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Conductometric Behavior of Sulfur–Ammonia Solutions[1]

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The conductances of solutions of sulfur and tetrasulfur tetranitride in liquid ammonia have been measured at 0°. Both solutes appear to be fairly strong electrolytes in this solvent, but a large fraction of the dissolved sulfur is present in nonconducting forms.

The spectral behavior of solutions of sulfur in liquid ammonia has been reported recently.[3] We wish to present here conductance data for both S–NH_3 and S_4N_4–NH_3 solutions, as well as some spectral observations of our own which we feel are of value in furthering our knowledge of these systems.

Results and Discussion

Electrical conductivities of S–NH_3 solutions 2×10^{-5} to 0.01 M in sulfur have been measured at 0°. The molar conductance (based on an atomic weight of sulfur of 32.066) decreases from 89.69 to 40.14 over this concentration range. In addition, the conductance of S_4N_4 solutions was found to decrease from 406.7 to 350.6 over the concentration range 10^{-4} to 2×10^{-3} M. The data for sulfur solutions are listed in Table I and those for S_4N_4 in Table II, while the resulting plots can be seen in Figure 1, where the molar conductance is plotted against $\sqrt{M}$.

Several features of this conductance behavior are of interest. The most obvious of these is the rather low conductivity of sulfur solutions in comparison with those of S_4N_4 at the same temperature. It is sulfur which is exceptional in its conductance properties, not S_4N_4, for the latter has been shown to be comparable in behavior to other electrolytes.[4]

The low conductivity of sulfur could be attributed to several factors. If the assumption is made that the mobilities of the conducting species are not unusual compared to those of other electrolytes, the low conductance would seem to be due to either or both of the following: (a) the conducting species is present as a very weak electrolyte, making it impossible to obtain a true Λ_0 value by extrapolation; (b) some of the dissolved sulfur is present in a nonconducting form, molecular or otherwise, causing the actual concentration of the conducting species to be several times smaller than the sulfur molarity.

Our data appear to conform to the Ostwald dilution law (in which $1/\Lambda$ is plotted *vs.* $C\Lambda$) up to about 10^{-3} M and yield by extrapolation a Λ_0 value of 84.6 ± 0.7, which is only one-fifth as large as the Λ_0 value found for S_4N_4 (416) at this temperature. Further, if we assume that we are dealing with 1–1 electrolytes, the ratio Λ/Λ_0 represents the degree of dissociation for either a molecular equilibrium ($MA \rightleftharpoons M^+ + A^-$) or an ion-pair equilibrium ($M^+A^- \rightleftharpoons M^+ + A^-$) and leads to the evaluation of apparent equilibrium constants for the two systems of 1.47×10^{-2} (sulfur) and 9.0×10^{-3} (S_4N_4). While comparable data are not available for solutions of normal electrolytes in ammonia at 0°, the results obtained for 1–1 electrolytes at −34° ($K_{NaBr} = 2.9 \times 10^{-3}$ and $K_{KCl} = 8.7 \times 10^{-4}$)[5] would suggest that we are dealing with fairly strong electrolytes in the present study.

We therefore infer that factor (a) does not contribute greatly in accounting for the lower conductance values found for sulfur solutions at low concentrations and we are left with the conclusion that much of the sulfur remains in a nonconducting form, possibly as polyatomic anionic species which may be in equilibrium with nonconducting molecular types. If it is assumed that the Λ_0 values for sulfur and S_4N_4 solutions should be approximately equal, it would appear that on the average, 80% or more of the sulfur must be nonconducting. If, however, S_4N_4 converts to $HNSNSNH_2$ in solution as has been suggested,[6] the true Λ_0 value for S_4N_4 would be calculated to be 208 rather than 416, owing to the molecular weight being halved, and the compounds formed by the reaction of elemental sulfur with ammonia would contain an average of two to three sulfur atoms.

The binary behavior of solutions of S_4N_4 at first appears to be inconsistent with the structure $HNSNSNH_2$ (proposed for the species formed in the ammonolysis of both S_4N_4 and S_2N_2). This species has three acidic hydrogens as indicated by the formation of the salt $Na_3S_2N_3$. One of these hydrogens can be removed more easily than the other two,[7] however, and it may be that only the first is acidic enough to ionize under the conditions of this study, giving rise to the 1–1 conductance behavior observed. In fact, the low dielectric constant of ammonia (approximately 20 at 0°) would argue against the presence of highly charged ions in substantial amounts.

