The Apparent Molal Volumes of Some Electrolytes in Anhydrous Ethylenediamine[1,2]

ROBERT E. DAVIS and JOHN PEACOCK with
FREDERIC C. SCHMIDT and WARD B. SCHAAP, Indiana University

Introduction

Very few density measurements and no partial molal volumes of electrolytes in solution in anhydrous ethylenediamine have been made. In conjunction with some conductance measurements made in this laboratory, density measurements were made on solutions of sodium bromide, silver nitrate, silver chloride, mercuric iodide, and cyanide. From these data the apparent molal volumes of these salts in solution were calculated with the hope that such data would indicate the nature of the species present in solution, both dilute and concentrated.

Experimental

The purification and handling of the anhydrous solvent has been previously discussed.[1,2]

All salts were of reagent grade and were dried to constant weight at 110° C. The water-soluble salts were twice recrystallized from distilled water. Density measurements made on solutions of the sublimed HgI_2 were identical, within experimental error, to those made with the unsublimed reagent grade salt.

Picnometers of 25 ml. capacity were calibrated at 25.00° C with both water and distilled mercury.

The solutions were prepared by weighing the salts directly into glass stoppered tubes of approximately 100 ml. capacity. The anhydrous solvent was distilled directly onto the salt in the tubes. All air was excluded by a positive pressure of hydrogen. Solutions were siphoned into the picnometers. Densities agreed with 0.03% on duplicate runs for each concentration.

Results and Discussion

The apparent molal volumes were calculated by means of the equation

$$\emptyset V_2 = \frac{m_2}{d_1} - \frac{1000}{md_1} (d_1 - d_o)$$

where d_1 and d_o are the densities of the solution and the pure solvent respectively.

The densities and apparent molal volumes are tabulated in Table I for each concentration. The plots of the apparent molal volumes versus the square-root of the molality is shown in Figure 1. Examination of these plots demonstrated that the Masson[3] equation $\emptyset V_2 = \emptyset V_2° + KC^{1/2}$

is applicable to these solutions. From the plots the volume of the salt at infinite dilution can be obtained by extrapolation. These values along with the Masson constant are shown in Table II.
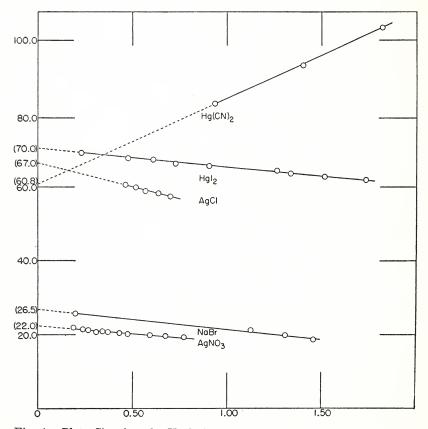

Fig. 1. Plots Showing the Variation of the Apparent Molal Volumes of Some Electrolytes in Anhydrous Ethylenediamine.

TABLE I

Densities and Apparent Molal Volumes in Ethylenediamine at 25° C.

$AgNO_3$

Molality	Density gm/ml.	$\emptyset V_2$
0.0648	0.9030	29.18
0.1283	0.9113	29.51
0.1616	0.9158	27.70
0.1657	0.9164	27.18
0.2154	0.9231	25.55
0.2574	0.9286	25.40
0.4035	0.9481	24.82
0.5183	0.9640	24.69
0.6859	0.9865	24.00

AgCl

0.2596	0.9144	60.65
0.3068	0.9182	60.0
0.3751	0.9240	58.3
0.4705	0.9315	58.1
0.5771	0.9401	57.4

HgI_2

0.1037	0.93057	66.41
0.2388	0.97680	65.40
0.3351	1.0108	67.08
0.6257	1.1096	63.15
0.9710	1.2190	66.83
1.3861	1.3520	62.85
2.016	1.5370	64.11
2.182	1.5723	58.39
2.279	1.6112	64.03
3.039	1.8254	59.81

NaBr

0.0467	0.8962	25.2
1.1010	0.9740	
1.4884	1.0020	21.7
1.9880	1.040	19.9
2.483	1.078	18.5

$Hg(CN)_2$

0.8524	1.0462	82.7
1.971	1.2280	93.3
3.957	1.5283	103.2

TABLE II

$\emptyset V_2°$ and The Masson Constant

Salt	$\emptyset V_2°$	K
$Hg(CN)_2$	60.8	$+22.7$
AgCl	67.0	-12.5
NaBr	32.6	-8.5
$AgNO_3$	29.5	-5.9
HgI_2	69.2	-5.7

Literature Cited

1. HIBBARD, B. B., and F. C. SCHMIDT. 1955. Physical-chemical Studies of Solutions in Anhydrous Ethylenediamine. I. Conductance Measurements of Solutions of Sodium, Silver, and Tetra-n-butylammonium Nitrates and Iodides. J. Am. Chem. Soc. 77: 225.

2. PEACOCK, JOHN, F. C. SCHMIDT, R. E. DAVIS, AND W. B. SCHAAP. 1955. Physical Chemical Studies of Solutions in Anhydrous Ethylenediamine. II. Conductances and Visosities of Solutions of Mercuric Bromide, Iodide, and Cyanide. J. Am. Chem. Soc. 77: 5829.

3. MASSON, D. O. 1929. Solute Molecular volumes in Relation to Solvation and Ionization. Phil. Mag. [7], 8: 218.