BINARY SYSTEM. LIQUID-LIQUID EQUILIBRIUM

1. PURPOSE OF THE WORK

Determination of the liquid-liquid phase diagram for the phenol-water system and determination of the critical dissolution temperature.

2. THEORETICAL NOTIONS

It has been found experimentally that by mixing two liquid components (at fixed temperature - T and pressure - P) a homogeneous system (a single phase) is not always formed. For these systems the terminology of partial miscibility (solubility) of the components is used, in the sense of the formation of two liquid phases in equilibrium that contain both components, but differ in their proportions. A borderline case is when phases L_1 and L_2 each contain practically only one of the components (immiscibility).

The equilibrium conditions between phases are:

$$T_{L_1} = T_{L_2} = T;\; P_{L_1} = P_{L_2} = P;\; \mu_i^{L_1}\left(T, P, X_i^{L_1}\right) = \mu_i^{L_2}\left(T, P, X_i^{L_2}\right);\quad i = 1, 2 \qquad (1)$$

(temperature and pressure in the two phases are constant and equal and, respectively, the chemical potentials of the 2 components are equal in the two phases).

The variables that characterize the equilibrium state are T, P, $X_i^{L_1}, X_i^{L_2}$. According to the law of phases, for a biphasic system (F = 2) the number of degrees of freedom of the system in the equilibrium state, l, is $l = C – F + 2 = 2$ (the number of parameters that can be changed independently without changing the number of phases in the system)

Therefore, it is necessary to fix two quantities (for example T and P) in order to obtain a determined system. Thus, the temperature variation (at constant P) entails a change in the phase composition. It has been found that for a number of systems the increase in temperature causes the difference between the compositions of the two phases to decrease, to a value of it called critical temperature (T_C) at which the system becomes single-phase. The graphical representation for different temperatures of the phase composition leads to an equilibrium (or solubility) curve of the system, which has a maximum point in temperature, called the *upper critical point*. Such systems are commonly referred to as systems with a *upper critical dissolution temperature*. There are also systems with *lower critical dissolution temperature* and also systems that have a closed domain of the 2 phases (they have both a higher critical point and a lower critical point). Examples of systems belonging to the 3 categories are presented in the Appendix.

A simple model that describes the behavior of systems with higher critical temperature is the model of regular solutions according to which the activity coefficients of the components are given by the expressions

$$\mu_1^E = RT\ln\gamma_1 = A\left(1-X_1\right)^2 \tag{2}$$

$$\mu_2^E = RT\ln\gamma_2 = AX_1^2 \tag{3}$$

where parameter *A* is considered constant. The chemical potentials will have the expressions

$$\mu_1 = \mu_1^0(T,P) + RT\ln X_1 + A\left(1-X_1\right)^2 \tag{4}$$

$$\mu_2 = \mu_2^0(T,P) + RT\ln\left(1-X_1\right) + AX_1^2 \tag{5}$$

where μ_1^0 and μ_2^0 are the standard chemical potentials of pure components. By introducing the expressions (4) and (5) under the equilibrium conditions (1), it is obtained

$$RT\ln X_1^{L_1} + A\left(1-X_1^{L_1}\right)^2 = RT\ln X_1^{L_2} + A\left(1-X_1^{L_2}\right)^2 \tag{6}$$

$$RT\ln\left(1-X_1^{L_1}\right) + A\left(X_1^{L_1}\right)^2 = RT\ln\left(1-X_1^{L_2}\right) + A\left(X_1^{L_2}\right)^2 \tag{7}$$

In the case of symmetrical curves, $X_1^{L_2} = 1 - X_1^{L_1}$. Introducing the symmetry condition into the equation (6)

$$RT\ln X_1^{L_1} + A\left(1-X_1^{L_1}\right)^2 = RT\ln\left(1-X_1^{L_1}\right) + A\left(X_1^{L_1}\right)^2 \tag{8}$$

or $A\left[\left(1-X_1^{L_1}\right)^2 - \left(X_1^{L_1}\right)^2\right] = RT\left[\ln\left(1-X_1^{L_1}\right) - \ln X_1^{L_1}\right]$ (9)

