tradictory to a picture of the solution phase according to which forces leading to compound formation are present in the liquid phase. If, however, the loose bonds in the solution phase involve hydrogen, a high thermal conductivity may result, even with a highly ordered assembly of molecules. Perhaps the hydrogen bonding between the halogen-like thiocyanate ions and the ammonia protons is not unlikely. The relatively high conductance of water depends in part on the hydrogen bonding between the molecules.

The heat of solution of NaSCN in liquid ammonia is more exothermic than the heat of solution in water by 13 or 14 kcal. This larger evolution of heat in ammonia than in water is true of most salts and the difference may be due[16] to the requirement for energy absorption in the disruption of water clusters which are held together by hydrogen bonds.

Acknowledgments.—The authors are pleased to acknowledge the financial support of this investigation by the John Simon Guggenheim Memorial Foundation, the Rockefeller Foundation and the Union Carbide Corporation.

(16) S. P. Wolsky, E. J. Zdanuk, and L. V. Coulter, *J. Am. Chem. Soc.*, **74**, 6196 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

Concentrated Solutions in Liquid Ammonia: Solubility of $NaNO_3$ and KBr and Other Salts; Vapor Pressures of $LiNO_3$–NH_3 Solutions[1]

BY GEORGE C. BLYTAS, DENIS J. KERTESZ AND FARRINGTON DANIELS

RECEIVED SEPTEMBER 5, 1961

The solubilities of several inorganic salts in liquid ammonia have been determined and the solubility curves of $NaNO_3$ and KBr over a limited concentration range are given. The KBr–NH_3 system has a negative temperature coefficient of solubility. Trends in solubility of salts are discussed in terms of polarizability and size of ions. The vapor pressures of $LiNO_3$–NH_3 solutions have been determined and are presented up to 200 psia.

In the accompanying paper[2] many physical properties of concentrated solutions of NaSCN in liquid ammonia are given together with a description of the experimental measurements and theoretical discussions. The same equipment and techniques were used in the present investigation in which phase diagrams of $NaNO_3$ and of KBr in liquid ammonia are presented. Solubilities of a few other salts are recorded and the vapor pressures of the system $LiNO_3$–NH_3.

The solid and liquid phase diagram of the $NaNO_3$–NH_3 system is shown in Fig. 1. A peritectic is formed which involves the compound $NaNO_3 \cdot 4NH_3$ with a melting point of −42.0°. There is a eutectic point at −81.0° at a composition of 78% by weight of ammonia. Hunt[3] has reported the freezing at 25° of a solution of 50.6% by weight of ammonia, whereas in this work there is a consistent evidence that the composition which first freezes at 25° is 43% ammonia.

The interesting but only partially complete phase diagram for KBr–NH_3 is given in Fig. 2. This system shows a negative temperature coefficient of solubility. The range of concentrations in this study was limited to solutions containing more than 67% by weight of NH_3 and more work should be done on this system. A similar behavior has been reported by Campbell[4] for Li_2SO_4 and water.

In Table I are recorded the liquidus points for several other salts in liquid ammonia.

TABLE I

SOLUBILITIES OF SALTS IN LIQUID AMMONIA

Salt	NH_3, weight %	Moles NH_3 per mole salt	Temp., crystal disappearance, °C.
LiSCN	96.55	106.8	−75
	79.75	15.04	−82
	50.89	5.04	−64
	44.11	2.95	16
	33.91	1.96	20
LiBr	75.35	15.59	39
LiI	92.66	99.2	−76.5
	65.58	14.98	−37.5
NaBr	50.21	6.09	16.0
	42.0	4.38	25.0
NaI	40.40	5.97	14.5
KSCN	51.38	6.03	−59
KI	37.07	5.89	−49.5
KNO_3	94.36	99.42	−74
	71.69	15.04	100
AgSCN	38.25	6.04	−12

The LiSCN–NH_3 system was chosen for study because it was anticipated that the salt would be highly soluble. The solutions however were so viscous that they were difficult to work with; in fact, at the higher concentrations of LiSCN the solutions were gel-like. The salt itself decomposed at 220 to 240°. Both in the case of the thiocyanate and the nitrate the lithium salts were more viscous than the sodium salts.

