7. LIQUID/LIQUID EQUILIBRIUMS AND THEIR PHASE DIAGRAMS

GOALS

● Prove that, in general, two liquids do not mix in all compositions and temperatures, as they would if they behaved as ideal solutions

● Verify that, as opposed to what is generally thought, the solubility of two substances (two liquids in this case) does not always increase with temperature and might actually decrease.

● By doing experiments, construct phase diagrams showing the stages of mixing two liquids that are separated into phases as temperature changes, both increasing and decreasing. Determine the critical solubility temperatures.

● Verify experimentally that when the phases separate, they do not necessarily have to be composed of the pure components.

THEORETICAL BACKGROUND

When attempting to mix two liquids at room temperature, they sometimes mix easily (the case of water and ethanol) while in other cases, there is no way of mixing them, no matter how much you stir (the case of oil and water). However, whether two liquids mix or not depends strongly on the temperature at which the process is taking place.

One system that illustrates this point very well involves water and phenol. At high temperatures, both liquids mix in all proportions. However, when the temperature drops, mixtures of these two components separate into two differentiated phases. Just like most mixtures that separate into phases, these phases are not usually made up of pure components as each one is a solution that is richer in one of the components than the overall composition of the mixture. There is therefore partial miscibility rather than complete immiscibility. The temperature to get a miscible mixture to separate into well-differentiated phases depends on the specific mixture that we are studying and the component proportions.

This behaviour seems to follow the generalised idea that the substances mix better if the system temperature rises. However, this is not always the case. In the other system that you will study, water and triethylamine, temperature has just the opposite effect. Water and triethylamine are mixed at temperatures relatively below room temperature and, as the mixture is heated, its phases separate, with the same characteristics as described for the phenol and water mixture.

The ultimate aim of our experiments here is to construct a graph that plots the temperatures at which phase separation takes place (or the miscibility, as the process is reversible) against the concentration of the mixtures. This graph marks the boundary between the temperatures and compositions where the system forms a single phase and where the system separates into two clear phases to the naked eye. This diagram presents a maximum in the case of the phenol/water, whose composition and temperature is usually called the critical solution composition and upper critical solution temperature UCST). On the other hand, in the case of the triethylamine/water system, the diagram shows a minimum whose coordinates are known as the critical solution composition and lower critical solution temperature (LCST).

To establish the temperature at which a mixture of a specific composition separates into phases, either by raising or lowering the temperature, you will work from the fact that while a miscible mixture is uniform and transparent to the human eye, a mixture separated into phases is not uniform and looks opaque or turbid when stirred. Turbidity appears because when a solution that has separated into phases is stirred, small droplets from either phase are dispersed, each with a different refraction index. This refraction index, differing from one phase to the other, causes the turbidity detected by the human eye.

When you stop stirring the miscible mixture, it keeps the same appearance, whilst a mixture that has separated into phases tends to clearly exhibit these phases due to the different density of each phase.

EXPERIMENTAL PROCEDURE

Material	**Material**
A Magnetic Stirrer with Hot Plate	A cork isolator sheet
A Thermometer	A metallic sheet with holes
6 little magnetic stirrers and a large one	2 beakers of 1 L, a tall/large one and a small one
A Separatory Funnel	Triethylamine (TEA)
A 10 mL Volumetric Flask	Deionised water
A 100 mL Erlenmeyer	
2 pipets of 25 mL	
Various Water/phenol and Water/TEA solutions on the test tubes (with the stirrers inside)	

1.- Phenol/water mixture

The student is provided with six closed test tubes containing 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 g of phenol to which the appropriate amount of water has been added up to a total weight of 6 g. If they are stirred, an opaque dispersion can be seen, indicating the immiscibility of water and phenol at room temperature.

Take a large beaker, remove the magnetic stirrer (if there is any) and fill it with 800 cm^3 of water. Take this beaker to a microwave to heat the water to 72-74ºC (6 minutes more or less, and **use oven-gloves** to handle the beaker once hot). **NOTE: water should not be above 80ºC**.

A Teflon-covered magnetic stirrer will be put in the beaker with the hot water and it will all be put on a stirring device to stir the water during the experiments. Each of the test tubes containing the phenol/water mixtures will be suspended in this beaker plus a thermometer that will check the water temperature at all times. Once the tubes have attained the beaker water temperature, check that the mixture has become transparent, indicating that, at this temperature, phenol and water mix for the composition being tested.

