[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Apparent and Partial Molal Volumes of Potassium Iodide and of Iodine in Methanol at 25° from Density Measurements

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With the aid of the magnetic float method, accurate values of the densities of potassium iodide and of iodine, and of mixtures of these substances, in methanol have been determined. From these data values of the apparent and partial molal volumes have been computed. The results indicate that the complex KI_3 exists in methanol solutions.

Recent papers from this Laboratory have described researches on iodide–iodine solutions with the aid of the e.m.f. centrifuge.[1] In order to interpret the measurements, the partial molal volumes of the substances entering into the reaction of the galvanic cell

$$(Pt);\ I_2,\ MI,\ I_2;\ (Pt)$$
$$r_2 \qquad\qquad r_1$$

have been necessary. (Here M = K or Na and r_1 and r_2 are radii in a centrifugal field.) These volumes were obtained from precision density measurements at a series of concentrations on solutions of the substances involved. The determination of the densities has been carried out by a modification of the magnetic float method originated by Lamb and Lee.[2] The description of the method and the accounts of the results so far obtained with it, using aqueous solutions, have already appeared.[3]

However, the chief utility of the e.m.f. centrifuge will be, almost certainly, in connection with studies on non-aqueous solutions. Measurements with this centrifuge have already been carried out with potassium iodide–iodine mixtures in methanol and the results will be described later. The necessary density measurements and the apparent, and partial, molal volumes computed from them are described in this communication.

Experimental

Very briefly the method for obtaining densities of solutions consists in the utilization of a float in the shape of an inverted flask, the weight of which is adjusted, when made, until it barely rises to the surface of the pure solvent at the temperature of the measurements. During a determination the float is placed in a vessel containing the solvent or solution, small weights are then placed on the upper surface of the float until it sinks gently to the bottom of the containing vessel, where the lower tip of the float may be observed, through a window of the thermostat, with a telescope, the eyepiece of which has a graduated scale. Since a bar magnet is in the stem of the float, it may be caused to rise by passing current through a solenoid which surrounds the stem. By varying the current the float may be caused to rise at different speeds which can be measured by observing the time of passage of the image of the float past selected marks in the telescope.[4] Plots of these relative speeds against the current may be extrapolated to values of the current at which the float would, theoretically at least, remain poised and motionless. The computations involved are described in earlier papers.

The method has been found to be particularly useful in dealing with a volatile solvent, such as methanol, the determinations being as readily and accurately made as with aqueous solutions. In the use of the conventional pycnometer it is very difficult to prevent errors due to evaporation.

Preparation of Solutions.—Synthetic methanol, from the best available source, was distilled twice through a column, 60 cm. high and 2 cm. in diameter, which was packed with glass beads. The first and last fractions were discarded and the middle $^1/_2$ to $^2/_3$ retained for use. The iodine used was resublimed. The potassium iodide was recrystallized twice. The solutions were made up by weight. The air in the empty flasks was replaced by air saturated with dry methanol, which was also used in blowing the solutions out of storage flasks.

The Data and Computations.—The results of the density measurements for methanol solutions of iodine are given in Table I, for potassium iodide in the same solvent in Table II, and for mixtures of these solutes in Tables III and IV. A single magnetic float cannot be used, for the accuracy we desired, for a range of density of more than about 3%. Since the difference of the densities of water and methanol is much greater than this, a value of the density of the latter has been obtained from other measurements. There is a slight variation in the published values of the density of pure methanol, at 25°, the figures varying from that of McKelvy and Simpson,[5] 0.78658, and 0.78641 from the work of Ewart

TABLE I

DENSITIES AND MOLAL VOLUMES OF SOLUTIONS OF IODINE, I_2, IN METHANOL AT 25°

I_2, g. per 1000 g. soln.	Density at 25°	Molal volumes Apparent ϕ	Molal volumes Partial $\bar{V}$
0.0	*0.786500*		
6.0623	0.790367	62.26	62.26
15.659	.796567	62.28	62.28
20.857	.799959	62.38	62.38
21.002	.800061	62.26	62.26
22.244	.800876	61.82	61.82