The solubilities of AgBr, AgI, $AgNO_3$, NH_4SCN, $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2$ and some other salts at 25° have been reported by Hunt.[3] The solubility of $LiNO_3$ in liquid ammonia has been studied by Portnow and Divilewitch.[5] The solubilities of NH_4I and NH_4NO_3 are also reported.[6]

---

(1) More complete details of this research may be obtained from the Ph.D. thesis of George C. Blytas filed in the library of the University of Wisconsin in 1961.

(2) G. C. Blytas and F. Daniels, *J. Am. Chem. Soc.*, **84**, 1075 (1962).

(3) H. Hunt, *ibid.*, **54**, 3509 (1932).

(4) A. N. Campbell, *ibid.*, **65**, 2268 (1943).

(5) M. A. Portnow and N. K. Divilewitch, *Zhur. Obs. Khim.*, **7**, 2149 (1947).

(6) International Critical Tables, Vol. IV, 44 (1933).

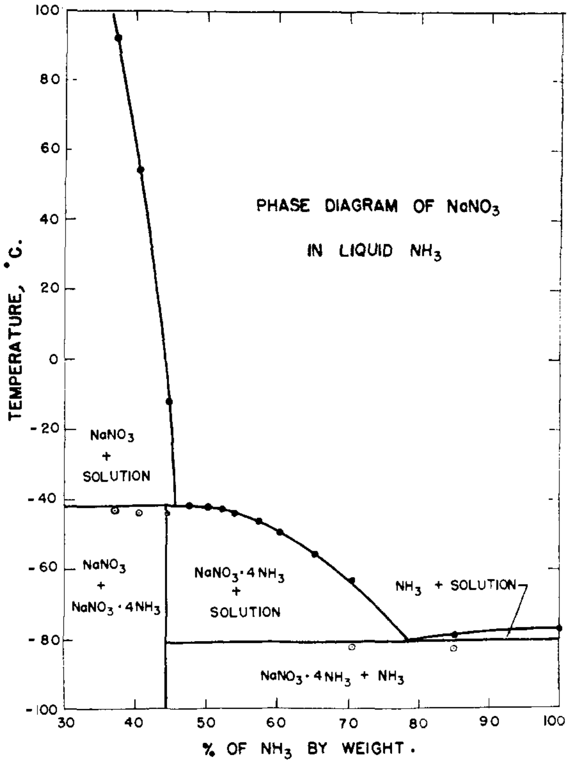

Fig. 1.

The vapor pressures of ammonia in concentrated solutions of $LiNO_3$ are given at different temperatures in Fig. 3. The log *P versus* $1/T$ graphs for a few concentrations of $LiNO_3$ and NaSCN in liquid ammonia are given in Fig. 4, where the per cent. by weight of NH_3 is indicated.

Discussion

The solubilities of salts in liquids of appreciable dielectric constants, such as liquid ammonia, are determined by the crystal structure of the salts, the character of the ions involved and the solvating power of the solvent. Factors such as ionic diameter, ionic charge and polarizability and polarizing power of the ions determine both crystal energy and the energetics of solution.

A comparison of the solubilities of salts in liquid ammonia can be made by noting the freezing points of solutions having the same solvent to solute mole ratio. Data from the present investigation, as well as from sources previously cited, are arranged in terms of component ions in Table II.

The general trend in solubility of anions is $SCN^- > I^- > Br^-$. The NO_3^- ion is more soluble when coupled with strongly electropositive cations such as NH_4^+, Li^+ and Na^+ and is less soluble in conjunction with less electropositive, polarizable ions as K^+ and Ag^+. The SCN^- ion shows the same tendency but to a lesser degree. For Br^- and I^- which are much more polarizable and less electronegative than NO_3^- or SCN^-, the effect is sometimes reversed, except for the NH_4^+ salts. The bromide salts are the least soluble in all cases.

The trend in solubility for the cations is $NH_4^+ > Li^+ > Na^+, K^+ > Ag^+ > Ca^{++}, Ba^{++}, Sr^{++}$, when in combination with the more electronegative anions, SCN^- and NO_3^-. In the case of the salts of the more polarizable anions, Br^- and I^-, the sequence for the alkali metal cations is indefinite. In all cases, salts of the ammonium ion, which may be considered a protonated solvent molecule, are the most soluble.

