

Investigation of ternary systems

Introduction

The three-component or ternary systems raise not only interesting theoretical issues, but also have great practical significance, such as metallurgy, plastic industry (think of molten, alloys, in which one or more solid phase hold equilibrium with liquid phase containing one or two common substances or dissolving polymers etc). In ternary systems the mutual solubility of components on each other is different. Any such system has a pressure and / or temperature range, in which miscibility for at least two components is limited.

The presence of the third component - if this can be partially or completely miscible in the other two components - changes the mutual solubility of the two partially miscible components. Describing the ternary systems' state additionally to the pressure and temperature, the composition is required, when a chemical reaction does not take place in the system. Since knowing the mole fraction of two components, the mole fraction of the third component is determined, and therefore the number of degrees of freedom is 4 in these kind of systems. At a given temperature and pressure therefore two composition data sets the system status clearly. In order to illustrate a ternary system phase diagram in the plane, two parameters - preferably the pressure and temperature - we must consider as constants. In this case, the three components are determined by the composition of an equilateral triangle. The peaks of the triangle represent the pure components of one-component systems. The sides of the triangle represent the mole fraction or weight % of each component (Figure 1), increasing counterclockwise

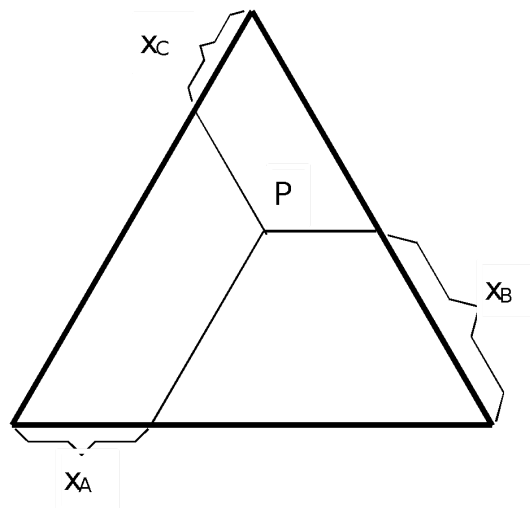


Fig. 1 Representation of a ternary system in a triangle diagram. The mole fractions of the components increase counterclockwise.

Features:

- Any point within this triangle represents the overall composition of a ternary system at a fixed temperature and pressure.
- By convention, the lightest component (A) is located at the apex or top of the triangle. The heavy (C) and medium (B) components are placed at the left hand corner and right hand corner, respectively.
- Every corner represents a pure condition. Hence, at the top we have 100 % A, and at each side, 100 % C and 100 % B, respectively.
- Each side of the triangle represents all possible binary combinations of the three components.

- On any of those sides, the fraction of the third component is zero (0%).
- As you move from one side (0 %) to the 100 % or pure condition, the composition of the given component is increasing gradually and proportionally. At the very center of the triangle, we find 33.33 % of each of the component.

The composition at point P inside the triangle can be obtained if we draw lines parallel to the sides crossing the points and the individual mole fraction of the components we read the relevant. The chart sides also provide the composition of liquid-pairs of a two-component systems (Fig. 2 I).

