MOLAR AND PARTIAL MOLAR VOLUMES IN AQUEOUS SOLUTIONS (10/21/03)

QUANTITATIVE TECHNIQUES

❒ Use of an Analytical Balance

Your assignment is to determine the partial molar volumes of solutions of water with an alcohol (specified on home page, following link to this experiment) using density measurements obtained with a Mettler-Toledo DA-300M density meter.

Background information for partial molar volumes can be found in almost any physical chemistry text or in the fifth edition of *Physical Chemistry* by Ira N. Levine, pp. 250-4 and 258-268.

PRE LABORATORY EXERCISE

Use a spreadsheet to do the calculations in the next 5 parts. Include a sample of each calculation in your pre lab report.

1. Find the literature values of densities of solute/water *solutions* for varying concentrations and use them to calculate solution volumes (V). Use the same solute you will use for the experiment and 1000g of solution as a basis for your calculations.

2. Next, find V* for each of the solutions, using equation 1:

$$V^*_{Soln} = n_A V^*_{m,A} + n_B V^*_{m,B} \qquad (1)$$

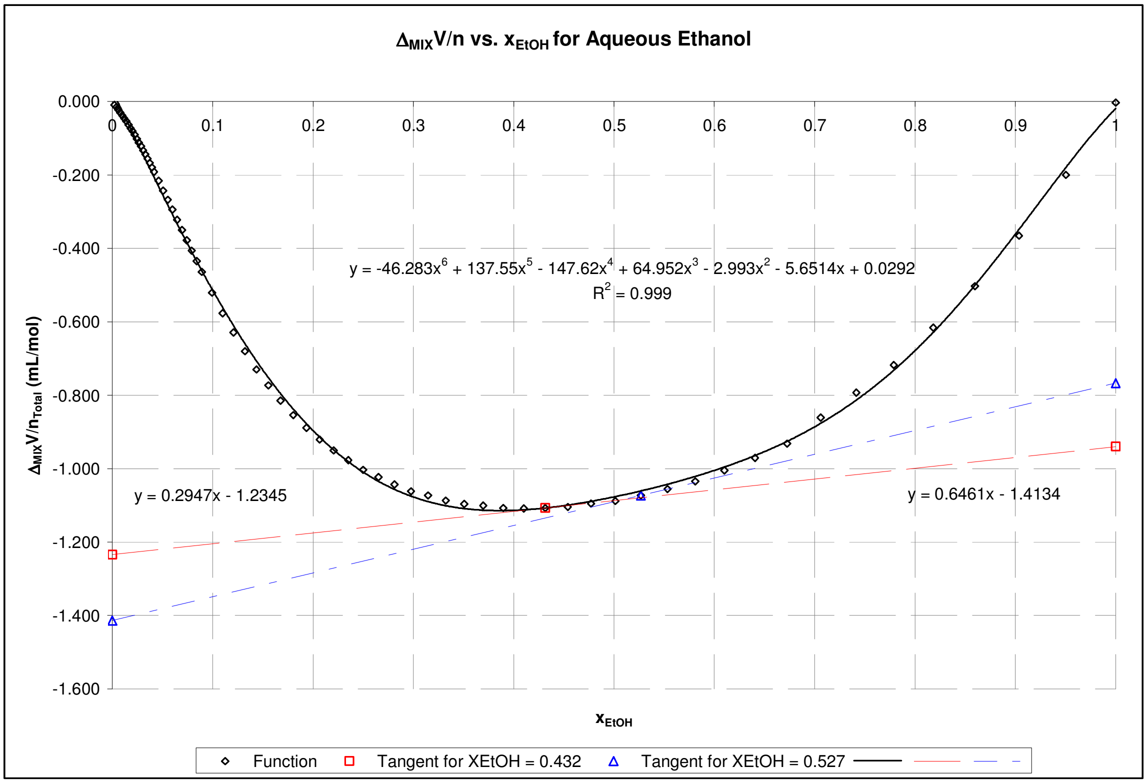
   Where:
   V^*_{SOLN} = the theoretical/ideal volume of a binary solution based on the molar volumes of the two components at constant temperature and pressure.
   n_A, n_B = the moles of components A and B (respectively)
   $V^*_{m,A}$, $V^*_{m,B}$ = the molar volume of components A and B (respectively)

3. Finallly, plot $\Delta V_{MIX}/nT$ vs. XB. Where ΔV_{MIX} is defined in equation 2:

$$\Delta V_{MIX} \equiv V_{SOLN} - V^*_{SOLN} \qquad (2)$$

   Where:
   ΔV_{MIX} = the difference between the real and ideal volumes of a solution.
   V_{SOLN} = the actual/real volume of a solution (calculated from density)
   n_T = the total number of moles in the binary solution ($n_A + n_B$)
   X_B = the mole fraction of the solute.

