[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Liquid Ammonia as a Solvent. III. The Solubility of Inorganic Salts at 25°

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In order to investigate the behavior of strong electrolytes in liquid ammonia it is advantageous to know their solubilities. It is the purpose of this article to report the solubilities of some inorganic salts in liquid ammonia at 25°.

Experimental

The same methods of measuring solubilities were used as described in the first paper of this series.[1] In the meantime, the vapor pressures of ammonia solutions of the salts of ammonia were determined and the following agreement between the two methods of measuring solubilities was found.

	NH_4NO_3	NH_4I
Solubility by vapor pressure	390.0 g.	368.5 g./100 g. NH_3
Solubility by methods of Paper I	390.0 g.	368.5 g./100 g. NH_3

M. Linard and M. Stephan[2] criticized our values as being too low because a vapor correction was not applied. The solubilities of the alkali halide salts were checked by weighing the amount of salt previously reported into a 25-mm. tube with the reported amount of ammonia, drawing the tube down to a long narrow capillary, sealing, and, when the salt had dissolved, weighing the tube. Then the tube was cooled, the tip broken and a few milligrams of ammonia allowed to escape. The tube was then placed in the 25° bath. Crystals always came out with this smaller amount of ammonia. The tubes were sealed as close to the liquid as possible. Using our method we found a value of 12.85 g./100 g. NH_3 for the solubility of sodium chloride at 0°. Linard's data show that we have a great variation in solubility with change in temperature. G. Patscheke[3] has shown that sodium chloride has a wide variation in solubility at various temperatures. Linard's results show that the vapor phase correction is no greater than was explained in Paper I.

We have taken special precautions to have all our materials extremely dry. Reagent grade chemicals were recrystallized three times from water and then from a suitable anhydrous solvent. They were dried to constant weight in a vacuum oven.

The formulas for ammonium oxalate, ammonium sulfate and sodium sulfate were incorrectly printed in the first paper of this series, subscripts of three being given instead of four. The solubility of sodium sulfate was incorrect also.

[1] Hunt, THIS JOURNAL, **54**, 3509 (1932).

[2] M. Linard and M. Stephan, *Z. physik. Chem.*, **163**, 185 (1933).

[3] G. Patscheke, *Z. physik. Chem.*, **163**, 340 (1933).

TABLE I

THE SOLUBILITY OF INORGANIC SALTS IN LIQUID AMMONIA AT 25°

Substance	G./100 g. NH_3	Substance	G./100 g. NH_3	Substance	G./100 g. NH_3
$NH_4C_2H_3O_2$	253.16(?)	$KBrO_3$	0.002	$LiNO_3$	243.66
NH_4HCO_3	0.00	$KClO_3$	2.52	Li_2SO_4	0.00
NH_4ClO_4	137.93	KIO_3	0.000	MnI_2	.02
NH_4I	368.5	AgBr	5.92	$NaNH_2$	.004
$(NH_4)_2HPO_4$	0.00	AgCl	0.83	Na_2SO_4	.00
$(NH_4)_2S$	120.0	AgI	206.84	$Sr(NO_3)_2$	87.08
$BaCl_2$	0.00	$AgNO_3$	86.04	ZnI_2	0.10
$Ba(NO_3)_2$	97.22	$Ca(NO_3)_2$	80.22	ZnO	.00
KNH_2	3.6	H_3BO_3	1.92		

$SbBr_3$, $BiCl_3$, $Bi(NO_3)_3$, $Cd(NO_3)_2$, $Co(NO_3)_2$, $FeBr_3$, $Pb(C_2H_3O_2)_2$, Mg_3N_2, $Hg(NO_3)_2$, $Ni(NO_3)_2$, S, $SnCl_4$ appear to be insoluble, while $Cu(NO_3)_2$, I_2, $Pb(NO_3)_2$, and HgI_2 were very soluble in liquid ammonia but all reacted with ammonia.

