Experiment 7

Partial Molar Volume

Purpose :

In this experiment the partial molar volumes of sodium chloride solutions will be calculated as a function of concentration from densities measured with a pycnometer.

Principle :

The total volume of an amount of solution containing *1 Kg* (*55.51 moles*) of water and *m moles* of solute is given by

$$V = n_1\overline{V}_1 + n_2\overline{V}_2 = 55.51\overline{V}_1 + m\overline{V}_2 \tag{1}$$

where the subscripts *1* and *2* refer to solvent and solute, respectively. Let $\tilde{V}_1^{o}$ be the molar volume of pure water ($= 18.016 / 0.997044 = 18.069 cm^3 mol^{-1}$ at $25\,°C$). Then we define the apparent molar volume ϕ of the solute by the equation

$$V = n_1\tilde{V}_1^{o} + n_2\phi = 55.51\tilde{V}_1^{o} + m\phi \tag{2}$$

which can he rearranged to give

$$\phi = \frac{1}{n_2}(V - n_1\tilde{V}_1^{o}) = \frac{1}{m}(V - 55.51\tilde{V}_1^{o}) \tag{3}$$

Now

$$V = \frac{1000 + mM_2}{d} \tag{4}$$

and

$$n_1\tilde{V}_1^{o} = \frac{1000}{d_o} \tag{5}$$

where *d* is the density of the solution and d_o is the density of pure solvent, both in units of $g \cdot cm^{-3}$, and M_2 is the solute molecular weight in *grams*. Substituting Eqs. (4) and (5) into Eq. (3), we obtain

$$\phi = \frac{1}{d}(M_2 - \frac{1000}{m}\frac{d - d_o}{d_o}) \tag{6}$$

$$= \frac{1}{d}(M_2 - \frac{1000}{m}\frac{W - W_o}{W_o - W_e}) \tag{7}$$

In Eq. (7), the directly measured weights of the pycnometer－W_e when empty, W_o when filled to the mark with pure water, and *W* when filled to the mark with solution －are used. This equation is preferable to Eq. (6) for calculation of ϕ, as it avoids the necessity of computing the densities to the high precision that would otherwise be necessary in obtaining the small difference $d - d_o$.

Now by the definition of partial molar volumes and by use of Eqs. (1) and (2),

$$\overline{V}_2 = (\frac{\partial V}{\partial n_2})_{n_1,T,P} = \phi + n_2 \frac{\partial \phi}{\partial n_2} = \phi + m\frac{d\phi}{dm} \qquad (8)$$

Also

$$\overline{V}_1 = \frac{V - n_2\overline{V}_2}{n_1} = \frac{1}{n_1}(n_1\tilde{V}_1^o - n_2^2 \frac{\partial \phi}{\partial n_2}) = \tilde{V}_1^o - \frac{m^2}{55.51}\frac{d\phi}{dm} \quad (9)$$

We might proceed by plotting ϕ versus m, drawing a smooth curve through the points, and constructing tangents to the curve at the desired concentrations in order to measure the slopes. However, for solutions of simple electrolytes, it has been found that many apparent molar quantities such as ϕ vary linearly with $\sqrt{m}$, even up to moderate concentrations. This behavior is in agreement with the prediction of the **Debye-Huckel** theory for dilute solutions. Since

$$\frac{d\phi}{dm} = \frac{d\phi}{d\sqrt{m}}\frac{d\sqrt{m}}{dm} = \frac{1}{2\sqrt{m}}\frac{d\phi}{d\sqrt{m}} \qquad (10)$$

we obtain from Eqs. (8) and (9)

$$\overline{V}_2 = \phi + \frac{m}{2\sqrt{m}}\frac{d\phi}{d\sqrt{m}} = \phi + \frac{\sqrt{m}}{2}\frac{d\phi}{d\sqrt{m}} = \phi^o + \frac{3\sqrt{m}}{2}\frac{d\phi}{d\sqrt{m}} \quad (11)$$

$$\overline{V}_1 = \tilde{V}_1^o - \frac{m}{55.51}(\frac{\sqrt{m}}{2}\frac{d\phi}{d\sqrt{m}}) \qquad (12)$$

where ϕ^o is the apparent molar volume extrapolated to zero concentration. Now one can plot ϕ versus $\sqrt{m}$ and determine the best straight line through the points. From the slope $d\phi / d\sqrt{m}$ and the value ϕ^o, both $\overline{V}_1$ and $\overline{V}_2$ can be obtained.

