TERNAR SYSTEM. LIQUID-LIQUID EQUILIBRIUM CURVE

1. PURPOSE OF THE WORK

Determination of the liquid-liquid equilibrium curve for the ternary water-ethyl acetate-ethyl alcohol system.

2. THEORETICAL NOTIONS

In the case of liquid systems consisting of two components at constant temperature (*T*) and pressure (*P*), the following situations are practically observed:

-the components of the system are totally miscible, the system constituting a single phase (a solution, a homogeneous system), for example the binary water-ethanol system.

- the components of the system are totally immiscible (eg Hg-water), which consists of two pure liquid phases.
- the components of the system are partially miscible (eg aniline-water), the system being composed of two liquid phases (solutions) of different compositions. Thermodynamically we talk about the liquid-liquid (L-L) equilibrium.

In ternary systems, L-L equilibrium can also be encountered, generally determined by the characteristics of the three binaries corresponding to the system consisting of three components.

The study of the equilibrium diagrams LL of the systems composed of three or more components are particularly important from a practical point of view, since numerous mixtures of organic substances, alloys, solutions of salts, molten salts, molten silicas, metallurgical slags belong to this category of systems.

A ternary system of components A, B and C is shown in a triangular diagram, as in fig. 1.

The peaks of the equilateral triangle ABC represent the pure components. Some point on one side indicates the presence of the two adjacent components in the mix and the absence of the third. Thus, the point on the BC side indicates the lack of substance A and gives the composition of the mixture in B and C. A ternary system is represented by a point inside the triangle. The composition of point P in A, B and C is given respectively by the distances Pa, Pb, Pc. Thus, all the points on the line AX, which unite the tip A with the opposite side, represent a system consisting of a constant ratio of substances B and C and variable amounts of substance A. On a parallel to one of the sides, for example YZ, all systems with constant B content and variable composition of A and C are found.

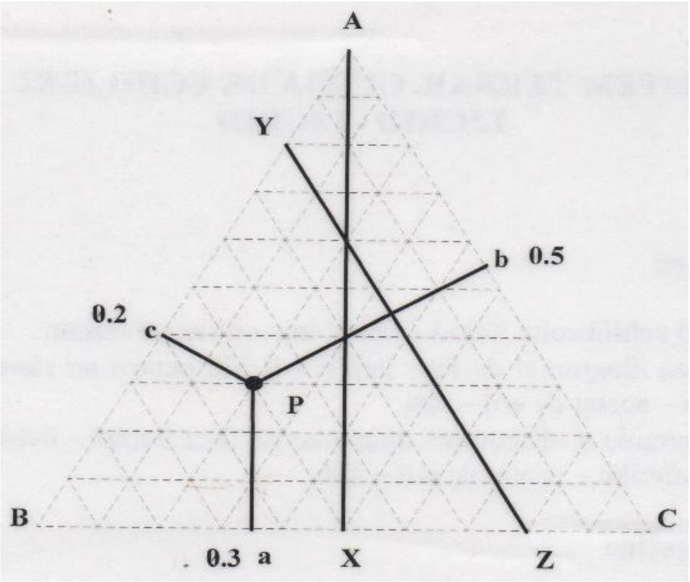

Fig. 1. Determination of the composition of a ternary mixture

Consider a ternary system in which liquid A is completely miscible with liquids B and C, the latter being only partially miscible (examples of such systems: acetic acid-chloroform-water; alcohol-ethyl acetate-water; water-benzene-alcohol). Assuming the system composed of the two partially miscible liquids B and C, at equilibrium (at constant *P* and *T*) the compositions of the two conjugated layers will be represented by points b and c.

