Exercise 16

INVESTIGATION OF PHASE EQUILIBRIA IN SYSTEMS WITH THREE LIQUIDS

Topics: phase, independent component, degrees of freedom of a system. Thermodynamic criteria for equilibrium in multi-component and multi-phase systems. Phase rule. Phase diagrams and their interpretation with particular emphasis on systems with two and three liquids. Emulsions. Light scattering by colloidal systems.

A system in which at least two phases coexist is in a state of phase equilibrium if, for fixed values of the intensive variables of the masses of these phases, they remain constant. In a multi-component system, the maximum number of phases that can coexist in equilibrium can be determined based on the so-called phase rule (also known as Gibbs' rule), which relates the number of degrees of freedom of the system (F) to the number of components (C) and the number of phases (P) in the system:

$$F = C - P + 2 \qquad (1)$$

In a ternary (three-component) system, a maximum of 5 phases can coexist in equilibrium, but such a system can only exist under tightly defined conditions of pressure and temperature. Typically, we deal with systems that are monophasic (single-phase), biphasic (two-phase), or triphasic (three-phase).

Among all the intensive variables determining the phase state of a system, only a subset are independent, while the rest are unique functions of them. The graphical representation of these dependencies is called a phase diagram. A phase diagram informs us about the phases that will coexist in equilibrium in a system with a specific composition, temperature, and pressure.

For a ternary system, the number of independent variables, as implied by equation (1), can be as high as 4. This makes it impractical to graphically represent the complete phase diagram on a two-dimensional plane. Even if pressure and temperature values are fixed, constructing a phase diagram would require three axes, as the system would still have two degrees of freedom (mole fractions or weight fractions of two components).

However, let's note that in a ternary system, the following condition is satisfied:

$$x_A + x_B + x_C = 1 \qquad (2)$$

where x_A , x_B and x_C represent the mole (or weight) fractions of individual components, reducing the number of independent variables to two for fixed pressure and temperature values. If we represent the composition of such a system on a plane using a coordinate system with axes corresponding to the sides of an equilateral triangle, then condition (2) will be automatically fulfilled. This is because any point Q within the triangle has the property that the sum of its distances to the sides of the triangle, measured parallel to the sides, is equal to the length of a side of the triangle. This triangular coordinate system, also known as the Gibbs-Roozeboom triangle, is illustrated in Figure 1.

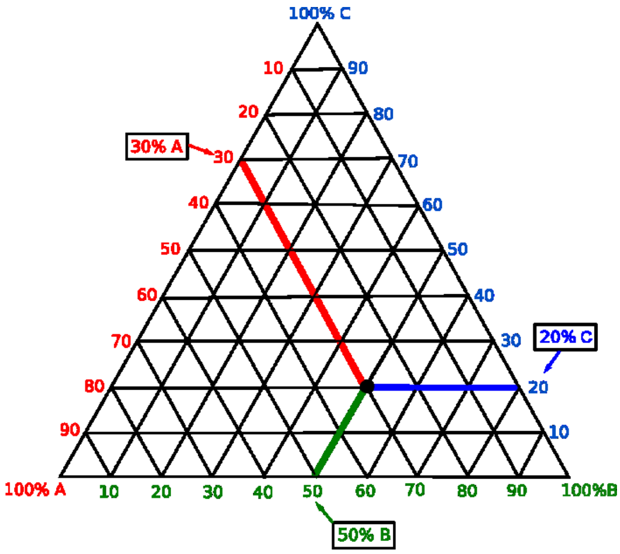

Figure 1. Gibbs' Concentration Triangle.

Vertices A, B, and C of the triangle represent pure components, while the sides represent binary systems, and the area of the triangle represents ternary systems. If the length of one side of the triangle is taken as the unit, the points lying on the sides directly determine the mole (or weight) fractions of two out of the three components. Points located within the triangle correspond to the mole (or weight) fractions of all three components. Compositions corresponding to these points (*e.g.* point Q) can be easily found by considering that systems with a constant content of a specific component are represented by a straight line drawn parallel to the side opposite the vertex corresponding to that component and at a certain distance from that vertex. In Figure 1, point Q represents a system with the composition: x_A = 0.3, x_B = 0.5 and x_C = 0.2. This property is also utilized to position a point on the graph corresponding to a specific system.