TABLE II

DENSITIES AND MOLAL VOLUMES OF SOLUTIONS OF POTASSIUM IODIDE IN METHANOL AT 25°

KI, g. per 1000 g. soln.	Density at 25°	Molal volumes Apparent ϕ	Molal volumes Partial $\bar{V}$
0.0	*0.786500*		
3.3462	0.788850	23.17	23.99
13.636	.796086	24.69	26.34
16.808	.798311	25.28	27.11
28.208	.806406	26.17	28.55
43.209	.817240	27.33	30.27

(1) B. R. Ray and D. A. MacInnes, *Rev. Sci. Instruments*, **20**, 52 (1949); D. A. MacInnes and B. R. Ray, THIS JOURNAL, **71**, 2987 (1949); D. A. MacInnes and M. O. Dayhoff, *J. Chem. Phys.*, **20**, 1034 (1952); D. A. MacInnes, *Proc. Am. Phil. Soc.*, **97**, 51 (1953).

(2) A. B. Lamb and R. E. Lee, THIS JOURNAL, **35**, 1666 (1913).

(3) D. A. MacInnes, M. O. Dayhoff and B. R. Ray, *Rev. Sci. Instruments*, **22**, 642 (1951); D. A. MacInnes and M. O. Dayhoff, THIS JOURNAL, **74**, 1017 (1952); M. O. Dayhoff, G. E. Perlmann and D. A. MacInnes, *ibid.*, **74**, 2515 (1952).

(4) A tendency of the float to rise at an angle from the vertical may be corrected by the adjustment of the position of a bar magnet in the thermostat. The magnet in use is a 2-inch piece of $^1/_4$ inch Alnico placed about 8 inches from the float and mounted horizontally so that it can be raised and lowered and turned about its center. Since the magnet corrodes rapidly in the thermostat water it is well to seal it in a glass tube. This detail was inadvertently omitted from the first paper[3] of this series.

(5) E. C. McKelvy and D. H. Simpson, THIS JOURNAL, **44**, 105 (1922).

Table III

Densities and Molal Volumes of Solutions of Iodine, I_2, in Potassium Iodide–Methanol Mixtures at 25°

I_2, g. per 1000 g. soln.	KI, g. per 1000 g. soln.	Density ρ	Molal volumes Apparent ϕ	Partial $\bar{V}_I$
0.0	0.0	*0.786500*		
12.521	16.598	0.806683	54.40	54.88
20.509	16.700	.812279	54.70	55.46
25.493	16.380	.815496	55.14	58.64
27.739	16.342	.817019	55.50	59.64
35.660	16.209	.822402	56.76	62.44
2.0135	43.122	.818610	52.38	53.12
8.6843	42.834	.823143	54.16	55.52
13.8060	42.612	.826649	54.54	55.06
22.8939	42.220	.832955	54.62	54.10

Table IV

Densities and Molar Volumes of Solutions of Potassium Iodide in an Iodide–Methanol Mixture at 25°

I_2, g. per 1000 g. soln.	KI, g. per 1000 g. soln.	Density ρ	Molal volumes Apparent ϕ	Partial $\bar{V}_{KI}$
20.847	7.3417	0.805529	15.58	17.67
20.631	10.924	.808087	16.60	19.68
20.578	13.409	.809917	17.35	22.74
20.509	16.700	.812279	19.12	26.91
20.550	21.517	.815848	20.87	28.68

