ChE 203 - Physicochemical Systems Laboratory

EXPERIMENT 3: DETERMINATION OF PARTIAL MOLAR VOLUMES

Before the experiment: *Read the booklet carefully. Be aware of the safety issues.*

Object

Determination of the density and specific volume of a non-ideal solution, and partial molar volumes of its components by using a pycnometer

Theory

Thermodynamics is concerned only with the macroscopic properties of a body and not with its atomic properties, such as the distance between the atoms in a particular crystal. These macroscopic properties form a large class and include the volume, pressure, surface tension, viscosity, temperature etc. They may be divided into groups as follows: The extensive properties, such as volume and mass, are those which are additive, in the sense that the value of the property for the whole of a body is the sum of the values for its constituent parts. The intensive properties, such as pressure, temperature, density, etc., are those values can be specified at each point in a system and which may vary from point to point, when there is an absence of equilibrium. Such properties are not additive and do not require any specification of the quantity of the sample to which they refer.

The partial molar properties are very important in dealing with the problems of the solution thermodynamics. For ideal gaseous or liquid solutions, the partial molar volumes, internal energies and enthalpies (V, U, H) are equal to their respective molar quantities for the pure components while (S_i, A_i, G_i) are not. For non-ideal solutions, all partial molar quantities of components differ in general from their corresponding molar quantities in pure, and the difference are frequently of interest.

Of all the extensive thermodynamic properties, the volume is the easiest to visualize. In general, the partial molar volume of a substance A in a mixture is the change in volume per mole of A added to a large volume of the mixture. The partial molar volumes of the components of a mixture vary with composition because the environment of each type of molecule changes as the composition changes from pure A to pure B.

The partial molar volume, V_j, of a substance J at some general composition is defined formally as follows:

$$V_j = \left(\frac{\partial V}{\partial n_j}\right)_{p,T,n'} \tag{1}$$

where the subscript n' signifies that the amounts of all other substances present are constant as well as the pressure and temperature. The definition in equation 1 implies that, when the composition of the mixture is changed by the addition of dn_A of A and dn_B of B, then the total volume of the mixture changes by

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B = V_A dn_A + V_B dn_B \tag{2}$$

The final volume of a mixture can be calculated by integration since the composition and partial molar volumes are constant as the amounts of A and B are increased.

$$V = \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B = V_A n_A + V_B n_B \tag{3}$$

For ideal solutions,

$$V = V_A^* n_A + V_A^* n_B \tag{4a}$$

For non-ideal solutions,

$$V = V_A n_A + V_B n_B \tag{4b}$$

It should be noted that quantities relating to pure substances are denoted by superscript *.

If equations (4a) and (4b) are divided by number of moles of solutions, the above equations may be written as,

In ideal solutions,

$$V_m = V_A^* x_A + V_A^* x_B \tag{5a}$$

In non-ideal solutions,

$$V_m = V_A x_A + V_B x_B \tag{5b}$$

is obtained, with V_m, molar volume of the solution and x_A and x_B mole fraction of component A and B. [2]

Experimental Work

Apparatus and Chemicals: Pycnometer (4), 250 ml round bottom flask, balance, pipette (4), HCl solutions in various concentrations, distilled water.

Procedure

1. At room temperature, determine the density for the following solutions: 20, 40, 60 and 80% (wt./wt.) of HCl solutions using the following steps.
2. Weigh the dry pycnometer, W_p.
3. Fill the pycnometer with distilled water making sure the water level in the pycnometer reaches the top of the capillary. Make sure that water is free of air bubbles and the outer surface of the pycnometer is completely dry.
4. Fill the pycnometer with water and determine its weight (W_g).
5. Using the density of water at 25 °C, $\rho = 0.997$ g/ml, calculate the volume of pycnometer. Fill the pycnometer with ($HCl+H_2O$) solution. Weigh it and calculate the density of the solution.

Safety Issues: HCl solutions are used in this experiment. It is very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive) and of ingestion. Check for and remove any contact lenses. In case of eye contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention immediately. In case of skin contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient. Wash clothing before reuse. Thoroughly clean shoes before reuse. If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. If swallowed, do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately for all cases of contact. [1]

Calculations

1. Calculate the specific volume (ml/g) (i.e. reciprocal density) of each solution and plot the percentage weight of HCl (abscissa) against specific volume.
2. Draw a smooth curve through points, and draw tangents to the curve at different concentrations. The intercept of these lines on 0% and 100% ordinates gives the partial specific volumes of water and HCl respectively at various concentrations.

3. Calculate the partial molar volume (ml/gmol) of components in solution, from partial specific volume (ml/g) and molecular weight (g/gmol).
4. Calculate the molar volumes of HCl solutions at different concentrations.
5. Calculate the specific volume of HCl solutions using partial specific volumes and weight fractions of components within the solution. Compare the results with your experimental data.
6. Finally, draw two plots showing the variation of the partial molar volume of HCl, and the partial molar volume of water with mole fraction (abscissa) on the same graph. (Do not draw a curve!)

References

[1] http://www.sciencelab.com/msds

[2] Atkins, P. W. and De Paula, J., *Physical Chemistry*, 8th Edition, Oxford University Press, 2006.