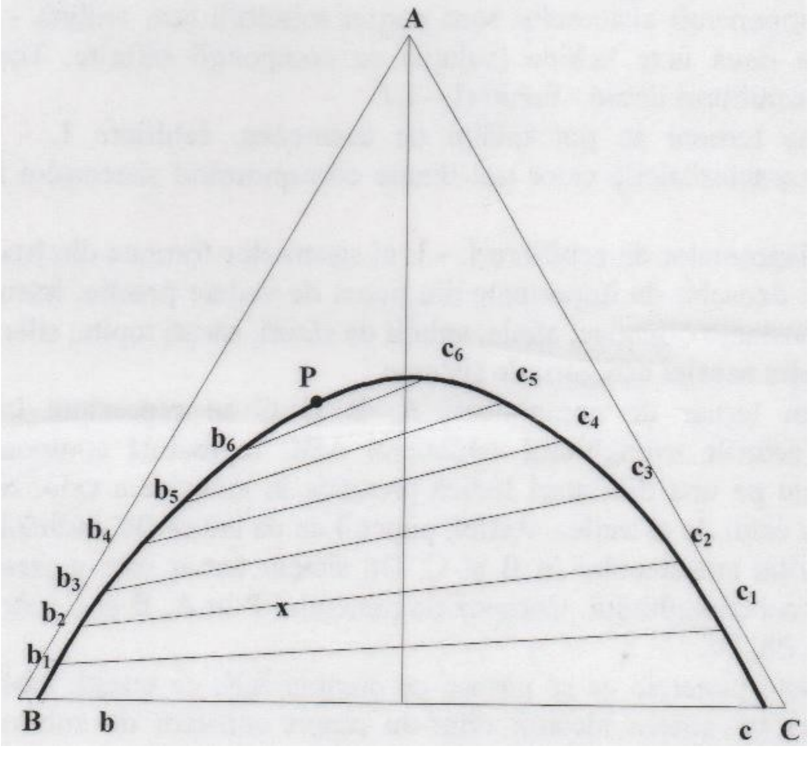

Fig. 2. The equilibrium curve of a ternary mixture

By adding to this system the substance A which is completely miscible with B and C, it will be distributed between the two layers, obtaining conjugated ternary solutions. The compositions of the two solutions will be given by points b and c inside the triangle. By gradually adding substance A to the two layers, larger amounts of this component will dissolve, while increasing the mutual solubility of the two liquids B and C. The composition of the two layers becomes more similar as A is added, and at point P the two conjugate solutions have the same composition, P being called a critical point. The bPc curve that represents the composition of the conjugate solutions is called the binodal (convex) curve. The maximum point of this curve M would coincide with P if component A were evenly distributed between the two layers. Above the bPc curve, the system consists of a single liquid phase and to define it (temperature and pressure being constant) the concentrations of two components must be indicated. Under the bPc curve, the system consists of two liquid phases in equilibrium and at constant temperature and pressure, has only one degree of freedom, so it is sufficient to indicate a concentration term to completely define the system. A mixture of overall composition X will be made up, according to the diagram, of two liquid phases of composition b_2 and c_2. The quantities in the two phases are given, according to the lever rule, by the ratio X_{c2} / X_{b2}.

The liquid-liquid equilibrium in the ethyl alcohol-ethyl acetate-water system, as well as any phase equilibrium in a multicomponent system, is described by a mathematical model comprising the stationary conditions of the total thermodynamic potential of the system (the necessary equilibrium conditions). and the normalization conditions for the molar fractions of the components in the two phases. Thus, noting with the exponents ' and '' the two phases in equilibrium and with indices 1, 2 and 3, respectively water, ethyl alcohol and ethyl acetate, we have the following system of equations:

- Equilibrium conditions in relation to mass transfer:

$$\begin{aligned}
&\mu_1'(T',P',x_1',x_2',x_3') = \mu_1''(T'',P'',x_1'',x_2'',x_3'')\\
&\mu_2'(T',P',x_1',x_2',x_3') = \mu_2''(T'',P'',x_1'',x_2'',x_3'') \qquad (1a)\\
&\mu_3'(T',P',x_1',x_2',x_3') = \mu_3''(T'',P'',x_1'',x_2'',x_3'')
\end{aligned}$$

- Thermal equilibrium condition:

$$T' = T'' \qquad (1b)$$

- Condition of mechanical equilibrium:

$$P' = P'' \qquad (1c)$$

- Conditions to normalize for molar fractions:

$$\begin{aligned} x_1' + x_2' + x_3' &= 1 \\ x_1'' + x_2'' + x_3'' &= 1 \end{aligned} \qquad (1d)$$

By introducing equations (1b) and (1c) into the system (1a) and considering the equations (1d), it finally results:

$$\begin{aligned} \mu_1'(T', P', x_1', x_2') &= \mu_1''(T'', P'', x_1'', x_2'') \\ \mu_2'(T', P', x_1', x_2') &= \mu_2''(T'', P'', x_1'', x_2'') \\ \mu_3'(T', P', x_1', x_2') &= \mu_3''(T'', P'', x_1'', x_2'') \end{aligned} \qquad (2)$$