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(3) J. T. Nelson and J. J. Lagowski, *Inorg. Chem.*, **6**, 1292 (1967).

(4) F. A. Smith, *J. Am. Chem. Soc.*, **49**, 2162 (1927), reported a Λ_0 value of 298 for S_4N_4 at −33.5° and values for other electrolytes which ranged from 227 to 349.

(5) V. F. Hnizda and C. A. Kraus, *ibid.*, **71**, 1565 (1949).

(6) M. Goehring, *Quart. Rev.* (London), **10**, 437 (1956).

(7) M. Becke-Goehring and R. Schwarz, *Z. Anorg. Allgem. Chem.*, **296**, 3 (1958).

TABLE I

CONDUCTANCE-CONCENTRATION DATA FOR SULFUR-AMMONIA SOLUTIONS AT 0°

$M \times 10^3$	Λ, ohm^{-1} cm^{-2} mol^{-1}	$M \times 10^3$	Λ, ohm^{-1} cm^{-2} mol^{-1}
0.0225	89.69	5.659	66.20
0.0388	88.04	9.938	62.03
0.1114	86.15	10.96	61.90
0.1404	85.00	12.53	59.57
0.2025	84.71	13.24	59.98
0.3478	82.31	15.06	57.69
0.3943	82.37	16.79	57.60
0.4183	81.93	19.88	54.82
0.5738	81.40	23.23	52.73
0.6065	80.43	23.58	52.37
0.8331	80.29	27.45	51.16
1.076	78.24	31.32	49.65
1.140	80.22	32.22	50.93
1.142	78.49	37.97	47.88
1.360	76.79	42.66	46.86
1.793	74.75	46.49	46.20
1.919	75.88	56.13	44.38
2.508	74.40	79.90	41.41
2.665	72.99	90.43	40.14
3.477	70.09		

TABLE II

CONDUCTANCE-CONCENTRATION DATA FOR S_4N_4 IN LIQUID AMMONIA AT 0°

$M \times 10^3$	Λ, ohm^{-1} cm^{-2} mol^{-1}	$M \times 10^3$	Λ, ohm^{-1} cm^{-2} mol^{-1}
0.1297	407.6	0.9267	378.3
0.1752	404.1	1.288	366.9
0.3271	398.0	1.820	350.6
0.7265	375.5	3.571	320.7

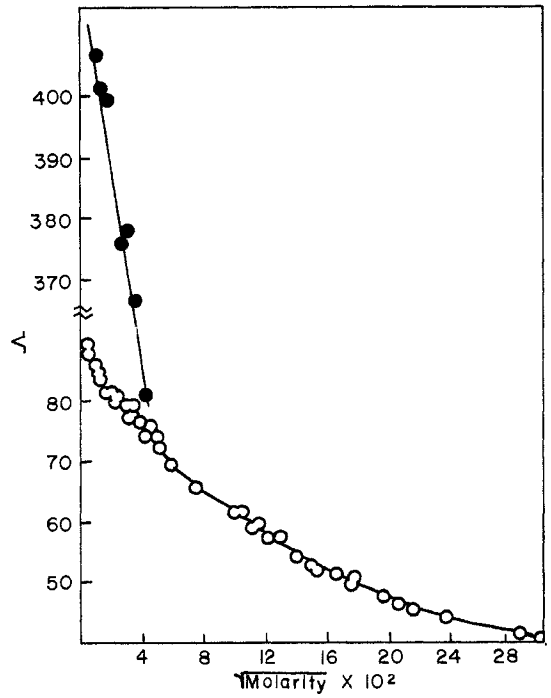

Figure 1.—Conductance–$\sqrt{\text{molarity}}$ plot for solutions of sulfur (○) and S_4N_4 (●) in liquid ammonia at 0°.

