[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

The Apparent and Partial Molal Volumes of Ammonium Chloride and of Cupric Sulfate in Aqueous Solution at 25°[1]

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Masson[4] discovered a linear relationship between the apparent molal volume and the square root of the volume concentration, which held even in concentrated solutions for a number of strong electrolytes. To test the validity of this law in the case of ammonium chloride and of cupric sulfate, their apparent molal volumes were calculated.

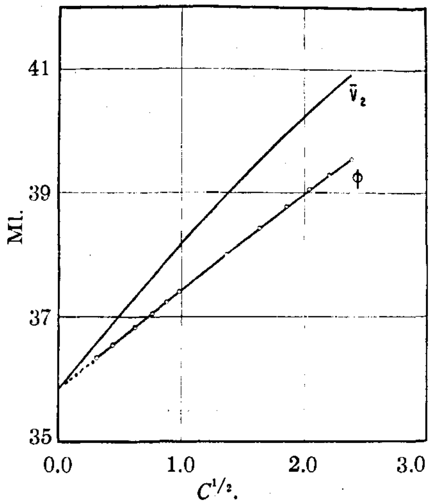

Fig. 1.—Apparent and partial molal volumes of ammonium chloride in aqueous solution at 25°.

The various solutions were made up from stock solutions of thrice recrystallized ammonium chloride or cupric sulfate and redistilled water on a weight-molal basis. The stock ammonium chloride solution was analyzed by precipitation of the chloride as silver chloride. The cupric sulfate solutions were analyzed by electrolytic deposition of the copper from slightly acid solution on platinum cathodes.

The density of each solution was determined in a 100-ml. pycnometer, filled in a water thermostat at 25 ± 0.005°. A similar pycnometer was used as a counterpoise, and brass weights calibrated by substitution against Bureau of Standards certified weights were used in all weighings. The relative humidity of the air was considered in all the necessary buoyancy corrections. At least three independent determinations of each density were made, the results agreeing to two or three parts per million.

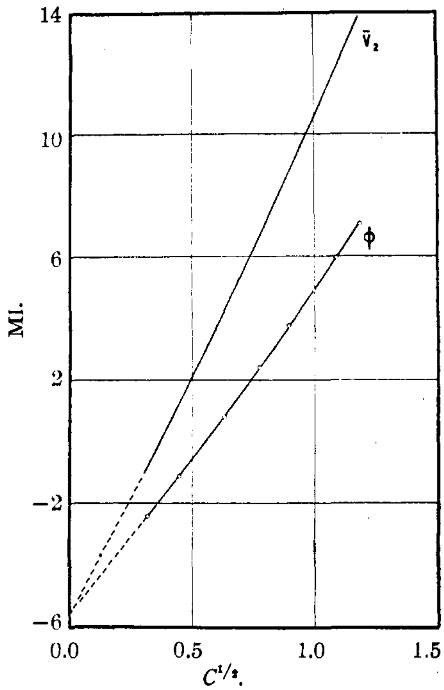

Fig. 2.—Apparent and partial molal volumes of cupric sulfate in aqueous solution at 25°.

The solution volumes, V, were calculated from the relation

$$V = (1000 + mM)/d$$

where m is the molality, M the molecular weight of the solute, and d the density. The apparent molal volumes, ϕ, of the solute were calculated from

$$\phi = (V - n_1\bar{V}_1^0)/m$$

where $n_1\bar{V}_1^0$ is the volume of 1000 g. of water at 25°, and m is the molality. The concentration, C, in moles per liter is given by the relation

$$C = 1000m/V$$

The values calculated are collected in Tables I and II, and the apparent molal volumes are plotted against $C^{1/2}$ in Figs. 1 and 2. The experi-

(1) Part of the dissertation presented to the Graduate College of the State University of Iowa by Gerald G. Pumplin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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(4) Masson, *Phil. Mag.*, **8**, 218 (1928).