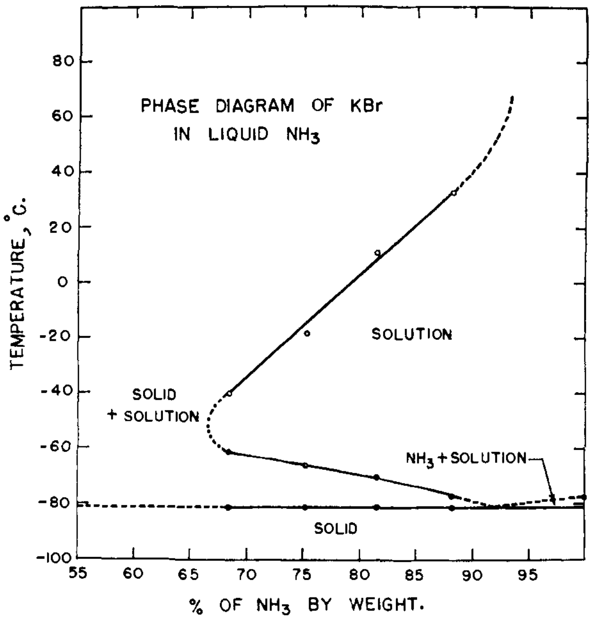

Fig. 2.

Table II

	SCN⁻		Br⁻		I⁻		NO_3^-	
	n^a	T, °C.	n	T, °C.	n	T, °C.	n	T, °C.
Na^+	6	−48	6	16	6	14.5	6	−45
	2	135					3	90
K^+	6	−59	15	−61 and >150	6	−49.5	15	100
NH_4^+	1.4	−12	6	−23	4	−51	2.1	−30
			2	87	2	57	1.4	0
Ag^+	6	−12	188	25	6.7	25	11.6	25
Li^+	5	−64	15.6	39	15	−38	15	−79
							2	40
Ca^{++}							11.8	25
Sr^{++}							18.8	25
Ba^{++}							15.7	25

[a] n = moles of solvent per mole of solute; T = liquidus points.

In water solutions, lithium salts are known to be very soluble in general. In ammonia lithium performs in a similar manner when coupled with strongly electronegative ions such as SCN^- and NO_3^-. However, when coupled with more polarizable ions, as Br^- and I^-, the lesser solvating power of NH_3 is not nearly as capable of removing the Li^+ from the covalent crystal lattice. The difference in the solubility between the bromide and iodide salts can be accounted for in terms of the less favorable crystal structure of the iodide resulting from the great size of the I^- ions.

In conclusion it appears that unless the crystal structure is unfavorable, the solubility of a salt in liquid ammonia is inversely related to the degree of covalency of the crystal interatomic bonds.

The vapor pressures of the $LiNO_3$–NH_3 system were investigated because of possible use in solar refrigeration by absorption and desorption. Although promising, there is a theoretical possibility of an exothermic reaction to give nitrogen and

