Variant 4

System: Water (H_2O) (A) – phenol (C_6H_6O) (B)

Tube №	1	2	3	4	5	6	7	8	9	10
C_A, mass. %	91,0	90,0	88,0	83,0	76,0	56,8	47,8	39,7	33,0	31,6
C_B, mass. %	9,0	10,0	12,0	17,0	24,0	43,2	52,2	60,3	67,0	68,4
T,^{0}C av.	36,3	44,3	50,4	59,4	63,9	64,8	61,7	54,7	40,0	32,0
T_1, K = 320; T_2, K = 330; C_A, mass. % = 60										

LABORATORY WORK 9
THE STUDY OF THE LIMITED SOLUBILITY IN LIQUID BINARY SYSTEM

Objective: To build mutual solubility diagram for liquid partially soluble systems.

Theoretical information

To study the equilibrium in heterogeneous systems using physic-chemical analysis method. Its essence is to observe any dependence of physical properties of the system on its composition, followed by a graphic representation of this relationship – the state diagram. The basis of the construction, analysis and interpretation of phase diagrams are the Gibbs's phase rule and two Kurnakov's principles.

According to the Gibbs's phase rule

$$C = K - F + n, \quad (3.1)$$

where C –number of freedom degrees, i.e. the number of independent thermodynamic parameters that can be changed without changing the number or type of phases in the system;

K - number of independent components;

F - number of phases;

n - number of independent thermodynamic parameters (typically, P and T).

Two-component systems in the condensed state (when there a gas phase is absent or it may not take into account) is usually considered under the condition P = const. Then the phase rule for such systems can be written as:

$$C = K - F + 1 = 3 - F. \quad (3.2)$$

According to the first Kurnakov's principle known as the ***principle of correspondence****, any phase or phase aggregate of the real equilibrium heterogeneous system on the phase diagram corresponds to a geometric image (point, line, part of the plane, etc.).*

*The second Kurnakov's principle (****principle of continuity****) can be formulated as follows. When a continuous change of any of the thermodynamic parameters that define the state of equilibrium in a heterogeneous system, the properties of the individual phases also change continuously; wherein the properties of the system as a whole is changed continuously as long as the system is stored in the number and type of phases. When the number or type of phases is changed in changing the property of the system as a whole, there is a discontinuity (jump break, etc.).*

Diagrams of systems with limited solubility of liquids

All liquids in one degree or another are soluble in each other. Based on the solubility of different nature, the liquids can be divided into several groups.

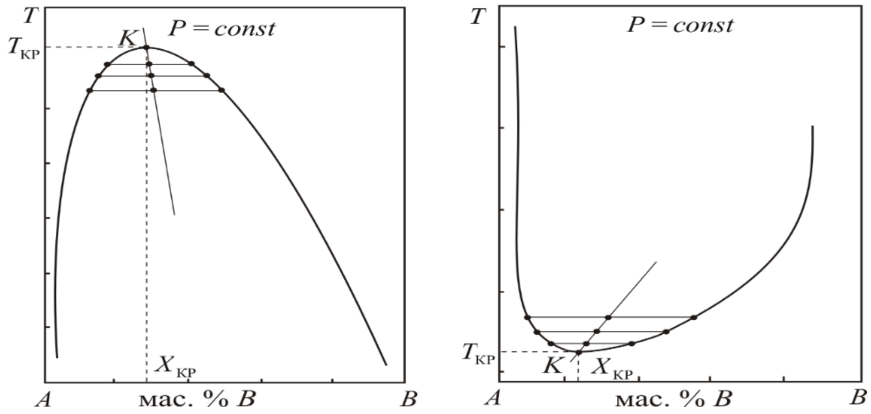
1. Liquids infinitely soluble in one another: methanol – water, benzene – chloroform and others.
2. Liquids hardly soluble in each other: benzene – water, mercury – water and others.
3. Liquids limitedly mutually soluble phenol – water, methanol – hexane and others.

Mutual limited solubility of liquids, except of their nature, strongly depends on the temperature This influence can be different: with an increase in the temperature in some cases mutual solubility increases, in others -– reduces. Therefore, there are three types of diagrams temperature – composition.

In the first case, the mutual solubility with increasing temperature increases and at a certain temperature the liquids shows unlimited solubility in each other. Temperature above which liquid is unlimited soluble in each other in any ratio, called upper critical solution temperature. An example may be systems water – phenol, water – aniline, etc. (Fig.3.2.).

In the second case, the temperature rise decreases mutual solubility and mutual solubility with decreasing temperature increases. The temperature below which the liquid is unlimited soluble in each other in any ratio, called the lower critical temperature. An example could be the system: o-toluidine – water, triethylamine – water, etc. (Figure 3.2.).

There are also mixtures which have a critical temperature of the two type – top and bottom. This systems: nicotine – water, glycerol – m-toluidine, etc. (Fig.3.3.).



а) б)

Fig. 3.2 a) the system with an upper critical solution temperature
b) systems with a lower critical solution temperature

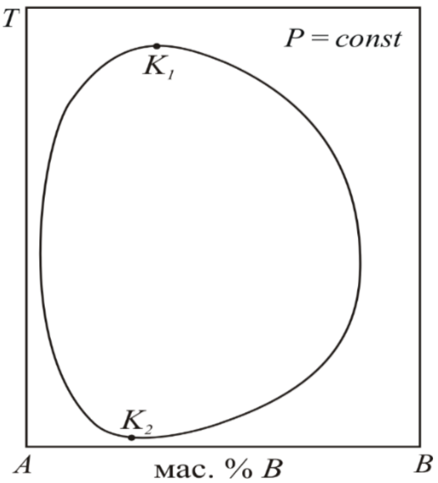


Fig. 3.3 Diagram of the system with two type
critical temperatures

The curves in the above state diagrams (charts limited solubility) are the set of points that define the compositions of saturated solutions at appropriate temperatures, i.e. points at which the system goes from heterogeneous to homogeneous state or vice versa.

