PHASE EQUILIBRIUM OF LIQUID–LIQUID TERNARY SYSTEMS

Author:
dr Magdalena Błachnio

Editor:
dr hab. Agnieszka Ewa Wiącek

Task 21

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I. Aim of the task

The aim of this task is determining solubility isotherm (binodal curve) of ternary sytems:

- water – toluene – methanol,
- water – toluene – acetone.

II. Introduction

1. Mutual solubility of liquids – temperature dependence.
2. Mutual solubility of liquids in ternary systems.
3. The principle of the Gibbs triangle construction.
4. Methods of determining the composition of solutions within the Gibbs triangle.
5. Definition of binodal curve and conoda.

References:

1. P. Atkins, „*Physical chemistry*", W. H. Freeman and Company, New York, 2006, 179-188.
2. A. Malijevsky "*Physical chemistry in brief*", Institute of Chemical Technology, Prague, 2005, 182-188, 211-214.
3. I. Levine „*Physical chemistry*", McGraw-Hill Higher Education, 2009, 370-372, 285-387.

III. Theory

The solubility of different substances in a given solvent is dependent on the impact of intermolecular interactions and external conditions. In the case of liquids, their mutual solubility, among other things, depends on the structural similarity of molecules. If two liquids with similar polarities (and, therefore, similar intermolecular interactions) are combined, the liquids are said to be miscible with each other because they will mix to form a homogeneous solution. The examples of solutions formed with miscible liquids include: *gasoline* (a mixture of many organic solvents such as benzene, toluene, xylenes, and others), *alcoholic drinks* (ethanol and water), *molten copper and zinc*.

Not all liquids mix together completely over a wide range of concentrations. There are liquid systems that mix together only partially, for example: aniline + water, phenol + water, hexane + nitrobenzene. If for two liquids, A and B, the impact of A – A and B – B intermolecular interactions is stronger than A – B intermolecular interactions, their mutual solubility will be limited. After mixing these two liquids you can obtain two liquid phases: one is a saturated solution of liquid A in B, the second is a saturated solution of liquid B in A. Both liquid phases will remain at equilibrium at a given temperature.

Mutual solubility of liquids is also dependent on the temperature – at a given temperature two liquids can be mixed in any ratio (unlimited), at another temperature they can have limited mutual solubility. Along with the change in temperature the composition and quantitative ratio of both phases will change. These dependences can be shown on the graph as the temperature function vs. the composition of solution (Fig. 1a, b, c).

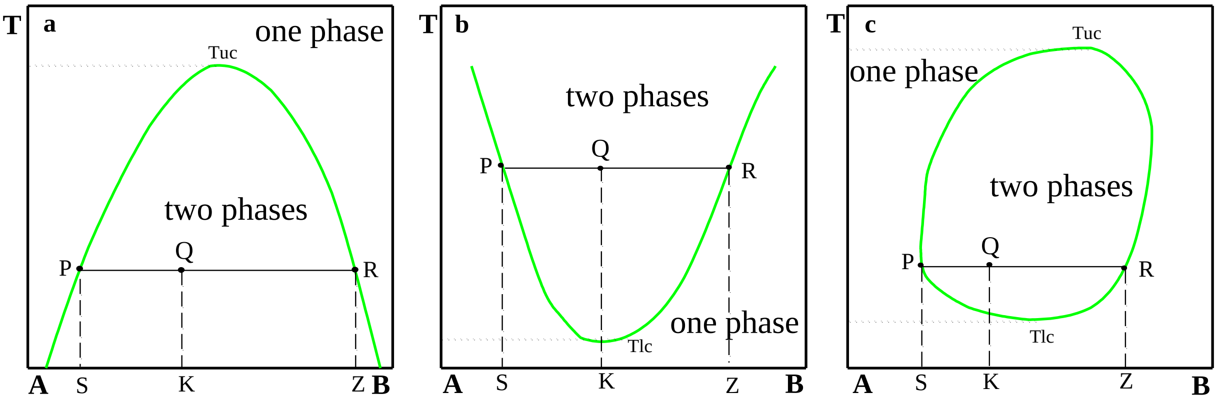

Fig. 1. Examples of mutual solubility of two liquids.

Figs. 1a, b, c show the characteristic curves determining the range of limited mutual solubility of two liquids. In Fig. 1a we can observe a two – component liquid system whose mutual solubility increases with increasing temperature (for example *hexane* and *nitrobenzene)*. The two – phase system becomes less extensive, because each phase in equilibrium is richer in its minor component: the *A* – rich phase is richer in *B* and the *B* – rich phase is richer in *A*. We can construct the entire phase diagram by repeating the observations at different temperatures and drawing the envelope of the two-phase region.