If we gradually introduce a third component into a binary system, the coordinates of points describing the overall composition of the system will shift, as the third component is added, along a straight line connecting the point representing the initial composition of the system with the vertex corresponding to the added component. For example, if component B is added to a system initially containing only components A and C, where the concentration of component A was 36%, the overall composition of the system will change as shown in Figure 2.

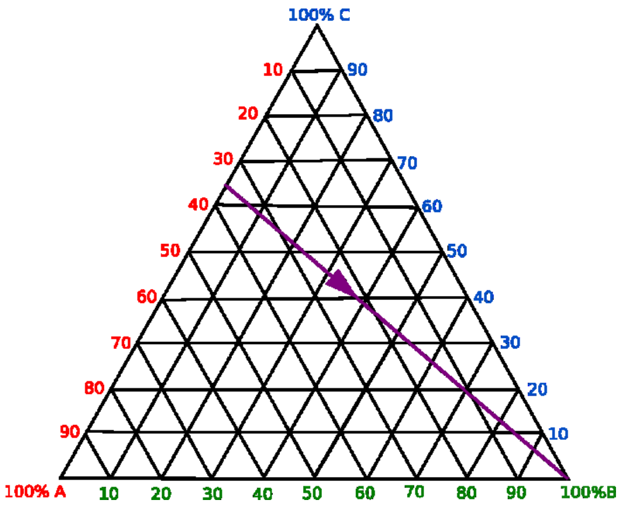

Figure 2. Change in the system's composition resulting from adding pure component B to a binary system containing components A and C in concentrations of 36% and 64% respectively.

In a system where two liquids exhibit limited mutual solubility (limited miscibility), while a third liquid component can mix indefinitely with the other two, an increase in the mutual solubility of the components with limited miscibility is observed. The phase equilibrium curve in such a system, determined for specific pressure and temperature values, is called a binodal curve, or simply a binode. Sometimes, this line is also referred to as the solubility curve. The binode is supported by the side representing the concentrations of the liquids with limited miscibility. If the liquids with limited miscibility are liquids B and C (as depicted in Figure 3), the enclosed area bounded by the arms of the binodal curve corresponds to conditions where two phases are formed: a saturated solution of liquid B in liquid C or in a liquid mixture of components A and C, and a saturated solution of liquid C in liquid B or in a liquid mixture of components A and B.

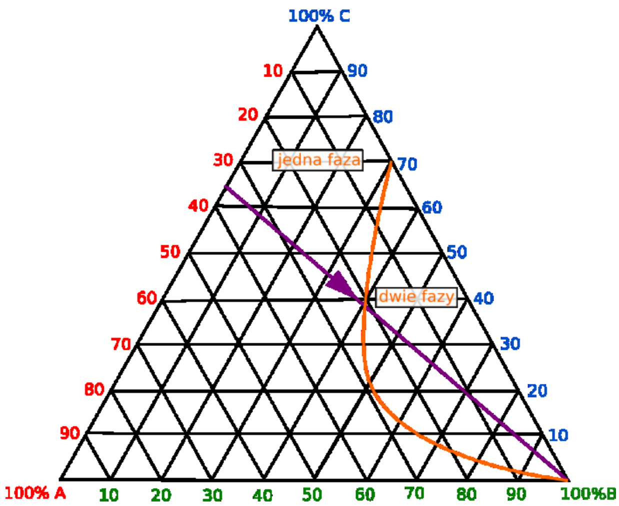

Figure 3. Change in composition and number of phases in a system resulting from adding a third liquid that can mix indefinitely only with one of the other components while having limited miscibility with the second component, to a mixture of two liquids with unlimited mutual solubility.