Given that phase in such systems on the aggregation state is liquid and the presence of two or more phases form immiscible layers above mentioned curves are called curves of the layering. Areas of limited solubility diagrams that are outside of the curves of the layering correspond to a single-phase (homogeneous) system. In areas which are within the bundle of curves, a heterogeneous system consisting of two layers of saturated solutions of each other substances.

The point, which corresponds to the critical temperature, determined by the *Alekseev's method (rule of rectilinear diameter), according to which a straight line passing through the middle of the tie lines (connodes) that connect the associated phase intersects the curve of the bundle at the critical point.*

To do this, conducted a series of several tie lines (horizontal lines), which connect the points corresponding to the coexisting phases. Through the middle of the obtained segments is carried out straight line, as shown in Figure 9.1. The upper end of the line (point *K*) will determine the upper critical point (temperature and composition of the system, which it is responsible).

The practical implementation of the work consists of two parts.

Determination of the temperature stratification in the systems of different composition of liquids, which partially dissolve each in other

To determine the stratification temperature Alekseev's method is used. Sealed ampoules with mixtures of various compositions are immersed in a water bath whose temperature was gradually raised, and determine the temperature at which the mixture becomes homogeneous. Check values of founded temperature gradually cooling the ampoules until the second phase will appear (clouding of the solutions in the ampoules). The difference between the cloud point temperatures and temperatures of the clarification should not exceed 1° C.

Order of work execution

In this work, using thin bent ampoule bottom in which are mixtures studied (Fig. 9.3). Tripod with numbered ampoules immersed in a water bath. Compositions of the mixtures listed in the tables in the workplace. Water bath with a set of ampoules put on an electric hot plate and begin heating.

The rate of heating water in the water bath should not exceed 10°C for 5 minutes, or temperature of the liquid in the ampoule will not respond to the temperature of the water bath. During heating, the contents stirred ampoules, which operate tripod oscillatory motion so that air bubbles in the bent portion of the ampoule being moved from one end to the second.

Warming the ampoules and their contents with stirring, the temperature recorded for each ampoule, whereby the turbid mixture suddenly becomes transparent, i.e. clarification temperature. When all of the mixture will become clear, the temperature was raised further to 3-5° C, then removed with electric bath and begin cooling.

During cooling, for each ampoule is recorded temperature at which the fluid again becomes turbid (the cloud point). Temperatures clarification and cloud point should be the same. Divergence within acceptable 0,5-1,0° C. The average of these temperatures is taken as the stratification temperature at which water and phenol are soluble in each other in the proportion in which they are contained in each ampoule. When the temperature in the bath to fall to 40–50°C, cooling is accelerated, throwing pieces of ice in a bath every 5–7 minutes.

The experimental results are entered into the table 3.1.

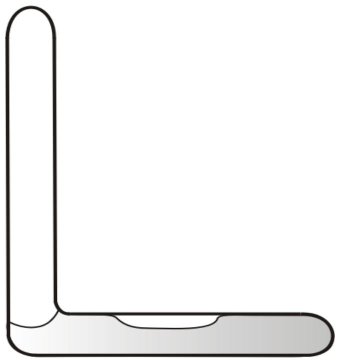


Рис. 3.4 The ampoule with the mixture for the study

Table 3.1 – Experimental results

Ampoule №	1	2	3	4	5	6	7	8	9	10
C_A, weight %										
C_B, weight %										
T, $^oC_{clar.}$										
T, $^oC_{opacity}$										
T, $^oC_{average.}$										

Construction and chart analysis limited solubility

In this part of the work on the experimental data, which are obtained by professional investigators, constructed and analyzed the phase diagram of a binary system of liquid that partially dissolve in each other.

Order of work execution

1. At the direction of the lecturer obtained an option data of studying the mutual solubility of organic substances.

2. According to the stratification temperature of mixtures of different composition is plotted solubility diagram of two-component system.

3. Analyzing stratification diagram, using the rule of rectilinear diameter, determine the coordinates of the critical point (temperature and composition of the mixture).

At the direction of the lecturer do the following task:

1) determine the composition of the conjugate solution at a temperature T_1;

2) determine the phase composition of the system, which corresponds the conditions of T_2 and C_A;

3) determined by the lever rule the relative the weight of phases of the system, which corresponds the above conditions.

Control questions

1. What factors affect the mutual solubility of liquids?

2. Specify the types of diagrams with a limited soluble liquids.

3. How in this work experimentally determined the temperature of cloud point andclarification of for mixtures of different composition in the study of the mutual solubility of liquids?

4. How to experimentally determine the critical temperature for mixtures of different composition?

5. On the basis of what data is plotteed solubility diagram of the system water – phenol?

6. What is the essence of the Alekseev's method, which is used to determine the upper critical point the ofsolubility?

7. Define the upper and lower critical temperature.

8. How is determined the composition of liquids in homogeneous and heterogeneous areas in the state diagram?