[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

# The Solubility of Some Salts in Ethylenediamine, Monoethanolamine and Ethylene Glycol[1]

BY HERBERT S. ISBIN[2] AND KENNETH A. KOBE[3]

The amino group of liquid ammonia and the hydroxyl group of water are quite similar in many respects. The many striking analogies between water and liquid ammonia, developed by Franklin and co-workers,[4] have led to a widespread interest in liquid ammonia research.[5] However, because of the involved experimental technique required in such investigations, other similar polar solvents may be preferred. Putnam and Kobe[6] have demonstrated that ethylenediamine is a desirable medium for theoretical studies as it is not only comparable in ionizing power to liquid ammonia, but also possesses more adaptable physical and chemical properties. Their tabulation of physical properties shows that polar properties, as dielectric constant, surface tension, dipole moment, etc., are comparable to liquid ammonia.

It is the object of this work to determine the solubility of a series of typical inorganic salts in ethylenediamine and compare with solubilities in liquid ammonia and in water. In addition, comparisons have been made for the related solvents monoethanolamine and ethylene glycol.

## Experimental

**Preparation of Solvents.**—The ethylene glycol and monoethanolamine were the technical grade chemicals of Carbide and Carbon Chemical Corporation and were purified by careful fractionation.[7] The ethylenediamine was dehydrated and purified by the method previously used.[6]

**General Treatment of Salts.**—Analytical grade salts were used and those not conforming to A. C. S. specifications were purified by recrystallization. Generally, drying at 150° was sufficient to remove all water, but the perchlorates were recrystallized from water above 50° and dehydrated at 250°. LiI·3en was prepared from $LiI \cdot 3H_2O$ by successive crystallizations from anhydrous ethylenediamine.

**Equilibrium.**—The solvent and excess solid phase were sealed in soft-glass test-tubes and rotated for at least one week in a water thermostat at 25.0 ± 0.08°. Analyses of a series of tubes were made at regular intervals until check values were obtained, which, in ethylenediamine were within 0.5% for salts more soluble than 3 g. per 100 g. of solvent, though with less soluble salts the differences were as high as 4%. For monoethanolamine and ethylene glycol the data were more consistent.

**Analysis of Solutions.**—All analyses were made on a weight basis by use of weighing pipets. Both the standard gravimetric determination of a halide and the volumetric method, using dichlorofluorescein as an adsorption indicator, were used. Neither the amines, after being neutralized with nitric acid, nor the glycol affected the accuracy of the determinations at the concentrations used. Chlorates, bromates and iodates were reduced to the corresponding halide by boiling with excess sulfurous acid. Perchlorates were reduced by fusing with sodium carbonate in a platinum crucible. Sodium and potassium thiocyanates and mercuric acetate were determined volumetrically with standard silver nitrate and potassium thiocyanate, respectively.

For the nitrate solutions the organic matter was oxidized with fuming sulfuric acid and 30% hydrogen peroxide and the salts ignited and weighed as sulfates.

**Determination of Solid Phases.**—The solid phase was analyzed by drying the excess solute on filter paper, weighing, titrating with standard nitric acid to the methyl orange end-point, and determining the halide with silver nitrate to the dichlorofluorescein end-point.

Experimental values of the mole ratio of ethylenediamine to salt are given:

| Salt | Moles en per mole of salt | | | | | |
|---|---|---|---|---|---|---|
| NaI | 3.0 | 3.0 | 3.3 | 2.9 | 3.1 | |
| $NaClO_4$ | 2.9 | 3.3 | 3.3 | 3.2 | 3.0 | 3.0 |
| LiBr | 2.0 | 2.0 | 2.1 | 1.9 | 2.0 | |
| LiCl | 2.0 | 1.9 | 2.0 | | | |
| LiI | 3.0 | | | | | |
| $BaCl_2$ | 3.75 | 4.1 | 4.0 | | | |
| $CaCl_2$ | 6.2 | 5.9 | | | | |
| $SrCl_2$ | 5.8 | 6.2 | 6.2 | | | |

## Results

The solubilities determined at 25° in ethylenediamine, monoethanolamine and ethylene glycol are compared in Table I with literature values in water[8] and liquid ammonia.[9]

A comparison of solvates, Table II, shows that ethylenediamine of solvation tends to parallel hydrate formation. Insufficient data are available to compare with ammoniate formation.

## Discussion

The solvent characteristics of ethylenediamine parallel those of liquid ammonia in all respects for the data available. All chlorides are but sparingly soluble. The relatively high solubility of sodium bromide and iodide, and potassium iodide, in comparison with the chlorides, differentiates both liquid ammonia and ethylenediamine from water. The abnormally high solubility of sodium bromide in liquid ammonia is reflected in ethylenediamine, for this solubility is even more than that of sodium iodide.

The inversion of the aqueous order of solubility for the chlorates and perchlorates in ethylenediamine is noteworthy. Although there are sev-

(1) Paper II; for I see ref. 6.

(2) Present address, Ford, Bacon and Davis, Inc., Washington, D. C.

(3) Present address, Department of Chemical Engineering, University of Texas, Austin, Texas.

(4) E. C. Franklin, "The Nitrogen System of Compounds," The Reinhold Publishing Company, New York, N. Y., 1935.

(5) Watt, *et al.*, *Chem. Rev.*, **32**, 219–29 (1943), and earlier reviews.

(6) Putnam and Kobe, *Trans. Electrochem. Soc.*, **74**, 609–624 (1938).

(7) Reitmeier, Sivertz and Tartar, THIS JOURNAL, **62**, 1943–1944 (1940).