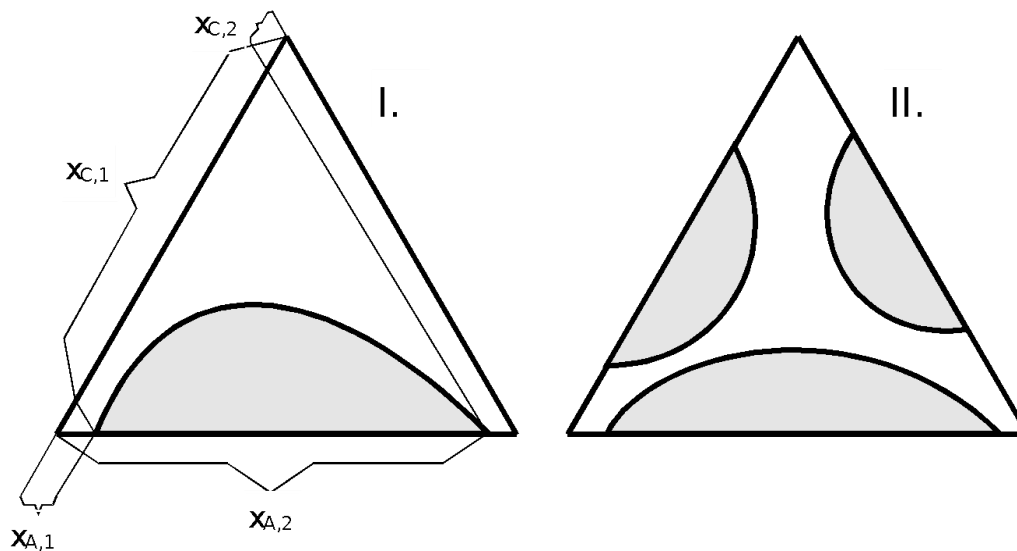
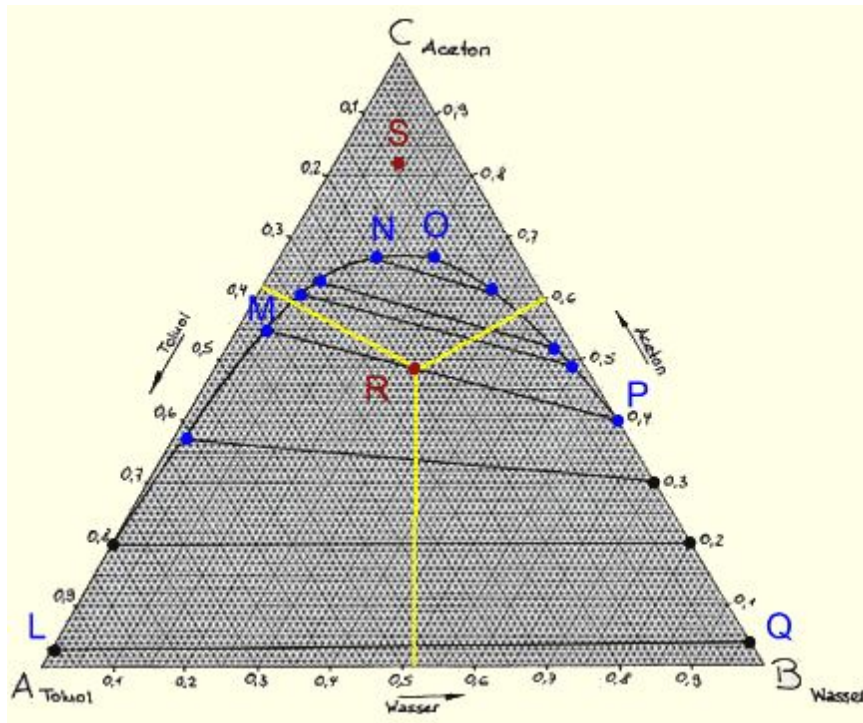


Fig. 2 The phase diagrams of the ternary systems **I**. One component-pairs miscibility is limited: under the curve, in the darker area the system is heterogeneous. **II**. All three components' miscibility in with each other is limited

Figure 2 (I) shows the composition of a ternary system, in which the miscibility of two components with each other is limited (water-chloroform), while the third (weak acid, for example. acetic acid) is miscible with both. The area under the curve indicates the heterogeneous phase. The system then falls apart into two phases, which are called conjugated phases. The system is homogeneous in the area outside the curve in the triangle. Where the curve intersects the side of the triangle, the system is present with two components: The $x_{A,1}$, $x_{C,1}$ point shows the solubility of water in chloroform, the $x_{A,2}$, $x_{C,2}$ represents the solubility of chloroform in water if the A-water, B-weak acid, C-chloroform notation is used. If miscibility of one liquids-pair is limited, we get a figure 2 (II)-type of chart. Further properties of ternary systems are presented through the example of the acetone-toluene--water system. As mentioned above, the area under the curve corresponding to any point composition system falls apart into two conjugated phases in equilibrium.

Representation of a ternary system

Equilibrium data of ternary systems are usually graphically shown using either right triangular or equilateral triangular diagrams. The diagram below shows the data for a ternary liquid system containing acetone, toluene and water. Any point located within the triangle or on one of its edges represent a different composition of the system.