The upper critical solution temperature, *T_{uc}*, is the highest temperature at which phase separation occurs. Above the upper critical temperature the components of mixture are miscible in a full range of concentrations forming the homogeneous, two – component, single – phase system. Better solubility at the higher temperature can be explained by the stronger thermal motion of molecules that overcomes any potential energy advantage in molecules of one type being close together.

The area of limited solubility is determined by the solubility curve, there is the coexistence of two liquid phases. Below this curve two mixed liquids always separate into two liquid phases. Two liquid phases which are in equilibrium with each other must be the saturated solutions – they are called the coupled solutions (conjugate solutions).

In Figure 1b there is a two – liquid system characterized by **the lower critical solution temperature, *T_{lc}*,** below it the liquids mix in all proportions and above it they form two phases. An example is *water and triethylamine*. In this case, at low temperatures the two components are more miscible because they form a weak complex. At higher temperatures the complexes break up and the two components are less miscible.

In the case of the system in Figure 1c we observe the enclosed area of mutual solubility and the presence of the lower and upper critical solution temperature. Above the upper temperature and below the lower one, the components of the system dissolve each other without restrictions. This phenomenon occurs because, after the weak complexes have been disrupted, leading to partial miscibility, the thermal motion at higher temperatures homogenizes the mixture again, just as in the case of ordinary partially miscible liquids. The most common example is *nicotine and water*, which are partially miscible between 61°C and 210°C.

The point *Q* in Figure 1a-c, on the area comprised by the solubility curve describes the system, which includes two liquid phases. The average composition of a two – phase system can be read on the axis of composition – the point *K*. The point *K* enables to determine the average molar mass of the solutions (*AK* and *KB*), but it does not inform about the division components between two liquid phases. Both liquid phases, *P* and *R* are saturated solutions and their composition, at a given temperature, can be read by projecting them on the axis of composition (*AS* and *ZB*). The liquid systems shown in Figures 1a, 1b, 1c can create two – component, single – phase system or two – component, two – phase system depending on a position of the analysed point in the diagram.

We can also observe limited, mutual solubility in the case of three liquids. The simplest system is when two pairs of liquids mix unlimitedly and the third pair mix limitedly.

The examples are:

- water – toluene – methanol,
- water – toluene – acetone,
- water – chloroform – acetic acid,
- water – chloroform – ethanol.

Water and toluene are both liquids at 25°C and are almost completely immiscible. So shaking together some water and some toluene, two phases are obtained; an aqueous phase containing traces of toluene and a toluene phase containing traces of water. Adding methanol to this heterogeneous system and shaking again we observe that the mutual solubility of water and toluene increases: the aqueous phase contains a larger quantity of toluene and the chloroform phase contains a larger amount of water. The compositions of the two phases in chemical equilibrium are called **binodal compositions** and the segment that joins these two compositions is indicated as **conoda.** All the couple of binodal compositions obtained for different amounts of added methanol form the **binodal curve**. On this curve there is one point at which the binodal compositions are identical. We note also that the amount of methanol is not the same in the two phases. In the triangular phase diagram this fact translates into asymmetric binodal curves and in conodas that are not parallel to the side corresponding to the binary water – toluene system.

At increasing methanol concentration the system tends to become homogeneous with a single phase containing all the components. This behaviour can be easily explained considering that methanol behaves as an amphiphilic solvent in respect to water and toluene. In fact its molecule has a hydrophilic moiety, the alcoholic group, –OH, and a hydrophobic one, the CH_3– one. Therefore the same amphiphilic molecule can interact with water, through the hydrophilic moiety, and with chloroform, through the hydrophobic one. As a consequence, the mutual solubility of water and toluene increases.

A similar behaviour is observed adding acetone to the water – toluene biphasic system. Assuming, the pressure and the temperature are constant, we can show the ternary system in **the Gibbs triangle** – Fig. 2.

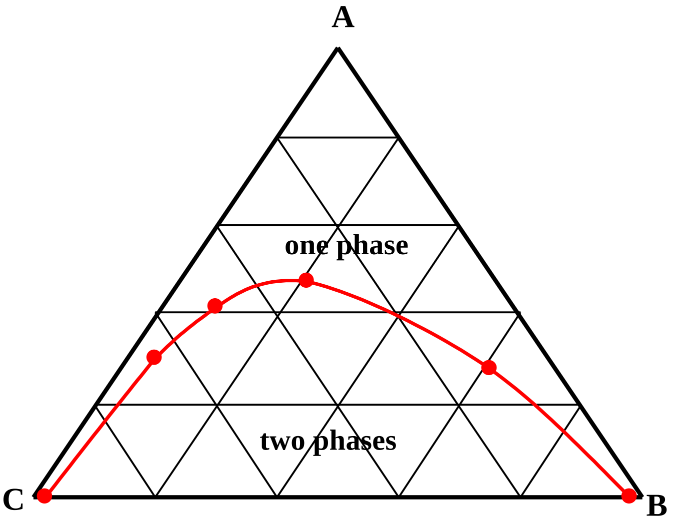

Fig. 2. Diagram of limited mutual solubility of two liquids in the ternary system.