(8) A. Seidell, "Solubilities of Inorganic and Organic Compounds," D. Van Nostrand Company, New York, N. Y., Third edition, 1940.

(9) H. Hunt, THIS JOURNAL, **54**, 3511 (1932); **55**, 3529 (1933).

TABLE I

SOLUBILITIES AT 25°

All solubilities are expressed in grams salt/100 grams solvent.

| Salt | Ethylenediamine | Monoethanolamine | Ethylene glycol | Ammonia (9) | Water (8) |
|---|---|---|---|---|---|
| NaCl | 0.33 | 1.86 | 7.15 | 3.02 | 35.98 |
| NaBr | 54.4 | 33.6 | 35.4 | 138.0 | 94.6 |
| NaI | 34.6 | 22.0 | 107.4 | 161.9 | 183.7 |
| KCl | 0.014 | 0.27 | 5.18 | 0.04 | 35.85 |
| KBr | 0.78 | 3.27 | 15.5 | 13.50 | 68.3 |
| KI | 74.9 | 42.3 | 49.9 | 182.0 | 148.7 |
| $NaClO_3$ | 52.8 | 19.7 | 16.0 | | 106 |
| $NaClO_4$ | 30.1 | 90.8 | 75.5 | | 209.6 |
| $KClO_3$ | 0.145 | 0.30 | 1.21 | 2.52 | 8.6 |
| $KClO_4$ | 2.81 | 1.36 | 1.03 | | 2.07 |
| LiCl | 1.39 | 30[a] | 14.3 | 1.41 (0°) | 84.66 |
| LiBr | 2.41 | 60[a] | 39.4 | | 170 |
| $NaIO_3$ | 0.00 | | | | 9.4 |
| $KIO_3$ | .00 | | | 0.000 | 10.6 |
| $KBrO_3$ | .00 | | | 0.002 | 8.0 |
| $KIO_4$ | Reacted | | | | 0.51 |
| NaCNS | 93.5 | | | 205.5 | 142.6 |
| $NaNO_3$ | 33.5 | | | 97.60 | 91.5 |
| KCNS | 83.0 | | | | 239 |
| $KNO_3$ | 0.37 | | | 10.4 | 37 9 |
| $CaCl_2$ | .00 | 14.0 | 20.6 | | 83 |
| $SrCl_2$ | .00 | 19.5 | 36.4 | | 55.8 |
| $BaCl_2$ | .22 | 45.2 | 36.8 | 0.00 | 37.2 |
| $HgCl_2$ | .4 | Dec. | | | 7.2 |
| $Hg(C_2H_3O_2)_2$ | .186 | Dec. | 17.8 | | 25 (10°) |

[a] Approximate, solutions very viscous.

TABLE II

COMPARISON OF SOLVATES AT 25°

| Water | Ethylenediamine |
|---|---|
| NaCl | NaCl |
| $NaBr \cdot 2H_2O$ | NaBr |
| $NaI \cdot 2H_2O$ | NaI·3en |
| KCl | KCl |
| KBr | KBr |
| KI | KI |
| $NaClO_3$ | $NaClO_3$ |
| $NaClO_4 \cdot H_2O$ | $NaClO_4$·3en |
| $KClO_3$ | $KClO_3$ |
| $KClO_4$ | $KClO_4$ |
| $LiCl \cdot H_2O$ | LiCl·2en |
| $LiBr \cdot 2H_2O$ | LiBr·2en |
| $LiI \cdot 3H_2O$ | LiI·3en |
| $CaCl_2 \cdot 6H_2O$ | $CaCl_2$·6en |
| $SrCl_2 \cdot 6H_2O$ | $SrCl_2$·6en |
| $BaCl_2 \cdot 2H_2O$ | $BaCl_2$·4en |

eral salts more soluble in liquid ammonia than in water, potassium perchlorate was the only salt found more soluble in ethylenediamine than in water. The thiocyanates are very soluble and sodium thiocyanate is the most soluble salt reported in both liquid ammonia and ethylenediamine. The solubilities of sodium and potassium nitrates are similar to those of the corresponding bromides.

As would be expected from the similarity of ethylenediamine, monoethanolamine and ethylene glycol, solubilities in monoethanolamine tend to occupy a position intermediate between the other two solvents. For the less soluble salts this value approximates the geometric mean of the solubilities in the other two related solvents. For the more soluble salts, the solubilities are unpredictable. The extraordinary viscosity of lithium salts in monoethanolamine is noteworthy.

Although no generalizations are apparent as to whether a hydroxyl or amino group will make a better solvent, the ratios of solubilities in ammonia to water are approximated by the corresponding ratios for ethylenediamine to ethylene glycol. These ratios are shown in Table III.

TABLE III

SOLUBILITY RATIOS AT 25°

| Salt | $\frac{C_2H_4(NH_2)_2}{C_2H_4(OH)_2}$ | $\frac{NH_3}{H_2O}$ |
|---|---|---|
| KCl | 0.0027 | 0.0011 |
| NaCl | .046 | .084 |
| KBr | .050 | .20 |
| LiCl | .097 | .017 |
| $KClO_3$ | .12 | .29 |
| NaI | .32 | .882 |
| KI | 1.50 | 1.22 |
| NaBr | 1.53 | 1.46 |

## Summary

1. The solubilities of a number of inorganic salts have been determined in ethylenediamine, monoethanolamine and ethylene glycol.

2. Although the solubilities in ethylenediamine are less than those in liquid ammonia, the former has been shown to possess similar solvent characteristics.

3. Ammonia/water solubility characteristics are approximated by the corresponding ethylenediamine/ethylene glycol ratios.

SEATTLE, WASHINGTON RECEIVED JULY 25, 1944