In particular:

- The points at the three apex, **A**, **B**, **C**, represent the three pure compounds. For example, in A, it is $x_A = 1$, $x_B = 0$, $x_C = 0$;
- Any point on a side (**A-B**; **B-C**; **A-C**), of the triangle represents a binary mixture of the two components which are at its extremity.
- Any point, like **S** or **R**, located inside the triangle represents a mixture of the three components A, B and C.

Such diagram has the property that the sum of the lengths of the perpendicular lines drawn from any interior point, like **R**, to the sides is equal to the height of the triangle. Thus if the height is scaled from 0 to 100, the percentage of component A in a system represented by **R** is the distance of **R** from the side opposite to the A apex. In a similar way, the content of B and C can be determined.

The degrees of freedom can be determined with Gibbs' phase rule. In any point like **S**, it is:

$$F = C - P + 2 = 3 - 1 + 2 = 4;$$

Where $C = 3$ components; $P = 1$ (outside the immiscibility region); and since this diagram is drawn at constant pressure and temperature, we have only 2 degrees of freedom; thus meaning that once having fixed the composition of two of the three components, the third one is consequently determined.

While in any point like **R**:

$$F = C - P + 2 = 3 - 2 + 2 = 3;$$

where $C = 3$ components; $P = 2$ (within the immiscibility region); and since again pressure and temperature are fixed, the system has only 1 degree of freedom and the compositions of the two

phases are univocally determined by the end-points (M and P) of the tie-line passing through the point R.

The solubility envelope

The curve LMNOPQ represents the saturation curve for the ternary system ABC. This line is also called solubility envelope since it delimits a region where the three components are not fully miscible. Any system, represented by point like R within the immiscibility region, will split into two phases, represented by M and P in equilibrium with each other. The immiscibility region is a biphasic region. The two points M and P lie on the same equilibrium line, called tie-line.

Any point of the solubility envelope behaves like R. Point O is called the **plait point** and it is characterized by the fact that the two phases have identical compositions. In this point the tie-lines converge in a point and the two phases become only one phase. All the pairs of points lying into solubility envelope, on one side and on the other of the **plait point**, are related by an equilibrium correlation represented by the tie-line. The solubility envelope for the same ternary system is going to change at different temperatures and pressures, since different equilibria are present among the components.

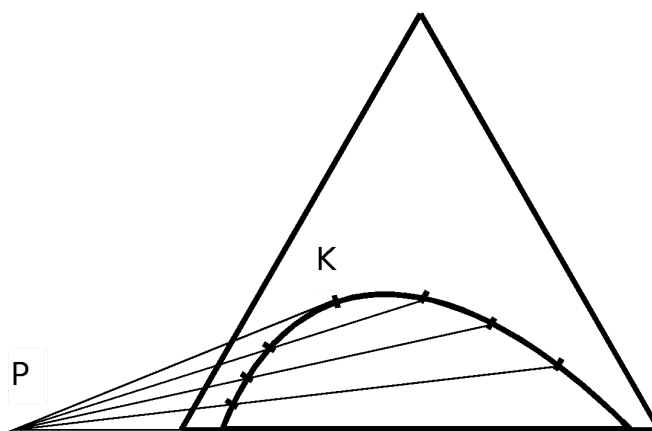


Fig. 3 Determination of the **plait point** (K on this figure)

Connecting the two points of two conjugated phase giving the composition the so-called tie-line is obtained. Linking the various tie-lines of conjugated systems the extensions normally outside the triangle, we get intersect point P (see Figure 3). The tie-lines are usually not parallel the triangle basis, as the third component is not equal partly dissolved in the two phases. The edited tangential of the extension of the tie-lines intersection indicates the system's (at a given temperature and pressure is valid) critical miscibility point where the system is homogeneous.

If not one but two or all the three liquid-pairs are limitedly miscible, as explained above, there two or three critical miscibility points in the system. During the practice the water - organic solvent - organic weak acid ternary system phase diagram will be determined.