The binode can be determined by gradually adding a third liquid to a binary and single-phase system (formed by liquids with unlimited mutual solubility) that can mix indefinitely with one of the components while having limited solubility with the other. At a certain specific composition (marked on Figure 3 as point O), a second stable liquid phase will appear in the system. The visual manifestation of the appearance of the second liquid phase will be the appearance of cloudiness due to vigorous shaking of the sample. The cause of this cloudiness is light scattering by the dispersed system formed as a result of shaking the two-phase system.

If the overall composition of the system is represented by a point within the enclosed area bounded by the arms of the binodal curve, it can be inferred that the system will separate into two phases. The compositions of these phases will be determined by the so-called tie line or simply, the tie. The tie has the property that all systems represented by points lying on it will split into phases with compositions defined by the tie's endpoints, which are determined by its intersections with the binodal curve. The position of the tie is determined experimentally by analyzing the compositions of coexisting phases in equilibrium. Ties often form a bundle of lines radiating from a single point or, less commonly, a bundle of lines parallel to the base of the triangle.

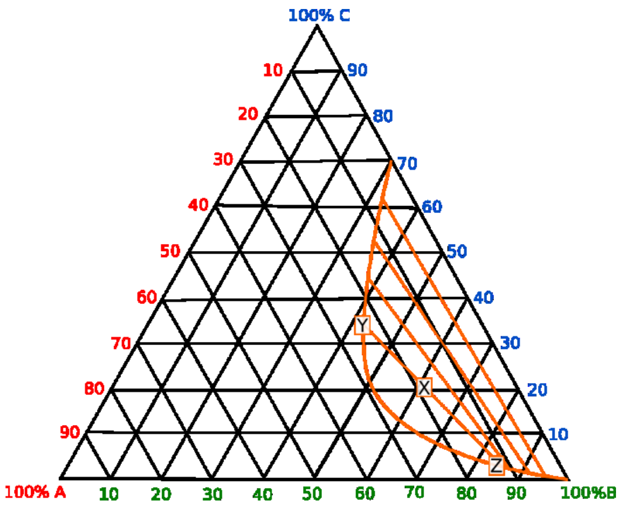

Figure 4. Tie lines (ties) determined by points representing the compositions of coexisting phases in equilibrium. A system with a composition indicated by the coordinates of point X will separate into two phases with compositions corresponding to points Y and Z.

Performing the exercise

The aim of the exercise is to determine the binodal curve for the system: acetic acid–water–chloroform.

In tightly sealed bottles, we prepare a series of 4 systems containing acetic acid and chloroform, as well as 4 systems containing acetic acid and water. The proposed compositions are provided in Table 1. These systems can be prepared by measuring appropriate volumes of individual components, using the following approximate values of their densities, d_i, applicable in the temperature range from around 285 K to around 300 K: *d* CH_3COOH = 1.1 g/cm^3, *d* $CHCl_3$ = 1.5 g/cm^3 and *d* H_2O = 1.0 g/cm^3.

After thorough mixing of the components, set aside the bottles for approximately 10 minutes. Then, gradually add the third component from a burette (water for systems with acetic acid–chloroform, and chloroform for systems with acetic acid–water) until the first appearance of cloudiness that doesn't disappear upon vigorous shaking of the system. The disappearance of cloudiness during shaking indicates that phase equilibrium has not yet been established in the system. On the other hand, the disappearance of cloudiness in systems left at rest is due to a decrease in the dispersion degree of the dispersed phase. Record the results in the table.

Table 1. Proposed compositions of binary systems used for determining the binodal curve.

component		1	2	3	4	5	6	7	8
acetic acid	volume [cm^3]								
	mass [g]	5	10	15	18	5	10	15	18
	% weight								
chloroform	volume [cm^3]								
	mass [g]	25	20	15	12				
	% weight								
water	mass [g]					25	20	15	12
	% weight								

Results analysis

Based on the masses of all three components, calculate their weight percentages in the mixture. After compiling the results in a table, plot them on the Gibbs' concentration triangle. The obtained points will outline the course of the binodal curve.