In the Gibbs triangle, an equilateral one, the vertices correspond to clean, single components *A*, *B* or *C*. The sides of the triangle describe the composition of the binary systems *AB*, *AC* and *BC*. Points inside the triangle contain a three component system. Because in an equilateral triangle the sum of the distances from any interior point to the three sides is equal, any point uniquely corresponds to the composition given by three molar fractions X_A, X_B and X_C, which sum to unity – Figure 3.

Binodal curve (solubility curve) determines a range of limited solubility of liquids *B* and *C*. The area under binodal curve represents three – component, two – phase systems, the area above the one corresponds three – component, single – phase systems. The end positions of bimodal curve indicate that there is slight miscibility between components *B* and *C*. If no miscibility existed between components *B* and *C*, ends of curve would coincide with corners *A* and *B*. The diagram also indicates that the third component *A*, is really miscible with either *B* or *C* in all proportions.

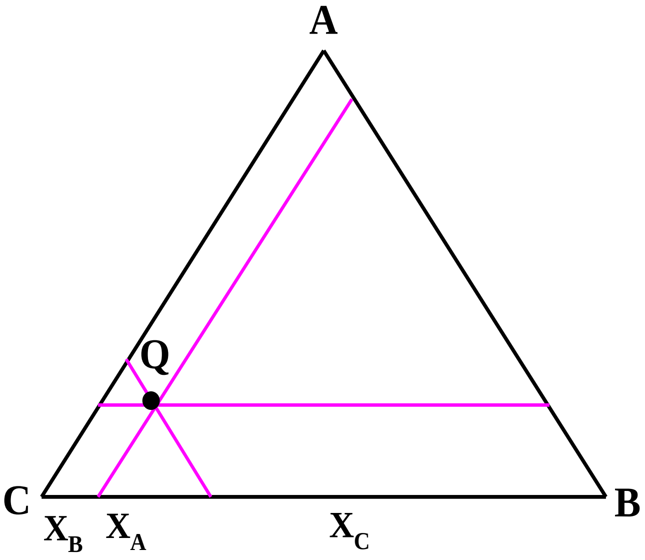

Fig. 3. The composition ternary system in point *Q* given by molar fractions.

If the total composition of the system is represented by the point lying in the area closed by the binodal curve, you can conclude that the system will divide into two phases. The composition of these phases determines the conjugate line – **conoda (tie line)**. Conoda has the property that all the systems represented by the points lying on it, separates into two phases with the composition specified by end points of conoda, i.e. determined by its intersection with the binodal curve. For example, the system with the composition assigned by coordinates of *Q* point (Fig. 4) separates into two phases with the composition corresponding to *P* and *R* points.

Quantitative relations of these phases can be specified by using the lever-arm principle:

$$\frac{quantity\ of\ phase\ of\ the\ composition\ P}{quantity\ of\ phase\ of\ the\ composition\ R} = \frac{length\ of\ QR}{length\ of\ QP}$$

The position of conoda will be determined experimentally by analysing the composition of the phases coexisting in equilibrium.

In Figure 4 the bimodal curve is not symmetrical and the conodas (tie lines) are not parallel to each other. This is simply because the solubility of *A* in the two phases (*B* and *C*) is not the same. In whatever direction the tie lines are slanted, they connect points of equilibrium compositions. These equilibrium compositions, *S* vs. *T* and *U* vs. *W*, and also *Y* vs. *Z* become increasingly similar with each subsequent tie line, starting from the base of the bimodal curve and proceeding upward. Similarly, the tie lines become shorter and finally converge to a composition. This is called **isothermal critical point** or **the plait point**.

