of the picrate, thiocyanate, iodide and bromide; and the minimum was located for the chloride and fluoride. Dissociation constants calculated from the conductance data are of the order of 10^{-18}; among the halides, the iodide is the strongest salt ($K = 5 \times 10^{-18}$) and the fluoride is the weakest ($K = 6 \times 10^{-19}$), which is the order one might expect in non-polar (not solvating) solvents.

II. Materials, Apparatus and Method

Salts.—The preparation of tetraisoamylammonium thiocyanate and iodide has already been described. The iodide used as the starting material for this series of experiments melted at 141°, which is 5° higher than our previous value. The picrate, bromide, chloride and fluoride were prepared by neutralizing the hydroxide with the corresponding acid in alcoholic solution. The picrate was recrystallized from alcohol; the other salts were used directly as obtained from (room temperature) evaporation of

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(1) Kraus and Fuoss. THIS JOURNAL, 55, 21 (1933).