If salts are ionized in ammonia as in water, salts with common ions should decrease each other's solubility and salts without common ions should increase the solubility of each other. This point was verified by determining the solubilities of the mixtures given in Table II: 0.2500 g. of the less soluble salt was mixed with variable amounts of the more soluble salt and ammonia added in excess. Ammonia was allowed to escape from the solution until a single small crystal of one salt came out of solution. Identical results were obtained by approaching the saturation point from opposite sides. The various experiments indicate the ratio of the two salts present in the solution when the solution was saturated with respect to one salt.

TABLE II

SOLUBILITIES OF MIXED SALTS

Moles Salt/10 moles NH_3

NaCl ⟷	$NaNO_3$	NH_4Cl ⟷	NH_4NO_3	NaCl ⟷	NH_4NO_3
0.0	1.95	0.0	8.2875	0.088	0.0
.0524	1.80	.4875	7.82	.534	1.562
.059	1.787	.576	7.70	.667	5.85
.0686	1.694	.692	7.4	.632	7.39
.0686	1.694	.734	6.54	.655	8.60
.0700	1.482	.903	4.83	.484	8.50
.0746	1.232	2.27	1.52	.0	8.2875
.087	0.46	3.01	0.255		
.088	.0	3.257	.0		

Discussion of Results

In general, the solubility of the halides increases as the atomic weight of the halogen increases. The salts of ammonia are the most soluble, salts of lithium are more soluble than salts of sodium, salts of sodium are more soluble than salts of potassium, and the solubilities of the nitrates of the alkaline earths decrease as the atomic weight of the metal increases. The halides of silver diverge the most radically of any salts from the aqueous solubilities, the iodide being 7.5×10^8 times as soluble in ammonia as in water. Silver iodide reacts with silver nitrate so that the solubility of mixtures of the two salts could not be determined. Mixtures of sodium nitrate and ammonium chloride react with explosive violence. All sulfates, phosphates, carbonates and oxides tested were insoluble. On comparing the solubilities of silver halides or any sulfates, one sees no correlation between physical properties and solvent power of the two solvents. As a general rule, the inorganic salts studied are more soluble in ammonia than in the aliphatic alcohols.

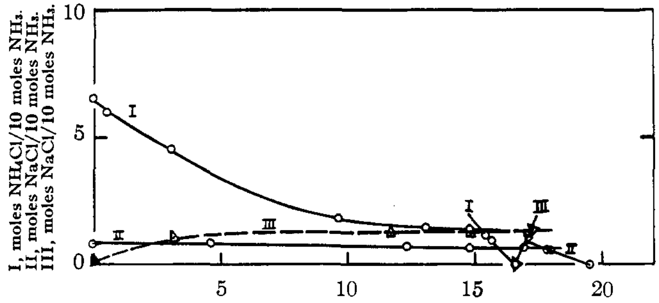

Fig. 1.—Solubilities of mixed salts: I, moles NH_4NO_3/10 moles NH_3 (scale 1 mole = 2 cm.); II, moles $NaNO_3$/10 moles NH_3 (scale 1 mole = 1 decimeter); III, moles NH_4NO_3/10 moles NH_3 (scale 1 mole = 2 cm.).

Some salts are very soluble but are unstable in liquid ammonia, as lead nitrate, while others, as nickelous nitrate, react only after a certain concentration is reached. The difference in solubility between similar salts, as potassium iodide and potassium iodate, makes this solvent a possible one to use for extractions in the preparation of pure chemicals. Compounds of the metals of groups I and II of the periodic table show the least tendency toward reaction with ammonia in liquid ammonia.

Figure 1 shows that the presence of a common ion decreases the solubility of a salt in ammonia. Curve III shows that salts without a common ion increase the solubility of each other. The solubility curves have the same general shape in ammonia as in water, indicating ionization of the salts.

Summary

1. The solubilities of twenty-six inorganic compounds in liquid ammonia have been determined quantitatively at 25°.
2. The solubilities for three sets of mixed salts, NH_4Cl–NH_4NO_3, NaCl–$NaNO_3$, and NaCl–NH_4NO_3 have been determined.

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