Description of the experiment

Prepare a mixture of organic solvent and weak acid designated by the practice instructor. a total volume of 20 cm³, a v/v% for the organic solvent of 15, 30, 50, 60, 70, 80, 85, 90, 95%. Measure the components with an automatic burette, into a clean, dry Erlenmeyer flask, and then close it. Titrate the mixtures carefully from 10 cm³, using a 0.05 cm³ graduated automatic burette with distilled water until a slight cloudiness is not observed. Search the components' densities in the

table and using the titre calculate the individual components' mole fraction and the weight % composition of solutions as well. Construct two phase diagrams: first, using the components' mole fraction, and second, using the weight % composition . The results should be recorded in the following format:

organic solvent $M_r = \quad \text{g mol}^{-1}$ $\rho = \quad \text{g cm}^{-3}$				weak acid $M_r = \quad \text{g mol}^{-1}$ $\rho = \quad \text{g cm}^{-3}$				water $M_r = \quad \text{g mol}^{-1}$ $\rho = 1.00 \text{ g cm}^{-3}$			
cm ³	mol	x	m %	cm ³	mol	x	m%	cm ³	mol	x	m%
2											
4											
...											

The critical miscibility point is determined by first constructing systems which form two phases being in equilibrium with each other. Then the weak acid content is determined by titration with NaOH. Then, weight % composition is calculated. So we get the tie-line of the original composition. From the extension of the points where tie-lines intersect, we can edit the line to the equilibrium curve, and receive the critical miscibility point, and its composition.

Prepare in clean, dry Erlenmeyer flasks the following mixtures:

A: 25 cm³ of distilled water, 25 cm³ of organic solvent, 5 cm³ weak acid.

B: 25 cm³ of distilled water, organic solvent 25 cm³, 15 cm³ weak acid.

Close up the flask containing A and shake the mixture for approx. 5 minutes. Transfer the mixture into a funnel, when the phases had separated, measure 2.00 cm³ of the aqueous phase, and 10.00 cm³ of the organic phase, and titrate with 1 mol dm⁻³ factorised NaOH solution, with two drops of phenolphthalein as an indicator. Repeat the measurements with the B mixture as well. Prepare the following table:

mixture	volume by titration (organic phase) cm ³	m_{acid} g	m_{phase} g	m%	volume by titration (water phase) cm ³	m_{acid} g	m_{phase} g	m%
A								
B								

Knowing the weight of the phases the weight % of the weak acid can be calculated. On the basis of the weight % we can construct the equilibrium chart then find and mark the two points of a mixture where the weak acid's weight percentage line intersects the equilibrium curve. We determine the two points designated by the prolongation of tie-lines segment, and edit this point affecting the equilibrium curve. Read and define the critical miscibility point weight % of the composition.

Appendix

Data of commonly used solvents

	Molecular weight g mol ⁻¹	Density (20 °C) g cm ⁻³	Viscosity (20 °C) mPa·s	Refractive index n _D (20 °C)	Boiling point (101325 Pa) °C	Dielectric constant (20 °C)
Acetic acid	60.05	1.0497	1.31(15)	1.372	117.9	6.15
Acetone	58.08	0.7900	0.30(25)	1.359	56.1	20.7(25)
Benzene	78.11	0.8750	0.65	1.501	80.1	2.284
n-Butanol	74.12	0.8089	2.95	1.399	117.7	17.8
CCl ₄	153.84	1.5940	0.97	1.460	76.8	2.238
Chloroform	119.38	1.4891	0.58	1.446	61.2	4.806
Ciklohexane	84.16	0.7786	0.98	1.426	80.7	2.023
Etil-acetate	88.11	0.9006	0.46	1.372	77.1	6.02(25)
n-Hexane	86.18	0.6593	0.31	1.375	68.7	1.890
Isobutanol	74.12	0.8063	4.21	1.397	99.5	15.8(25)
Methanol	32.04	0.7910	0.55	1.328	64.6	32.63(25)
n-Propanol	60.10	0.8036	2.26	1.386	97.2	20.1(25)
Toluene	92.14	0.8668	0.59	1.497	110.6	2.379(25)
Water	18.02	0.9982	1.00	1.333	100.0	78.54