Apparatus and Chemicals :

50-ml pycnometer; six *250-ml* Erlenmeyer flasks; *200-ml* volumetric flask; *100-ml* volumetric flask; funnel; *100 ℃* thermometer; *250-m1* beaker; spatula; dropper; glass bar; magnetic stirring bar; magnetic stirrer.

NaCl.

Procedures :

(1) Make up *200 ml* of approximately *3.2m* (*3.0M*) NaCl in water by weighing the salt accurately and use a volumetric flask.

(2) Solutions of *1/2*, *1/4*, *1/8*, and *1/16* of the initial molarity are to be prepared by successive volumetric dilution; for each dilution pipette *100 ml* of solution into a *200-ml* volumetric flask and make up to the mark with distilled water.

(3) The pycnometer is rinsed with distilled water and thoroughly dried before each use. The pycnometer should be weighed empty and dry (W_e).

(4) Fill the pycnometer with distilled water and hang it in the thermostat bath (*30.0 ℃*) with the main body below the surface. Allow at least *15 min* for equilibration.

(5) Remove the pycnometer from the bath and quickly but thoroughly dry the outside surface with a towel or filter paper. Weigh the pycnometer(W_o).

(6) By the similar procedures, record the weight (W) of pycnometer when filled with each NaCl solutions as prepared in **step (2)**.

Calculations :

(1) Although to a great extent the weights themselves enter into the calculations, it is necessary also to have the density d of every solution to within an accuracy of at least one part per thousand:

$$d = \frac{W_{sol'n}}{V} = \frac{W - W_e}{V_P} \qquad (13)$$

The volume of the pycnometer V_P is obtained by use of the density of pure water at 30.0 °C, d_o (with the value $0.9957\,g \cdot cm^{-3}$), and $W_o - W_e$.

(2) The molalities m (concentration in *mole* per *Kg* of solvent) which are needed for the calculations can he obtained from the molarities M (concentration in *mole* per *liter* of solution) obtained from the volumetric procedures by using the equation

$$m = \frac{1}{1 - \frac{M}{d}\frac{M_2}{1000}}\frac{M}{d} = \frac{1}{\frac{d}{M} - \frac{M_2}{1000}} \qquad (14)$$

Where M_2 is the solute molecular weight ($58.45\ g/cm$) and d is the experimental density in $g \cdot cm^{-3}$ units.

(3) Calculate ϕ for each solution using Eq. (7) and plot ϕ vs. $\sqrt{m}$. Determine the slope $d\phi/d\sqrt{m}$ and the intercept $\phi°$ at m equal zero from the best straight line through these data points.

(4) Calculate $\overline{V_2}$ and $\overline{V_1}$ for $m = 0, 0.5, 1.0, 1.5, 2.0$, and 2.5. Plot them against m and draw a smooth curve for each of the two quantities.

(5) In your report, present the curves (ϕ vs. $\sqrt{m}$, $\overline{V_2}$ and $\overline{V_1}$ vs. m) mentioned above. Present also in tabular form the quantities d, M, m, and ϕ for each solution studied. Give the values obtained for the pycnometer volume V_P and for $\phi°$ and $d\phi/d\sqrt{m}$.

References :

(1) **P. W. Atkins and J. de Paula**, "*Physical Chemistry*," 9th ed., pp. 157-158, Oxford University Press, U.S.A (2010).

(2) **D. P. Shoemaker**, **C. W. Garland**, and **J. W. Nibler**, "*Experiments in Physical Chemistry*," 5th ed., pp. 187-194, McGraw-Hill, Singapore (1989).

(3) **D. P. Shoemaker** and **C. W. Garland**, "*Experiments in Physical Chemistry*," 2nd ed., pp. 126-132, McGraw-Hill, U.S.A. (1967).

(4) **F. Daniels** and others, "*Experimental Physical Chemistry*," 6th ed., pp. 87-92, Europe-Asia book company, Taiwan (1956).