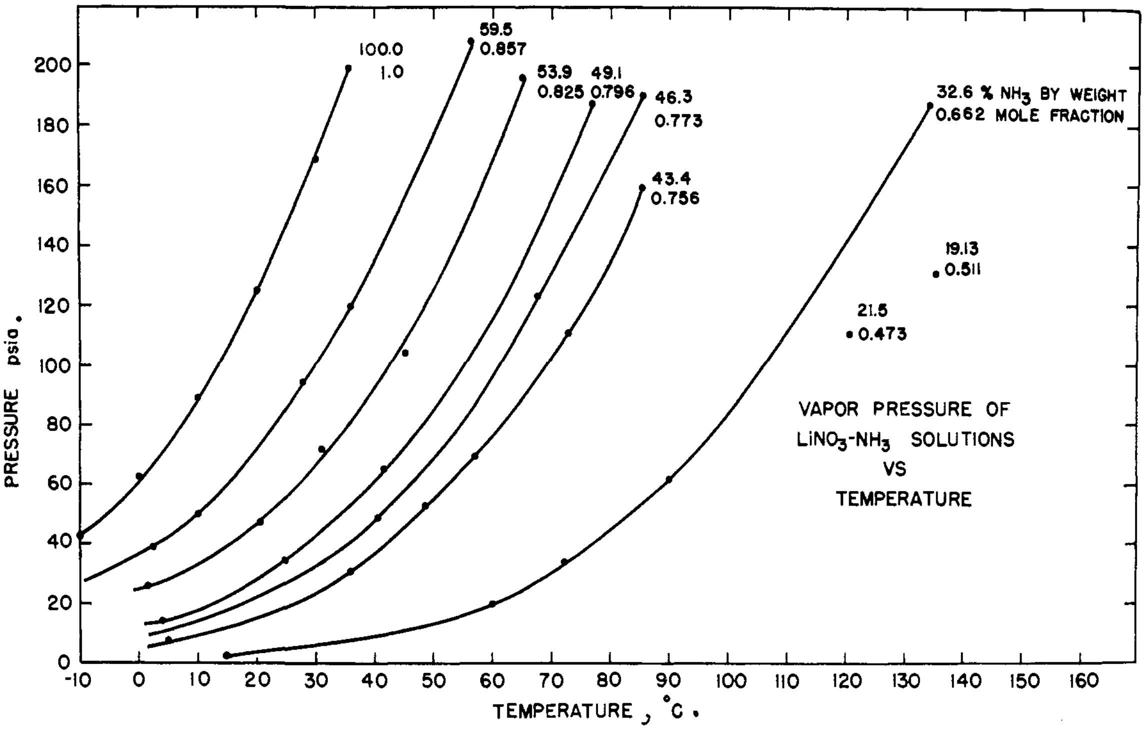

Fig. 3.

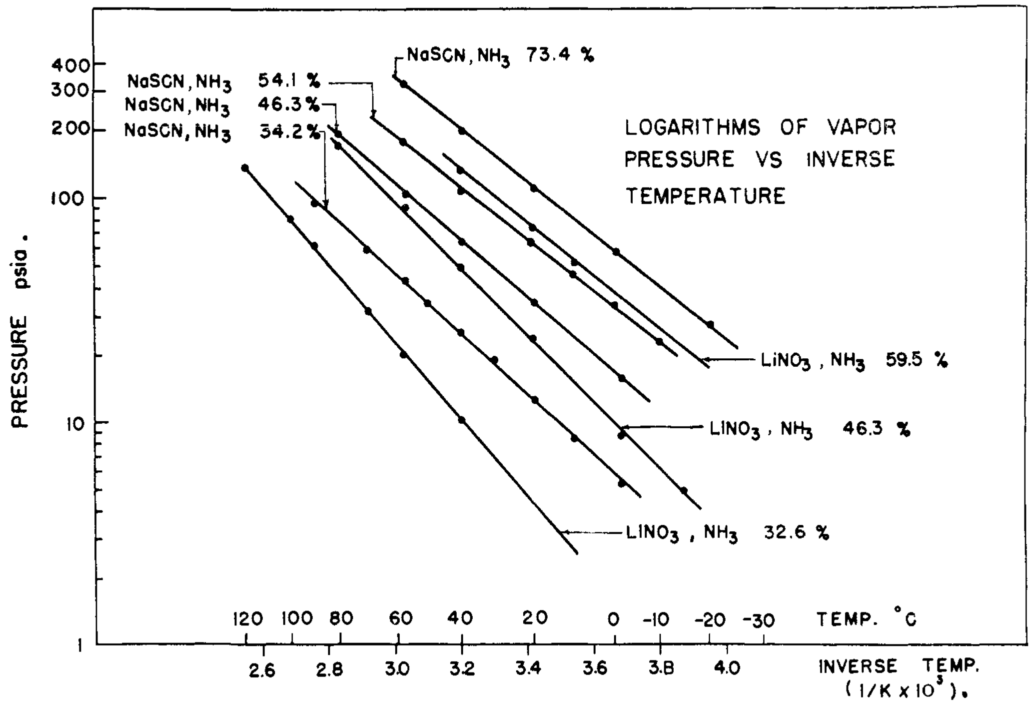

Fig. 4.

steam and lithium oxide with explosive violence. The NaSCN–NH_3 system[2] is as good and is less viscous and less expensive.

The log *P versus* 1/*T* graphs are straight lines even when the solutions go up to the range of the critical temperature of ammonia. This implies that the Clausius–Clapeyron conditions are satisfied. This is indeed the case, since (a) the density of very concentrated solutions is appreciably greater than that of the pure solvent, and (b) the vapor pressure of the solution is much lower than the pressure of pure solvents, so that the simple gas law is still reasonably applicable.

Acknowledgments.—The authors are pleased to acknowledge partial support of the program by the John Simon Guggenheim Memorial Foundation, the Rockefeller Foundation and the Union Carbide Corporation.