The spectral observations which we have made on these solutions are in essential agreement with those reported recently[3] over the concentration range of that study, namely, bands at 430 and 580 mμ which obey Beer's law up to 10^{-3} M with a third band at 295 mμ, which we did not study extensively. In addition, however, we have found strong positive deviations from Beer's law for both the 430- and 580-mμ bands at higher concentrations. The 580-mμ band (which has the lower absorbance at low concentrations) increases more rapidly and has an absorbance about 10% greater than that of the 430-mμ band at 0.1 M. A plot of this behavior is given in Figure 2. The deviations of these bands may be due to a rapid increase in the equilibrium concentrations of the species responsible for them, at the expense of others, perhaps the species which absorbs at 295 mμ. Alternately, the absorbance at 430 and 580 mμ could be augmented further by the formation of polysulfide species which absorb at 400 and 600 mμ.[8]

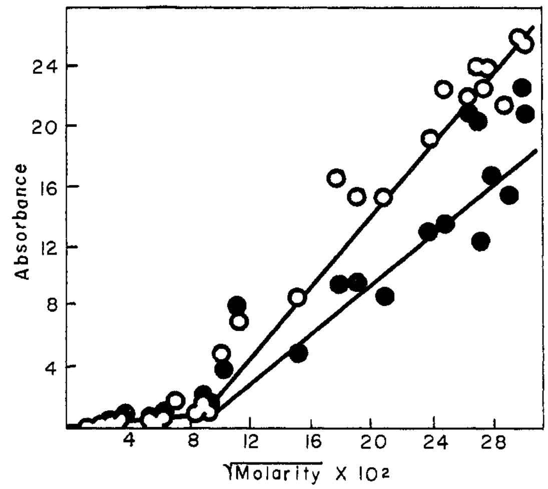

Figure 2.—Plot of absorbance *vs.* $\sqrt{\text{molarity}}$ for 430-mμ (●) and 580-mμ (○) bands in sulfur-ammonia solutions at −40°.

It now seems clear that solutions of sulfur in ammonia contain several species in equilibrium, at least one of which is a relatively strong electrolyte, but that a large fraction of the sulfur is nonconducting. The information now available is insufficient to indicate the nature of the dissolved species but does show that H_2S and S_4N_4 are not among them.

Experimental Section

Materials.—Sublimed sulfur was recrystallized three times from reagent grade benzene and stored over phosphorus pentoxide *in vacuo*. The molecular weight (cryoscopy in naphthalene) was 248–252. Commercial ammonia was distilled three times from sodium and stored in a stainless steel can until needed as described previously.[9] Tetrasulfur tetranitride was prepared from sulfur monochloride and ammonia (mp 179°).[10] Hydrogen sulfide (Matheson) was fractionally distilled twice from newly activated alumina.

Conductance.—The conductance cell with shiny platinum electrodes was constructed of heavy Pyrex glass to withstand the pressure at 0° (5 atm) and was equipped with a Teflon valve to isolate it from the vacuum system. The cell constant of 0.3468 cm^{-1} was determined with an aqueous KCl solution.[11]

Measurements were made at 0 ± 0.01° with a Model 221B

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[8] W. L. Jolly, Report UCRL-2008, Office of Technical Services, Department of Commerce, U. S. Government Printing Office, Washington, D.C., 1958.

[9] F. R. Longo and E. C. Evers, *J. Phys. Chem.*, **70**, 426 (1966).

[10] H. R. Van Valkenburgh and J. C. Bailar, *J. Am. Chem. Soc.*, **47**, 2134 (1925).

[11] J. E. Lind, J. J. Zwolenick, and R. M. Fuoss, *ibid.*, **81**, 1557 (1959).

Wayne-Kerr universal bridge. Solution volumes were calculated from the solvent weights (corrected for the amount present as vapor) and the density of ammonia (0.6386 g/cm^3).[12]

Spectra.—Solutions were maintained at $-40 \pm 2^\circ$ in quartz cells (1-, 5-, and 10-mm path length) by filling the attached cold finger with Dry Ice. Spectra were recorded on a Beckman DK-2 spectrophotometer. Solutions were prepared in Pyrex vessels attached to the cell units with Teflon valves, through which the solutions were forced into the cells with dry argon.[13]

Concentrations determined polarographically[14] after transfer to the spectral cell agreed within 3% with those calculated from the weights of sulfur and ammonia (density 0.6900 g/cm^3).[12]

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[12] C. S. Cragoe and D. R. Harper, Bureau of Standards Scientific Paper No. 430, U. S. Government Printing Office, Washington, D. C., 1921, p 313.

[13] Further details of the experimental method can be found in the Ph.D. thesis of A. P. Z.

[14] M. E. Hall, *Anal. Chem.*, **22**, 1137 (1950).