Now leave the water in the beaker, and so also the phenol/water mixture in the test tube, to cool slowly and keep checking the temperature until the mixture starts to change colour and become opaque. Note down the temperature at which the change takes place, always following the same criteria. Repeat the process with the other tubes, noting down the temperatures at which the transparent/turbid change takes place.

The test tubes being used will not be cleaned; they should be closed properly and left in the racks.

2.- Triethylamine/water mixture

The student is provided with five closed test tubes containing 1.0, 2.5, 4.0, 5.0, and 7.0 g of triethylamine to which the appropriate amount of water has been added up to a total weight of 10 g. If they are stirred, it can be seen that there is an opaque dispersion, indicating the immiscibility of water and triethylamine at room temperature.

The process to obtain the phase separation temperatures is similar to the previous experiment, although now the initial temperature of the water in the beaker should be below 12/13ºC, adding small quantities of ice to the water to bring the temperature down. In this case, you can see that after putting the opaque triethylamine/water mixture into the beaker water, it becomes transparent as it cools. In this case, let the beaker water warm up by heating it gently with the actual stirrer/heater in the lab (**do not go beyond the second position on the heater dial**). In this case, you will see that as it heats up, at a certain temperature the transparent solution begins to turn opaque again. As in the previous case, use the same criteria with all five concentrations to get the temperature corresponding to this process.

The test tubes being used will not be cleaned; they should be closed properly and left in the racks.

3.- Separation and analysis of the phases present at room temperature

For this new experiment, the student should prepare a mixture of water and triethylamine, bearing in mind that triethylamine is a corrosive substance that smells quite unpleasant. This requires the use of a fume hood, glasses and rubber gloves.

A 100 mL Erlenmeyer flask will be weighed empty and with its lid, and after adding 15 mL of water weigh the flask full and with the lid on, to thereby calculate the weight of water in it. Then add 20 mL of triethylamine using the same burette, weighing the **Erlenmeyer flask** again with its lid on the same lab scales to get the weight of the triethylamine in the flask.

After stirring the mixture in the Erlenmeyer flask, transfer it, inside a cabinet, to a separatory funnel where the mixture is stirred again and left to rest for around 5-10 minutes until the two transparent phases separate. The denser, water-rich phase will be in the lower part, below the triethylamine-rich phase. After taking the lid off the separatory funnel very carefully, open the tap and let the water-rich phase run out into the same Erlenmeyer flask with a lid that you used to prepare the mixture, after cleaning, drying and weighing it empty with its lid. After transferring this phase to the Erlenmeyer flask, it will be weighed again with its lid on to determine the weight of the aqueous phase. **Always use the same lab scales or balances** Note down the laboratory temperature during the experiment.

Part of this aqueous phase will be transferred to a small 10 ml volumetric flask that will have been previously weighed when dry and empty. Using a syringe, adjust the liquid from the aqueous phase up to the marker and weigh it again to calculate the density of this aqueous phase. Once this part has been completed, the solutions used (in the separatory funnel), the lined flask and the Erlenmeyer flask with lid will be put in a labelled waste container and to show that they contain residue from triethylamine and water mixtures.

Questions to be resolved

● With the data from the phase separation experiments, draw phase diagrams for the phenol/water and triethylamine/water mixtures, representing the temperatures at which the systems change from miscible to immiscible against the molar fraction of the phenol, in the first case, and the triethylamine in the second.

● Make an approximate estimation of the Upper Critical Solution Temperature (UCST) for the phenol/water system and the Lower Critical Solution Temperature (LCST) for the triethylamine/water system.

● With the volumes and weights used to prepare the triethylamine and water mixtures, calculate the density of both pure components.

● Using the density of the aqueous phase separated in the separatory funnel and supposing that the density of the mixture is additive regarding the densities of the pure components, calculate the weight fraction for each component in the aforementioned aqueous phase.

$$\frac{1}{\rho_{aqueous-phase}} = \frac{\omega_{TEA}}{\rho_{TEA}} + \frac{\omega_{water}}{\rho_{water}}$$

● Using the data from the previous section, calculate how many grams of water and triethylamine are in each phase that can be seen separately in the separatory funnel.

● Plot those points in the phase diagram.