[CONTRIBUTION NO. 136 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Partial Molal Volumes of Lithium Chloride and of Sodium Nitrate in Liquid Monomethylamine

BY E. A. KELSO WITH W. A. FELSING

Introduction

The purpose of this investigation was to determine the densities and the partial and apparent molal volumes of salts at different temperatures in liquid monomethylamine. This investigation is one of a series[1] dealing with the thermodynamic properties of the methylamines and their solutions, with special reference to their use in the absorption type of refrigerating units.

It was found by Anderson[2] that the conductance of lithium chloride in liquid monomethylamine seemed to be abnormal over certain concentration ranges, possibly indicating compound formation. Bonnefoi[3] has shown the existence of compounds of the formula $LiCl{\cdot}CH_3NH_2$, $LiCl{\cdot}2CH_3NH_2$, $LiCl{\cdot}3CH_3NH_2$, and $LiCl{\cdot}4CH_3NH_2$. Since in the electrical conductivity of this salt in the liquid amine it was desirable to know how much of the solvent, in the more concentrated region, was tied up with the salt (*i. e.*, the ions), it was decided to determine the partial molal volumes of this salt (and of sodium nitrate) from density measurements.

Experimental

The experimental method consisted of determining at different temperatures the densities of methylamine solutions of these salts in a specially designed pycnometer, the volume of which was accurately known over a range of calibrations.

The Pycnometer.—The Pyrex pycnometer consisted of a bulb (approx. 9 cc.) sealed to a 1-mm. uniform bore capillary approximately 25 cm. long. To the other end of this capillary was sealed a no. 7 ground joint, to which was sealed a 6 cm. small diameter and small bore tube ending in another no. 7 ground joint. The pycnometer is shown in Fig. 1. The calibration was carried out by filling with mercury at 0°; the volume at any other temperature was calculated from the volume at 0° and the volume coefficient of expansion of Pyrex glass as calculated by Felsing and Thomas[1a] from the determinations of Buffington and Latimer.[4]

The Thermostat.—A Dewar flask 12 cm. in diameter and 20 cm. deep (inside measurements) served as a thermostat. A stirrer, heater, and cooling coil (supplied from a reservoir of cooling liquid by means of a circulating pump) together with a mercury-in-iron thermoregulator actuating a high-sensitivity relay system assured a temperature constancy of better than ±0.02° at any desired temperature. Thermometers calibrated by the U. S. Bureau of Standards were used throughout.

The Loading Apparatus.—The loading apparatus is shown in Fig. 1. The entire system was connected to a high-vacuum line.

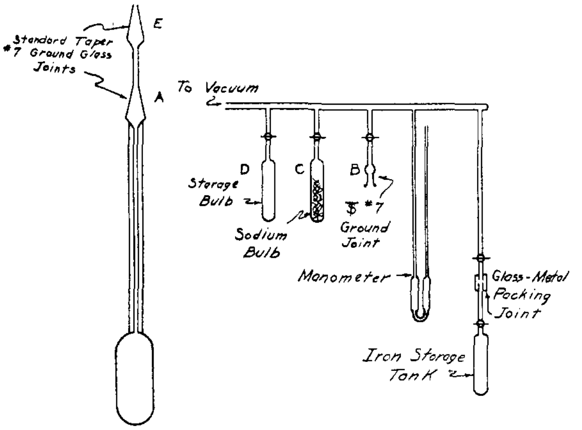

Fig. 1.—Density tube and methylamine loading apparatus.

Purification of Materials. (a) **The Solvent.**—The monomethylamine was prepared from Eastman C. P. hydrochloride. The salt as received was dried in an oven at 110° and over sulfuric acid in a desiccator. The *dry* salt was purified by the method of Bertheaume,[5] using purified and dry chloroform to remove the di- and trimethylamine hydrochlorides, and by the method of François,[6] using yellow mercuric oxide to remove any trace of ammonia. The gaseous amine was liberated by treatment of the purified hydrochloride with 50% potassium hydroxide, using the apparatus of Felsing and Wohlford.[1b] It was dried by passage over potassium hydroxide pellets followed by contact, as a liquid at 0°, with sodium wire. It was stored in a steel cylinder. (b) **The Salts.**—The lithium chloride was C. P. salt, recrystallized three times from conductivity water. It was dried at 110° in a stream of dry hydrogen chloride. The sodium nitrate was C. P. material recrystallized four times from conductivity water and was dried at 150°.

Method of Obtaining Data.—Solutions were prepared as follows. A definite volume of an aqueous stock solution of the salt was introduced into the bottom of the weighed pycnometer by means of a long thin capillary. The water

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[1] (a) Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929); (b) Felsing and Wohlford, THIS JOURNAL, **54**, 1442 (1932); (c) Felsing and Jessen, *ibid.*, **55**, 4148 (1933); (d) Felsing and Buckley, *J. Phys. Chem.*, **37**, 779 (1933); (e) Felsing and Ashby, THIS JOURNAL, **56**, 2226 (1934); (f) Felsing and Phillips, *ibid.*, **58**, 1973 (1936).