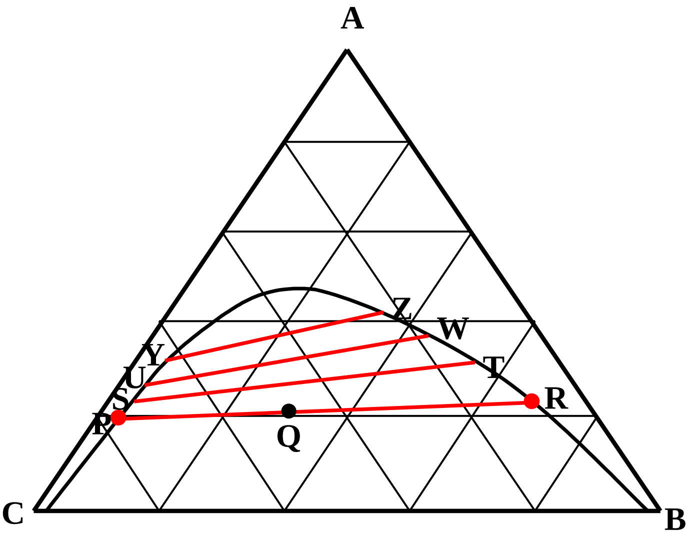

Fig. 4. Conjugate lines (conodas) determined by the points representing the composition of the phases coexisting in equilibrium.

IV. Experimental

A. Devices and materials

1. Device:

– digital burette,

Fig. 5. Digital burette.

2. Equipment:

– calibrated pipettes (1 cm^3) - 2 p.,
– calibrated pipettes (5 cm^3) - 2 p.,
– calibrated pipettes (10 cm^3) - 2 p.,
– test - tube with rubber stoppers - 16 p.

3. Materials:

– toluene,
– methyl alcohol,
– acetone,
– distilled water.

B. Program

1. Preparation of the digital burette for titration.
2. Preparing of binary solutions of toluene + methanol and toluene + acetone.
3. Titration obtained solutions with distilled water.
4. Development of the results.

C. Use of device

1. Operation of digital burette for titration.

- turn the burette on when you have prepared solutions for titration,
- unscrew the **red cap** at the tip of burette,
- turn the burette display on with the black button on the left side in the **On/Off** position (zero will appear on the screen),
- press the black button on the right to the **Fill** position (arrow under the zeros on the display set under the first two zeros) and turn the titrate wheel up on the right side of electronic head casing to fill the burette (burette moves to the top). Under the plastic part of the burette, you can see the metal teeth and behind them the transparent container with the liquid for titration. If you see at the top of the container a large air bubble, turn the titrate wheel down with fast movement to remove liquid from the container. Repeat this operation until you get rid of the air (small bubbles can stay inside),
- it is not allowed to turn the titrate wheel up if the black button is not in the **Fill position!,**
- if during the above steps any digits appear on the display you can reset the burette by pressing the button on the left to the **Clear** position (zero will appear on the display),
- press the black button on the right side to the **Titr.** position (arrow under the last two zeroes) – the burette is ready to titrate,
- titrate the particular samples by turning the black titrate wheel down on the right side of burette,
- during titration you get the volume of liquid in cm^3 on display,
- after the end of titration of each sample, press the **Clear** button (to zero the display) then you can titrate the next sample. A completely filled burette contains of 25 cm^3 of liquid – during the titration its upper part lowers (you can see how much titrant is left),
- if necessary, the burette may be refilled at any time during titration by pressing the button on the right side to the **Fill** position (by turning the titrate wheel up),
- after making all titrations leave the button on the right side in the **Fill** position and turn the burette off by pressing the black button on the left to the **On/Off** position,
- turn the **red cap** off at the tip of burette,
- if during the usage of burette you feel strong resistance it is forbidden to turn it with force, you should ask the Demonstrator for help.

D. Methods

1. Preparing binary solutions of toluene + methanol and toluene + acetone.

Into the tubes with matched stoppers measure toluene and methanol and also toluene and acetone with calibrated pipettes in the quantities listed in Table 1.

Table 1.

No. tube	Toluene		Methanol (Acetone)		Water	
	cm^3	% v/v	cm^3	% v/v	cm^3	% v/v
I	9		1			
II	8		2			
III	6		4			
IV	4		6			
V	2		8			
VI	1		9			
VII	0.5		9.5			
VIII	0.2		9.8			

2. Titration of the obtained solutions with distilled water.

Successively titrate the obtained solutions with distilled water to get the first stable turbidity (vigorously shake the tube after adding each portion of water). Titrate the first four two – component solutions by adding one drop of distilled water due to low solubility of water in the studied solutions. Into the next tubes you can pour the quantity of water close to the last titration at a time to reduce time of analysis. The remaining amount of water should be added in the portions of 1-2 drops. After titration pour the solutions into the bottle labelled **LIQUID WASTE** under a fume cupboard. Rinse the tubes with the same small amount of acetone (approx. 5 cm^3) and dry. Acetone used for washing tubes must be also poured into **LIQUID WASTE**.