TABLE I

THE APPARENT AND PARTIAL MOLAL VOLUMES OF AMMONIUM CHLORIDE IN AQUEOUS SOLUTION AT 25°

m	$C^{1/2}$	d	V	ϕ, obsd.	ϕ, calcd.	$\bar{V}_2$
0.0	0.0000	0.997074	1002.935	...	35.83	35.83
.1	.3152	.998789	1006.569	36.34	36.33	36.58
.2	.4449	1.000451	1010.244	36.55	36.54	36.89
.4	.6269	1.003665	1017.669	36.84	36.83	37.32
.6	.7650	1.006759	1025.169	37.06	37.05	37.64
.8	.8801	1.009753	1032.725	37.24	37.23	37.90
1.0	.9804	1.012644	1040.342	37.41	37.38	38.12
2.0	1.3615	1.026015	1078.924	38.00	37.98	38.95
3.0	1.6379	1.037810	1118.209	38.43	38.40	39.53
4.0	1.8585	1.048315	1158.034	38.78	38.74	39.96
5.0	2.0428	1.057796	1198.227	39.06	39.02	40.31
6.0	2.2009	1.066455	1238.661	39.29	39.26	40.59
7.3800[a]	2.3875	1.077299	1294.720	39.54	39.54	40.91

[a] Saturated.

TABLE II

THE APPARENT AND PARTIAL MOLAL VOLUMES OF CUPRIC SULFATE IN AQUEOUS SOLUTIONS AT 25°

m	$C^{1/2}$	d	V	ϕ, obsd.	ϕ, calcd.	$\bar{V}_2$
0.0	0.0000	0.997074	1002.935	...	−5.59	−5.59
.1	.3158	1.013235	1002.692	−2.42	−2.45	−0.83
.2	.4466	1.029136	1002.711	−1.12	−1.10	1.24
.4	.6314	1.060390	1003.265	0.82	0.87	4.27
.6	.7729	1.090990	1004.388	2.42	2.41	6.66
.8	.8918	1.121023	1005.960	3.78	3.74	8.71
1.0	.9961	1.150589	1007.858	4.92	4.92	10.55
1.1964	1.0883	1.179083	1010.096	5.99	5.98	12.19
1.4182[a]	1.1832	1.210706	1012.954	7.07	7.09	13.90

[a] Saturated.

mental values are shown by the circles. The curves do not deviate greatly from straight lines, those for ammonium chloride falling on a straight line up to about 3.5 molar. Masson[4] gives for ammonium chloride at 15°: $\phi = 35.30 + 1.633 C^{1/2}$. A second order equation of the form $\phi = a + bC^{1/2} + dC$ was assumed to hold for the curves and the coefficients were evaluated by the method of least squares. The equations found are

$$NH_4Cl: \phi = 35.828 + 1.6088C^{1/2} - 0.02266C$$
$$CuSO_4: \phi = -5.594 + 9.6841C^{1/2} + 0.87224C$$

The solid lines of the ϕ–$C^{1/2}$ curves are plotted from the values calculated from the respective derived equations, and it may be observed from the figures and the tables that they fit the experimental data quite well.

The partial molal volumes of the solutes were calculated by the equation developed by Gucker[5]

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

where the values of ϕ were those from the derived equations.

The data on the cupric sulfate solutions are especially interesting because of the negative values of the partial and apparent molal volumes in dilute solution. This same phenomenon has been observed for lithium hydroxide, sodium hydroxide, and magnesium sulfate solutions. These negative values and low values in general for cupric sulfate indicate a very large amount of electrostriction of the solvent produced by the cupric ions, the water dipoles being compressed around the cupric ion by the intense electrostatic field produced by the high charge-density of the ion.

Summary

The apparent and partial molal volumes of aqueous solutions of ammonium chloride and of cupric sulfate have been calculated from density data. The results on the apparent molal volumes have been discussed with relation to Masson's law.

IOWA CITY, IOWA RECEIVED MARCH 6, 1937

(5) Gucker, *J. Phys. Chem.*, **38**, 311 (1934).