[2] P. P. Anderson, Ph.D. Dissertation, The University of Texas, June, 1936.

[3] Bonnefoi, *Compt. rend.*, **127**, 516 (1898); *cf.* Gibbs, THIS JOURNAL, **28**, 1421 (1906).

[4] Buffington and Latimer, *ibid.*, **48**, 2305 (1926).

[5] Bertheaume, *Compt. rend.*, **150**, 1251 (1910).

[6] François, *ibid.*, **144**, 567 (1907).

was then removed by evacuation at slowly increasing temperatures, finishing at 100°. After admitting dry air, the pycnometer was weighed. The pycnometer was then connected to the loading system, the whole evacuated, and liquid methylamine condensed into the pycnometer by surrounding it with a dry ice-acetone mixture. The amount condensed was adjusted by experience to be sufficient to fill the pycnometer to the lower graduations of the capillary when at 0°. The small glass tube between the two ground joints was then sealed off, and the two portions weighed to ascertain the true weight of amine introduced. By means of the ground joint on the capillary, the pycnometer could be emptied back into the system without loss of amine.

Readings on the capillary were made after allowing at least one-half hour for temperature equilibrium to be attained. The weight of the liquid amine was corrected for the amount of gaseous amine above the liquid. The vapor was assumed ideal and the vapor pressure values were those of Felsing and Thomas.[1a]

All weights were corrected to vacuum.

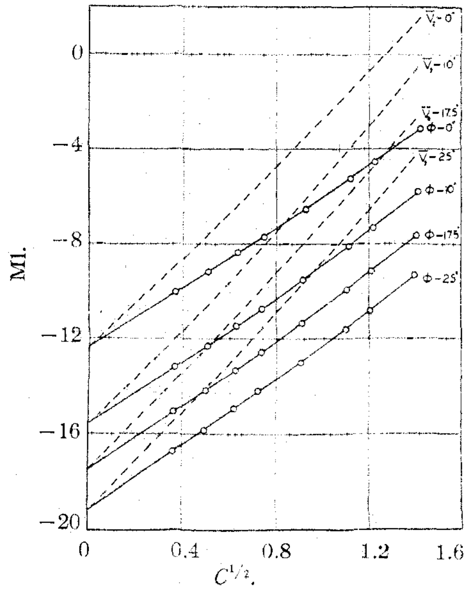

Fig. 2.—Partial and apparent molal volumes of lithium chloride in methylamine.

Experimental Data and Calculated Quantities

For lithium chloride, densities were determined at 0, 10, 17.5, and 25°; for sodium nitrate, at 0, 10, 18 and 25°. These densities are represented by the following relations, which reproduce the observed data to within ±0.01%.

LITHIUM CHLORIDE d (g./ml.)

at 0° $= 0.68667 + 0.05088C - 0.00441C^{3/2}$
at 10° $= .67464 + .05289C - .00452C^{3/2}$
at 17.5° $= .66550 + .05413C - .00458C^{3/2}$
at 25° $= .65623 + .05511C - .00465C^{3/2}$

SODIUM NITRATE, d (g./ml.)

at 0° $= 0.68667 + 0.07429C - 0.00495C^{3/2}$
at 10° $= .67464 + .07636C - .00559C^{3/2}$
at 18° $= 0.66490 + 0.07752C - 0.00569C^{3/2}$
at 25° $= .65623 + .07778C - .00520C^{3/2}$

The apparent molal volumes were calculated from the *observed* densities by the method of Gucker,[7] using the relation

$$\Phi = \frac{1000}{C} - \frac{1}{d_1}\left[\frac{1000d}{C} - M_2\right]$$

where C is the concentration of the solute in moles/liter of solution, d_1 the density of the solvent, d the density of the solution, and M_2 the molecular weight of the solute. These values are given by the following relations, which reproduce the calculated values to within ±0.1%.

LITHIUM CHLORIDE

Φ at 0° $= -12.36 + 6.0469C^{1/2} + 0.27971C$
10° $= -15.59 + 6.1411C^{1/2} + .53926C$
17.5° $= -17.51 + 6.3741C^{1/2} + .42964C$
25° $= -19.21 + 6.6034C^{1/2} + .28775C$

SODIUM NITRATE

Φ at 0° $= 17.45 + 3.2508C^{1/2} + 2.0660C$
10° $= 14.80 + 3.8672C^{1/2} + 2.3715C$
18° $= 13.42 + 4.2635C^{1/2} + 2.0986C$
25° $= 12.32 + 4.9056C^{1/2} + 1.6339C$

The partial molal volumes were then calculated by the expression given by Gucker[7]

$$\overline{V}_2 = \Phi + C^{1/2}\left[\frac{1000 - C\Phi}{2000 + C^{3/2}\partial\Phi/\partial C^{1/2}}\right]\frac{\partial\Phi}{\partial C^{1/2}}$$

The calculated values for $\overline{V}_2$ and for Φ are presented in Figs. 2 and 3. They represent an over-all accuracy of at least 0.1%.