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Autocatalysis in the Copper(II) Nitrate Decomposition in Alkali Nitrate Solvents

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The autocatalytic nature of the reaction $Cu^{2+} + NO_3^- = CuO + NO_2^+$ in molten sodium nitrate–potassium nitrate equimolar solvent is confirmed. A steady-state assumption applied to the nitryl ion concentration is shown to be more applicable than the rapid equilibrium assumption used by other workers. Evidence is given to support a proposed mechanism which indicates that solid copper(II) oxide enhances the reaction between NO_2^+ and NO_3^- ions. This suggests that the catalytic nature of CuO is not specific to the Cu^{2+} ion and that CuO should catalyze any acid–base reaction in nitrate solvents for which NO_2^+ ion can be considered an intermediate species. Also other metallic oxides could possibly act as catalyst for such reactions.

Many metallic cations can generally be classed as Lux–Flood acids since they will react with basic oxyanions (oxide ion donors) to give the corresponding metal oxide and the conjugate acid of the base. Frequently the apparent acidic nature of the cation is enhanced by the relative insolubility of the metal oxide in a specific solvent.

The acid–base reaction of a divalent cation with the weak-base nitrate ion in molten alkali metal nitrate solvents can be written as $M^{2+} + NO_3^- \rightleftarrows MO + NO_2^+$. The representation of the metal ion in this equation as M^{2+} does not indicate lack of solvation of the metal ion. The manner in which various metal ions are solvated in nitrate melts has not been accurately determined, and the use of some arbitrary number of solvation anions seems unnecessarily cumbersome. Presumably the nitryl ion, a product in the above reaction, reacts further with the solvent according to the reaction $NO_2^+ + NO_3^- \rightleftarrows 2NO_2 + 0.5O_2$. There is evidence to indicate that this reaction is the rate-determining step when condensed oxyanions such as $S_2O_7^{2-}$ or $Cr_2O_7^{2-}$ are used as acids.[1] Attempts to detect the nitryl ion spectroscopically and polarographically[2] have not been successful, which suggests that the nitryl ion is not present in significant quantities in acidified alkali nitrate melts. However, recent investigations in which several organic aromatic molecules were nitrated by passing them through a $LiNO_3$–$NaNO_3$–KNO_3 ternary eutectic containing potassium pyrosulfate, a strong acid, lend support to the existence of the nitryl ion in such melts.[3]

The specific reaction between Cu(II) and NO_3^- in nitrate melts has been studied by Slama,[4] who reported that the reaction is autocatalytic in nature. The copper(II) oxide which is produced acts as a catalyst to increase the rate of disappearance of the Cu(II) ion. However, no detailed study of this catalytic process was made. It is of interest to know whether the catalytic activity of the copper oxide is specific to this reaction or whether it is a general catalyst for other acid–base reactions in molten nitrate solvents. This paper is a report of a detailed investigation of this catalytic activity in an equimolar sodium nitrate–potassium nitrate melt.

Experimental Section

Reagent grade chemicals were used unless otherwise specified. The preparation of the equimolar sodium nitrate–potassium nitrate solvent has been previously described.[5]

Anhydrous copper(II) nitrate was prepared by the reaction of nitrogen tetroxide and copper shot in anhydrous ethyl acetate according to the procedure of Addison[6] and by the reaction of nitrogen pentoxide and copper(II) nitrate trihydrate according to the procedure of Hardy and Field.[7] In this latter method the nitrogen pentoxide was prepared according to the procedure of Caesar and Goldfrank[8] since contamination with nitrogen tetroxide did not interfere with the dehydration reaction. The copper(II) nitrate–nitrogen tetroxide adducts formed were thermally decomposed under vacuum to copper(II) nitrate. The infrared spectra of the anhydrous copper(II) nitrate thus obtained agreed

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[1] (a) F. R. Duke and S. Yamamoto, *J. Am. Chem. Soc.*, **81**, 6378 (1959); (b) F. R. Duke and M. L. Iverson, *ibid.*, **80**, 5061 (1958).

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[4] I. Slama, *Collection Czech. Chem. Commun.*, **28**, 985 (1963).

[5] R. N. Kust and F. R. Duke, *J. Am. Chem. Soc.*, **85**, 3338 (1963).

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[7] C. J. Hardy and B. O. Field, *ibid.*, 3513 (1964).

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