Result: $T = \frac{A}{R}\cdot\frac{1-2X_1^{L_1}}{\ln\left[\left(1-X_1^{L_1}\right)\big/X_1^{L_1}\right]}$ or $T = \frac{A}{R}\cdot\frac{1-2X_1}{\ln\left[\left(1-X_1\right)\big/X_1\right]}$ (10)

The condition for a binary system to have a single liquid phase (to be stable) is

$\frac{\partial^2 \Delta^{am}G}{\partial X_1^2} \geq 0$ at constant *T*, *P*. The composition at which the derivative becomes equal to zero represents the stability limit and corresponds to a turning point of the curve $\Delta^{am}G(X_1)$.

At the critical point $T = T_C$, $X_1 = (X_1)_C$ and the two derivatives of the function $\Delta^{am}G(X_1)$ are canceled, respectively

$$\left(\frac{\partial\,\Delta^{am}G}{\partial X_1}\right)_C = 0 \tag{11}$$

and
$$\left(\frac{\partial^2 \Delta^{am}G}{\partial X_1^2}\right)_C = 0 \tag{12}$$

According to the definition relation, $\Delta^{am}G = \sum_{i=1}^{N} X_i(\mu_i - \mu_i^0)$. For the model of regular solutions, is obtained the relation: $\Delta^{am}G = RT(X_1 \ln X_1 + X_2 \ln X_2) + AX_1X_2$ (13)

Relations (11) and (12) lead to

$$RT \ln\left(\frac{(X_1)_C}{1-(X_1)_C}\right) + A(1-2(X_1)_C) = 0 \tag{14}$$

and respectively,
$$\frac{RT}{(X_1)_C\left(1-(X_1)_C\right)} - 2A = 0 \tag{15}$$

For the critical temperature is obtained
$$T_C = \frac{2A(X_1)_C\left(1-(X_1)_C\right)}{R} \tag{16}$$

T_C has the maximum value when $X_1 = X_2 = 0.5$. So the critical temperature can be calculated from the value of parameter A in the regular model

$$T_C = \frac{A}{2R}. \tag{17}$$

It follows that equation (10) can also be written in the form:

$$T = 2 \cdot T_C \cdot \frac{1-2X_1}{\ln\left[\left(1-X_1\right)/X_1\right]} \tag{18}$$

and represents the expression of the solubility curve (equilibrium) for the model of regular solutions. Consistency with the experimental data is only in a few cases satisfactory, therefore more complicated models have been proposed, such as the van Laar equations, NRTL, UNIQUAC, etc.

An empirical method called the linear diameter method (originally formulated by Cailletet in the late 19th century to determine the critical volume for pure liquefied substances) is applied to determine the critical point. According to this rule, the arithmetic mean of the compositions of the two phases in equilibrium is a linear function of temperature, and the intersection of the line on which these mean values are inscribed with the solubility curve corresponds to the critical dissolution temperature. The rule is better checked when the compositions are expressed in mass fractions.

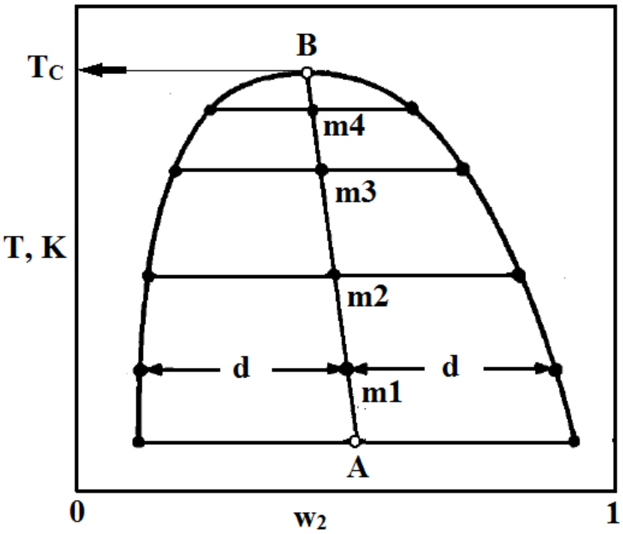


Fig. 1. Schematic presentation of the linear diameter rule.