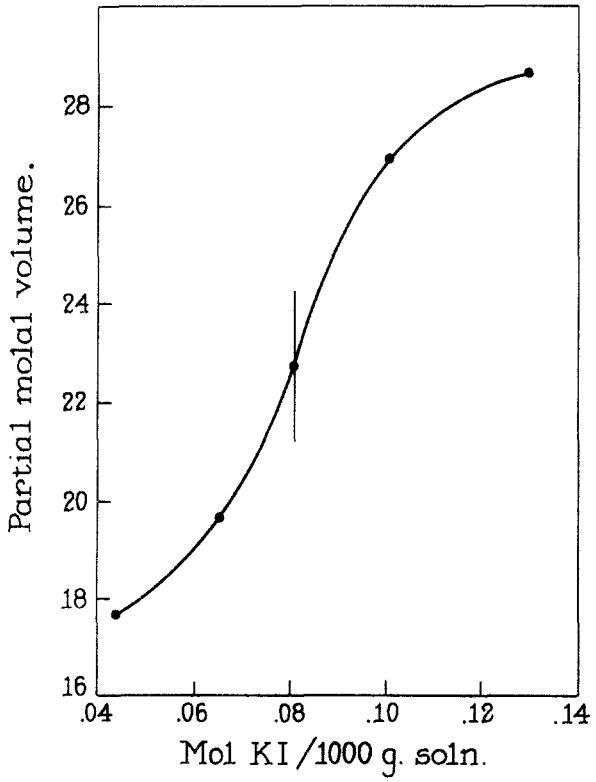

Fig. 1.—Partial molal volumes of KI in 0.08 molal I_2, indicating point of inflection at composition KI_3.

and Raikes.[6] For our purposes a mean value of 0.786500 has been adopted.

The apparent molal volume of a single solute may be obtained from the expression

$$\phi = \frac{V - V_0}{n} = \frac{1000/\rho - (1000 - g)/\rho_0}{g/M} \quad (1)$$

in which V is the volume of solution, V_0 that of the solvent in the pure state and n the number of moles of solute. In the alternative expression to the right, ρ is the density of the solution, ρ_0 that of the solvent, g the number of grams of solute in 1000 g. of solution and M the molecular weight of the solute. The computed values of ϕ are listed in the third columns of the tables.

To obtain the apparent molal volume of one solute when two are present in solution the expression

$$\phi_1 = \left[\frac{1000}{\rho} - \frac{1000 - m_1 - m_2}{\rho_0} - \frac{m_2}{M_2}\phi_2\right]\frac{M_1}{m_1} \quad (2)$$

may be used. Here m_1 and m_2 are the number of grams of the two solvents in 1000 g. of solution and M_1 and M_2 the corresponding molecular weights. Thus to compute ϕ_1 an appropriate value of ϕ_2 must be assumed. In Table III in which m for KCl has been kept nearly constant while that of I_2 is varied, the values of ϕ_{KI} were obtained from Table II, whereas in Table IV, in which m_I varies little, ϕ_{I_2} was taken from Table I.

The partial molal volumes are given by the relation

$$\bar{V} = \phi + m(d\phi/dm) \quad (3)$$

In Table I for iodine in methanol, it will be observed that ϕ is substantially constant, *i.e.* that $d\phi/dm = 0$, so that $\bar{V} = \phi$. The values of the apparent volume, ϕ, for potassium iodide in methanol may be represented by the empirical equation

$$\phi = 21.45 + 11.5\sqrt{m} \quad (4)$$

from which

$$m(d\phi/dm) = 5.75\sqrt{m} \quad (5)$$

which, with equation 3, gives the partial molal volumes listed in the last column of Table II.

Plots of the apparent molal volumes ϕ against the values of molality, m_2, for the solutions containing two solutes, m_1 and m_2, in which m_1 was kept constant show S-shaped curves if the ratio m_1/m_2 passes through unity. When three points on a curve were not on a straight line, values of $d\phi/dm$ were obtained by computing the constants a and b of the parabola $\Delta\phi = a\Delta m + b\Delta m^2$ from the data. From this expression $m(d\phi/dm) = m(d\Delta\phi/d\Delta m) = am + 2bm\Delta m$. This was used only for the middle value of three points. For the highest and lowest values the variation of ϕ with m is so nearly linear that $d\phi/dm$ could be estimated directly.

A plot of the values of the partial molal volumes of potassium iodide, in 0.082 to 0.081 molal iodine as solvent, is shown in Fig. 1. It will be seen that there is a point of inflection of the curve at the molality of the salt, indicated by the vertical line, at which it equals that of the iodine, thus indicating that the complex KI_3 is present in the solution. As is well known, this complex also exists in aqueous solutions.

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(6) F. K. Ewart and H. R. Raikes, *J. Chem. Soc.*, 1907 (1926).