E. Results and conclusions

1. Put the results of titrations in Table 1.
2. Give composition of the ternary solutions in % v/v.
3. Put the obtained composition of the ternary solutions in the Gibbs triangle and plot the transition isotherm from a single – phase system into a two – phase system, plot a binodal curve.
    3.1. Draw an equilateral triangle (in the case of a manual plot 10 cm as a length of triangle side is recommended),
    3.2. In accordance with the principle of determining composition of ternary solution in the Gibbs triangle, plot the data obtained from the measurements for all solutions,
    3.3. Select all the measuring points, and then combine them by plotting a piece of binodal curve.
4. Explain the cause of turbidity of solutions during the titration process.

Exemplary determination of composition of measuring point in the Gibbs triangle.

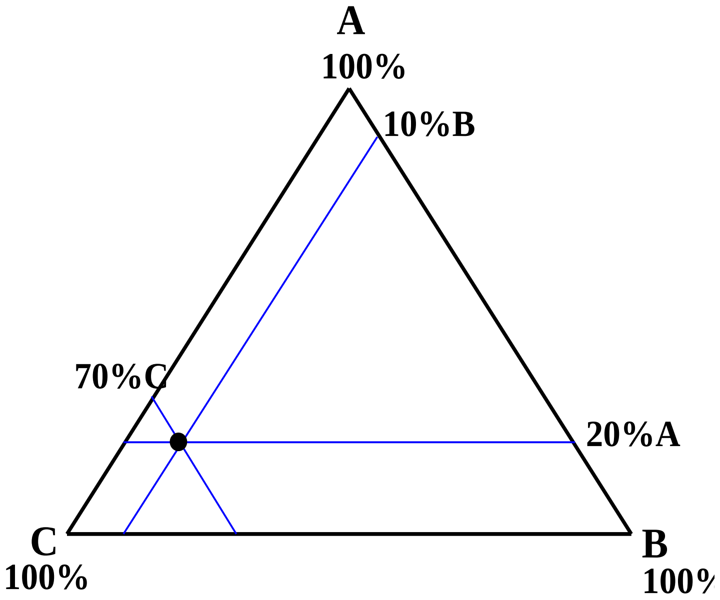

Fig. 6. The composition of the measuring point: 20% A, 10% B and 70% C.

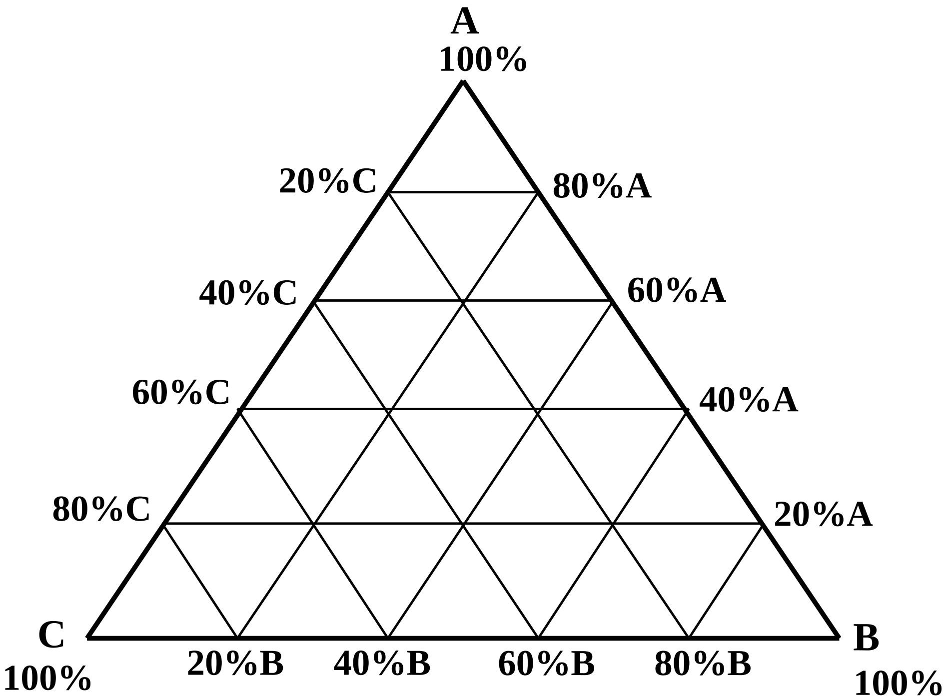

Fig. 7. The Gibbs triangle – determination of a composition of ternary solutions.