3. EXPERIMENTAL PART

3.1. APPARATUS AND SUBSTANCES

- thermostatic water bath, test tube, stirrer, thermometer, stand, distilled water, phenol.

3.2. PROCEDURE

The experimental study of the miscibility in the water (1) - phenol (2) system is performed using an installation of the type outlined in fig. 2.

A phenol-water mixture of known composition is introduced into test tube 1 (the phenol is weighed, the water is introduced with a graduated pipette). Weigh 5 g of phenol once and gradually add water to obtain mixtures of different compositions.:

Phenol mass (m_2), g	5	5	5	5	5	5	5	5	5
Water volume (v_1), mL	2	4	6	10	14	20	25	30	35

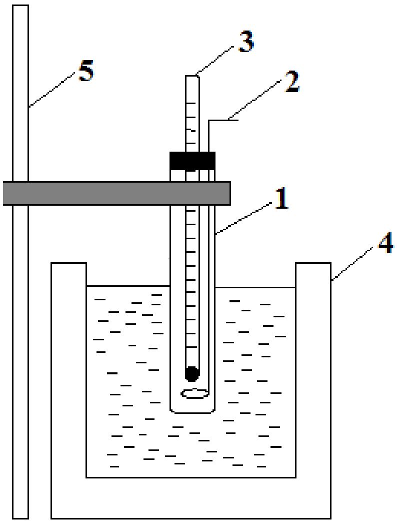


Fig. 2. Experimental installation (1 - test tube, 2 - stirrer, 3 - thermometer, 4 - thermostated water bath, 5 - stand)

Insert the test tube into the thermostated water bath. Heat slowly on the water bath. As the temperature increases, the two phases that form an emulsion pass into a single homogeneous liquid phase, at a temperature marked by the disappearance of the opalescence. Note the temperature at which the opalescence disappears (t_1). By cooling the system and observing the temperature at which the second phase occurs again (t_2), the dissolution temperature of the system is controlled. The average of the readings is taken. In the same way, the dissolution temperature for the other mixtures is determined.

4. EXPERIMENTAL DATA PROCESSING

4.1. The experimental data are entered in a table of the type:

m_2, g	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**
v_1, mL	**2**	**4**	**6**	**10**	**14**	**20**	**25**	**30**	**35**
t_1, °C									
t_2, °C									
T, K [(t_1+t_2)/2+273]									
x_2									
w_2									

4.2. Calculation of the composition of mixtures in mass and molar fractions of phenol:

$$x_2=\frac{n_2}{n_1+n_2}=\frac{\frac{m_2}{M_2}}{\frac{\rho_1\cdot v_1}{M_1}+\frac{m_2}{M_2}} \quad ; \qquad w_2=\frac{m_2}{m_1+m_2}=\frac{m_2}{\rho_1\cdot v_1+m_2};$$

4.3. The solubility curves are drawn, representing on the ordinate the absolute temperature, and on the abscissa the composition expressed as a mass fraction and, respectively, as a molar fraction.

4.4. Draw the linear diameter and estimate the critical temperature and critical composition.

4.5. Using the T_C value determined in point 4, the solubility curve corresponding to the model of regular solutions is calculated with equation (18). The data is placed in the table below:

X_1	0,01	0,1	0,2	0,3	0,4	0,499	0,6	0,7	0,8	0,9	0,99
T, K											

This theoretical curve is plotted on the same graph as the experimentally determined T-x_2 solubility curve in point 3.

Data from the literature

$M_1=M_{H_2O}=18{,}03$ g/mol ; $\rho_1=\rho_{H_2O}=0{,}9982\ g/cm^3$

$M_2=M_{fenol}=94{,}11$ g/mol ; $\rho_2=\rho_{fenol}=1{,}070\ g/cm^3$

5. QUESTIONS

Using the solubility curves constructed in point 4.3, answer the following questions:

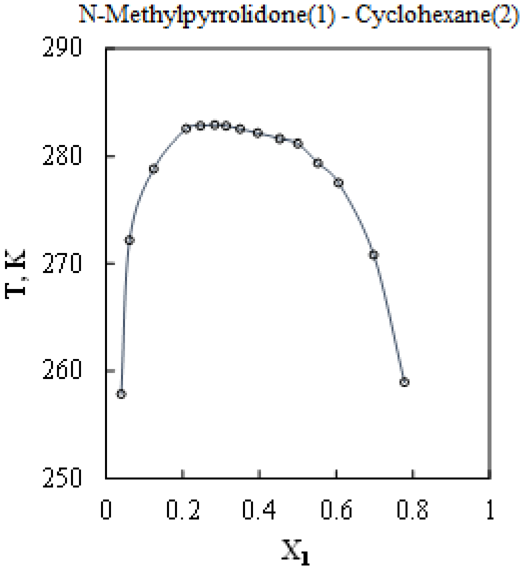
5.1. In two test tubes are phenol-water mixtures with a phenol concentration of 0.3 and 0.65 (mass fractions, respectively) at 70 °C. If the two tubes are cooled equally, in which of them is the appearance of opalescence first observed?

5.2. What are the equilibrium phase compositions and in what quantities are they found if a mixture of 5 g phenol and 5 g water is heated to 45 °C?

Appendix

Systems with higher critical temperature of dissolution at atmospheric pressure

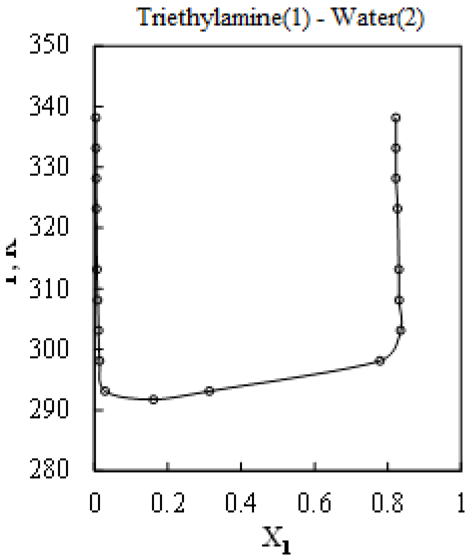
System	Upper Temperature, °C
Methanol + Tetrachlorethylene	10
Methanol + n-Pentane	14,75
Methanol + n-Hexane	33
Methanol + n-Heptane	51,5
Methanol + iso-Octane	42,5
Hexane + Nitrobenzene	19



Liquid-liquid phase diagram for the N-methylpyrrolidone - Cyclohexane system (exp. data ref. [2])

b) Systems with lower critical dissolution temperature:

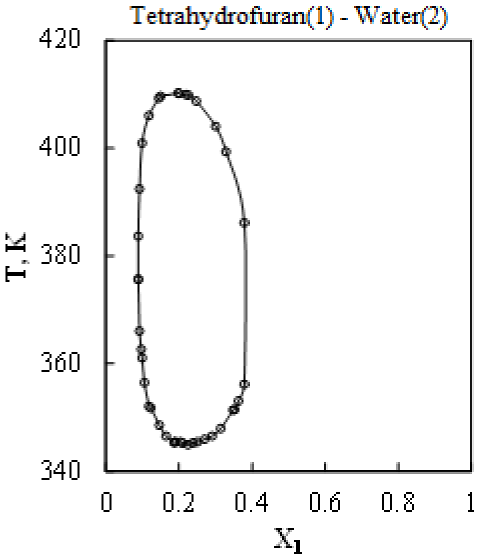
System	Lower Temperature, °C
Diethylamine + Water	143
Triethylamine + Water	18,5
CO_2 + o-Nitrophenol	23
I_2 + Methylpiperidine	48



Liquid-liquid phase diagram for the Triethylamine - Water system (exp. data ref. [3])

c) Systems with lower and upper critical dissolution temperature:

System	Lower Temperature, **°C**	Upper Temperature, **°C**
Tetrahydrofuran + Water	72	137
Nicotine + Water	60.8	208
2- Methylpiperidine + Water	79	227
3- Methylpiperidine + Water	57	235
4- Methylpiperidine + Water	86	189
Glycerin + m-Toluidine	6,7	120



Liquid-liquid phase diagram for the Tetrahydrofuran - Water system (exp. data ref. [4]).