4. Find the partial molar volumes of each component ($V_{PM,\,i}$) as a function of the mole fraction of the solute. The partial molar volume of the solvent (water) at a given mole fraction of the solute can be obtained from the y intercept at $X_B = 0$ ($y_{XB=0}$) of the slope of a line tangent to the curve of the plot, $\Delta V_{MIX}/n_T$ vs. X_B, using equation 2. The partial molar volume of the *solute* at this same mole fraction can then be determined for the y intercept of the tangent line at $X_B = 1$ ($y_{XB=1}$), again using equation 2 and shown in figure 1.



a) Finding the slope of the tangent line

The slope of the tangent for each point is determined by obtaining the derivative of a function fitting the curve of the plot $\Delta V_{MIX}/n_T$ vs. X_B.

b) Finding the tangent line intercepts

The y intercepts of the tangent line at $X_B = 0$ and $X_B = 1$ can be determined using the point slope form:

$$y - y_1 = m(x - x_1) \qquad (4)$$

Where y_1, x_1 are the $\Delta V_{MIX}/n_T$, X_B coordinates at a specific point (respectively), m is the slope of the tangent line (at y_1, x_1), and x is equal to zero ($y_{XB=0}$ intercept) or one ($y_{XB=1}$ intercept).

c) Calculating the partial molar volume

Once the y intercepts have been found, they can then be used to calculate the partial molar volume of a binary mixture using equation 5