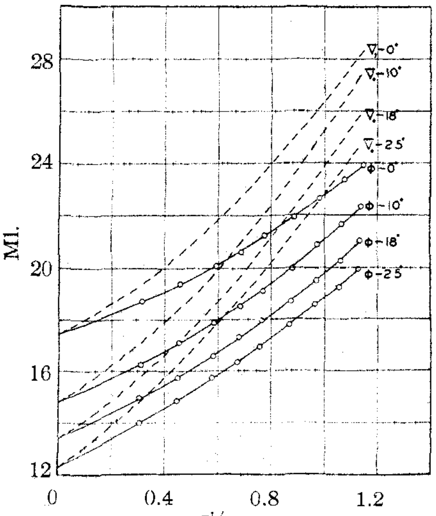

Fig. 3.—Apparent and partial molal volumes of sodium nitrate in methylamine.

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(7) Gucker, *J. Phys. Chem.*, **38**, 307 (1934).

Fitzgerald[8] cites some density data for lithium chloride and for sodium nitrate solutions in methylamine at 0°. However, a smooth curve cannot be drawn through his determined points; his values are mostly higher than those of this investigation and were only incidental to some conductivity and viscosity determinations.

The results for the apparent molal volumes of lithium chloride are very interesting when compared with the values obtained in other solvents.

APPARENT MOLAL VOLUME OF LiCl AT 25°

Solvent	Dielectric constant	Φ	Observer
Water	78	17.06	Geffcken[9]
Methyl alcohol	31.2	− 3.8	Vosburgh[10]
Ethyl alcohol	26.5	− 4.4	Vosburgh
Methylamine	<10.5	−19.21	K. & F.

As the dielectric constant decreases, the apparent molal volume also decreases. The value of <10.5 for the dielectric constant for methylamine was determined by Schlundt[11] on an impure sample. The correct value for pure methylamine is probably much lower than 10.5.

Negative values of the apparent and partial molal volumes have been obtained by other investigators for lithium and sodium hydroxides and for magnesium and copper sulfates in water. The negative values for lithium chloride obtained in this investigation seem to point definitely to a solvation of the lithium ions in the methylamine solution. Such solvation would explain, in part, the trends in electrical conductance observed by Anderson,[2] especially in the more concentrated region. The positive values for sodium nitrate would indicate a probable lack of extensive solvation.

Summary

1. The densities of solutions of lithium chloride and of sodium nitrate in liquid monomethylamine have been determined at different temperatures and have been recorded as functions of the concentration.

2. The apparent and partial molal volumes have been calculated and presented.

3. An approximate correlation between the apparent molal volume of lithium chloride and the dielectric constant of the solvent has been presented.

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(8) Fitzgerald, *J. Phys. Chem.*, **16**, 621 (1912).

(9) Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931).

(10) Vosburgh, Connell and Butler, *J. Chem. Soc.*, 933 (1933).

(11) Schlundt, *J. Phys. Chem.*, **5**, 503 (1901).

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLUMBIA UNIVERSITY]

The Synthesis of Dipeptides from α-Keto Acids[1]

BY DAVID SHEMIN AND ROBERT M. HERBST

The classical peptide syntheses of Emil Fischer, and the elegant methods of Bergmann have proved to be of great value both practically and theoretically. However, the possibility of synthesizing peptides from α-keto acids appeared attractive since biological materials other than amino acids could be utilized. The methods developed in this report are primarily of theoretical interest, although their further development in some specific instances may prove to be of practical value.

The conversion of α-keto acids into the corresponding amino acids has been accomplished in a variety of ways. The oximes of α-keto acids have been reduced to amino acids either with tin and hydrochloric acid,[2] or with sodium amalgam.[3] Knoop and Oesterlin[4] have succeeded in reducing α-keto acids to amino acids catalytically with hydrogen in the presence of ammonia. Herbst and Engel[5] have been able to convert α-keto acids into the corresponding amino acids by interaction with another α-amino acid, a reaction which has been accomplished recently in biological systems.[6,7] Of biochemical interest are the reduction of the oxime of pyruvic acid to *dl*-alanine by actively fermenting yeast,[8] the synthesis of alanine from pyruvic acid and ammonia by liver tissue slices,[9] and the formation of *l*-aspartic acid from oxalacetic acid and hydroxyl-

(1) This report is from a dissertation submitted by David Shemin in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

(2) Gutknecht, *Ber.*, **13**, 1116 (1880).

(3) Gränacher, *Helv. Chim. Acta*, **5**, 610 (1922).

(4) Knoop and Oesterlin, *Z. physiol. Chem.*, **148**, 294 (1925); **170**, 186 (1927).

(5) Herbst and Engel, *J. Biol. Chem.*, **107**, 505 (1934); Herbst, THIS JOURNAL, **58**, 2239 (1936).

(6) Braunstein and Kritzmann, *Enzymologia*, **2**, 129 (1937).

(7) Virtanen and Laine, *Nature*, **141**, 748 (1938).

(8) Maurer, *Biochem. Z.*, **189**, 216 (1927).

(9) Neber, *Z. physiol. Chem.*, **234**, 83 (1935).