5. PARTIAL MOLAR VOLUMES IN A MIXTURE OF TWO LIQUIDS

GOALS

● Determine the density of water and ethanol mixtures with different compositions.

● Working from density measurements, determine the volume really occupied by the different compositions that have been prepared and compare them with the volume you would expect by simply adding together the volumes occupied by the quantities of pure components used to prepare a mixture.

● Determine the partial molar volumes of the mixture components in an intermediate composition of the different mixtures being studied.

THEORETICAL BACKGROUND

In General Chemistry II (reviewed in more detail in Physical Chemistry I), we saw that when two liquids are mixed in certain quantities, the resulting volume is rarely the strict sum of the volumes occupied separately by each component. This emerges as the consequence of the different sizes and shapes of the molecules and means that the molecule packaging in the mixture is not exactly the average of what is given by the pure components.

One way of demonstrating this fact, usually unnoticed in real life, is to prepare solutions that contain weighed quantities of the two components of a binary mixture (implying a known number of mols for each of them) and measure the volume occupied by the mixture (V). When you know the molar volumes of the pure components ($V_{m,1}$ and $V_{m,2}$), you can determine the expected additive volume (V^0) for these mixtures:

$$V^0 = n_1 V_{m,1} + n_2 V_{m,2}$$

However, as we mentioned above, the real volume of the mixture (V) rarely coincides with this additive volume. In general,

$$V < V^0 \quad \text{or} \quad V > V^0$$

One way of expressing these discrepancies is writing the real volume as a function of what are known as partial molar volumes of the components ($\overline{V}_{m,1}$ and $\overline{V}_{m,2}$), that are the volumes really occupied in the **mixture** by one mol of each component:

$$V = n_1 \overline{V}_{m,1} + n_2 \overline{V}_{m,2}$$

If the $\overline{V}_{m,i}$ of each component are equal to $V_{m,i}$ then the mixture is additive and the real volume that is obtained is equal to the additive or expected volume, which does not usually happen.

The important question is: can these partial molar volumes be calculated in a specific mixture? The answer is yes and is one of the goals of this experiment. Consequently, we should remind ourselves the definition of the partial molar volumes for the components of a mixture:

$$\overline{V}_{m,1} = \left(\frac{\partial V}{\partial n_1}\right)_{n_2,T,P} \qquad \overline{V}_{m,2} = \left(\frac{\partial V}{\partial n_2}\right)_{n_1,T,P}$$

One procedure to obtain these derivatives is to prepare different mixtures that keep the number of mols of a component constant and vary the number of mols of the other, determining the volume occupied by the mixtures they form.

To determine the volume that is really occupied by each specific mixture, we resort to determining a property that is very easy to measure in a liquid or liquid mixture: its density. The density (its symbol is ρ) is a measurement of the mass corresponding to a certain volume of a liquid, expressed in g/mL or kg/L.

EXPERIMENTAL PROCEDURE

Equipment	Reactants
10 mL Volumetric Flask	Deionised water
Thermostatic bath	Ethanol
syringe	
7 flasks with their lids	
A thermometer with 0.1 ºC resolution	
Eye dropper or Pipets	

Components and mixtures

You are going to prepare five mixtures of water and ethanol. Actually, to keep costs down, you may find 96% or 99% ethanol. In any case, for simplicity, you will suppose that it is pure ethanol, which does not distort the aim of this practical. To do this, you have to put 0.70 mols of water or, in other words, 12.60 grams of water in each of the small glass containers, using pipettes to weigh out the closest possible quantity. You will pour quantities of around 0.23, 0.25, 0.27, 0.29 and 0.31 mols of ethanol on each one, noting it down precisely. These will be the mixtures in our experiment. All the mixtures will be prepared by weighing them on the same lab. balances or scales.

Equipment

In these experiments we will determine the densities of the two components (water and ethanol) **<u>in their pure state</u> and the five pre-prepared mixtures**. In order to determine the density, there is a thermostatic bath that can regulate the measurement temperature. The Teachers will explain how it works. Measurements are taken at a temperature close to 30ºC that will be measured accurately with a thermometer.

Volumetric flask

There is also a volumetric flask with a (manufacturer-certified) volume of 10.0 (±0.1) mL, that you will assume to be correct. In another experiments, an accurate measurement of this volume is preferred and a calibration must be carried out, using a liquid whose density is known very exactly (generally water), but not in these experiments.

To determine the density, first <u>close the dry flask with its lid</u> and weigh it on the laboratory balances to the nearest 0.0001g. Fill it with the liquid or mixture in question up to the marker and <u>put it in the thermostatic bath at the study temperature</u>. After the appropriate thermostating time, adjust the liquid level to the marker using a syringe. After checking that this marker does not move over the next few minutes, indicating that it is properly thermostated by the bath, remove the flask from the bath, dry the outside carefully with filter paper or toilet paper and weigh it again.

The weighing difference, divided by the 10 mL of the flask will give you the density of the test liquid.

Questions to be resolved

1. Determine the density of the five pre-prepared <u>mixtures</u>. Additionally, determine the density of the <u>pure components</u> at the same temperature.

2. Using Excel, construct a table that contains, in this order and for each mixture, the grams of water and ethanol weighed, the corresponding mols of water and ethanol, the total mass, the density measured experimentally and the volume that the mixture really occupied in the container where it was prepared.

3. With this data, and using the equation that defines the partial molar volumes, use an appropriate graphical representation to calculate the partial molar volume of the ethanol at the intermediate composition of the interval being studied. Using the equation that gives the real volume depending on the partial molar volumes, calculate the partial volume of the water for the same composition used before.

4. Using the densities of water and ethanol, calculate the molar volumes of the pure components (supposing that the 96 % alcohol is pure ethanol).

5. With data from section 4, calculate the additive volume of the intermediate mixture at which you calculated the partial molar volumes.

6. Check whether the additive and the real volume are the same or different.

7. Plot the molar volume of the mixture against the molar fraction of ethanol. Analyse the plot. The molar mixture volume is defined as follows:

$$\Delta V_m = \frac{V_{real} - V_{additive}}{n_{total}}$$

Aspects to consider for a successful experiment

Before weighing, check the zero on the scales, as it can oscillate with use in the lab.

To dry the flask properly, clean it with a little acetone and dry it with a hair dryer but not too much or it might be deformed, changing its volume.

Do not weigh the flask if it is hot. As it gets cooler, the water vapour from the atmosphere condenses on its walls and the weight of the flask on the scales will increase.

The marker level criterion can be subjective but it should always be read the same way.

There should be no liquid, not even in the form of droplets above the marker. To remove it, dry it with a little rolled up filter paper inserted in the flask or suck it up with the syringe and needle that are provided for the marker.