$$\frac{\Delta V_{MIX}}{n_T} = V_{PM,\,i} - V_{m,i} \qquad (5)$$

EXAMPLE 1

The partial molar volume of *ethanol* at $x_{Ethanol} = 0.432$

$$\frac{\Delta V_{MIX}}{n_T} = V_{PM\,,\,EtOH} - V_{m,\,EtOH}$$

$$-0.9398mL = V_{PM\,,\,EtOH} - 58.37mL$$

$$V_{PM\,,\,EtOH} = -0.9398mL + 58.37mL = 57.43mL$$

EXAMPLE 2

The partial molar volume of *water* at $x_{Ethanol} = 0.527$

$$\frac{\Delta V_{MIX}}{n_T} = V_{PM\,,\,H_2O} - V_{m,\,H_2O}$$

$$-1.4134mL = V_{PM\,,\,H_2O} - 18.07mL$$

$$V_{Pm,\,H_2O} = -1.4134mL + 18.07mL = 16.66mL$$

5. Make plots of the partial molar volume of the solute and H_2O versus x_B and compare them to figure 2:

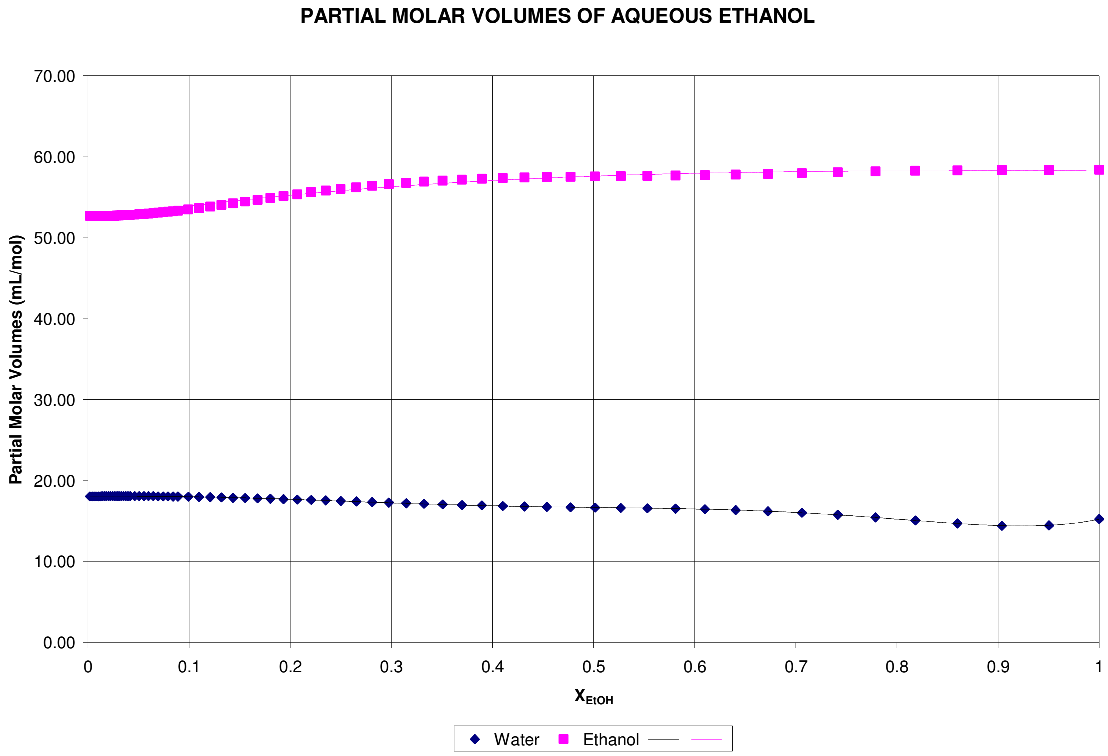


Figure 2: Partial molar volumes of ethanol and water, both as functions of the mole fraction of ethanol in water.

LABORATORY PROCEDURE

1. Prepare 25 - 30 solutions with varying weight %'s of the solute (non-water component). To conserve the solute, prepare solutions that weigh no more than 50g (total). Use stoppered Erlenmeyer flasks to prevent evaporation losses of the more volatile component.

2. Determine the densities at 25^oC using the Mettler-Toledo DA-300M Density meter: Perform at least (3) trials using the pure solute (alcohol). Use this density to determine the molar volume and estimate the relative standard deviation (RSD) of your measurements. In the abstract portion of your final report, report the molar volume +/- RSD. Determine the %error from the literature value in the error analysis section of your report.

Instrument Operating Instructions

a. Turn power on.

b. Connect the air tube to the input port (lower port) and push the button called SAMPLING. This flushes the cell with dry air.

c. Press the CHECK button and wait for the machine to beep.

d. Press the F.MEAS button. If the dry air purge above was OK, press the F.MEAS button again and wait for a beep. This sets the cell to the density of dry air at 25^oC.

e. After the beep you will see “Set water” on the display. At this point remove the air tube from the inlet port. Next, inject your sample (slowly!), using a 10mL plastic syringe. Inject at least 5mL of the syringe to pre-rinse the density cell. Leave the syringe attached to the inlet port.

f. Make sure there are no air bubbles in the cell (look in the window). Wait for 2 minutes for thermal equilibrium and then press the F.MEAS button again. Wait for the machine to beep. It will then set the density reading to the density of water at 25 ^oC. Record this density.

g. The above procedure is used to calibrate the machine. At this point, replace the water with one of your solutions and wait for the density reading to stabilize. Do not touch any buttons or you will have to repeat the previous steps.

h. Insert the remainder of the prepared solutions into the instrument in the same manner as above. Be sure to obtain the density of 100% of the solute (methanol or ethanol). Estimate the standard deviation of your density measurements with at least one of the solutions.

i. Evaluate the experimental data for the partial molar volumes as you did for the pre lab exercise with the literature data.

j. Describe and analyze the results. Compare experimentally determined molar volumes of water and the solute (methanol or ethanol) with those determined using literature values. Compare partial molar volumes with those in figure (2).

CLEAN-UP PROCEDURES

- Flush the density meter with about 10mL of distilled water.
- Turn off the instrument, clean-up glassware with micro followed by distilled water.. Leave stoppers *off* of flasks.
- Pour 2-3 cups of water (~600mL) of tap water down the small sink used to drain the density meter.
- Turn off the instrument and return all items to their original location.