System (2) is a system of three equations with four unknowns: the molar fractions of water and ethanol (components 1 and 2 respectively) in each phase. By eliminating, for example, x_1'' and x_2'' between the three equations that make up the system, we obtain the equation of a curve in coordinates (x_1', x_2'), which represents exactly the equilibrium curve described above. On the other hand, however, by setting a value for one of the molar fractions, for example x_1', the system (2) has a unique solution in x_2', x_1'' and x_2''. Thus, pairs of series $\{(x_1', x_2'), (x_1'', x_2'')\}$, are obtained, each series uniquely describing the equilibrium state of a mixture of ethyl acetate, water and ethanol, located in the two-phase domain of the diagram. Each of these pairs represents a point on the equilibrium curve, so that it is structured into two branches, each being associated with one of the equilibrium phases.

Determination of the solubility curve ethyl alcohol-ethyl acetate-water

If a system consisting of two immiscible substances, water and ethyl acetate, is added a third, (ethyl alcohol), soluble in each of them, they can become mutually soluble. The amount of ethyl alcohol added to the ethyl acetate-water mixture to obtain a homogeneous system (one phase) is determined by the L-L equilibrium curve. With the help of the triangular diagram, one can determine the compositions (at constant temperature and pressure) in which the three substances constitute a system consisting of two phases or a homogeneous system (one phase).

3. EXPERIMENTAL PART

3.1. APPARATUS AND SUBSTANCES

- 3 x 25 mL burettes, 2 x 50 mL dry Erlenmayer vessel, distilled water, ethyl acetate and ethyl alcohol.

3.2. PROCEDURE

a) With a burette, 10 mL of ethyl acetate is introduced into a **dry** Erlenmayer flask, then add 0.5 ml of distilled water from another burette and allow ethanol to drop until a clear solution is obtained after stirring, saturated in the two components. Read the volume of ethanol added. To the liquid thus obtained add more 0.5 mL of distilled water, shake and re-drop ethanol until the appearance becomes homogeneous. Read the number of mL of ethanol added. Add 1 mL of distilled water (6 times) and repeat, then add 2 mL of distilled water successively (until a mixture of 15 mL of distilled water and 10 mL of ethyl acetate is reached; each time add ethanol until the mixture is homogenized, each time noting the volume of ethyl alcohol added). Put leftover solution from flask in waste vessel, then wash the flask and use it for b).

b) 10 ml of distilled water is introduced with a burette into an Erlenmayer flask and ethyl acetate is added **dropwise** until a non-homogeneous system (two-phase existence) is obtained and the number of mL of ethyl acetate added is read.

c) Put 10 mL of ethyl acetate into a **dry** Erlenmayer flask with a burette and add water **dropwise** until a non-homogeneous system (two-phase existence) is obtained and read the number of mL of water added.

4. EXPERIMENTAL DATA PROCESSING

4.1. The experimental data are passed in a form table:

No. crt	**$V_{acetate}$, (mL)**	**V_{water}, (mL)**	**$V_{ethanol}$, (mL)**	**Acetate (% mol)**	**Water (% mol)**	**Ethanol (% mol)**
1.	**10**	**0,5**				
2.	**10**	**1,0**				
3.	**10**	**2**				
4.	**10**	**3**				
5.	**10**	**4**				
6.	**10**	**5**				
7.	**10**	**6**				
8.	**10**	**7**				
9.	**10**	**9**				
10.	**10**	**11**				
11.	**10**	**13**				
12.	**10**	**15**				
13.		**10**	**0**			
14.	**10**		**0**			

4.2. Considering the volumes being additive (the volumes are measured for the pure substances before mixing), the composition of the three components, expressed in molar percentages, is calculated for each case.

$$(\%mol)_i = x_i \cdot 100\,; \qquad x_i = \frac{n_i}{\sum\limits_i n_i} = \frac{\dfrac{m_i}{M_i}}{\sum\limits_i \dfrac{m_i}{M_i}} = \frac{\dfrac{\rho_i \cdot V_i}{M_i}}{\sum\limits_i \dfrac{\rho_i \cdot V_i}{M_i}}\,;$$

4.3. The liquid-liquid equilibrium curve through the experimentally determined points is shown on a triangular diagram.

Data from the literature

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

$M_{CH_3COC_2H_5} = 88{,}11\ \text{g/mol}$; $\rho_{CH_3COC_2H_5} = 0{,}8970\ \text{g/cm}^3$

$M_{C_2H_5OH} = 46{,}07\ \text{g/mol}$; $\rho_{C_2H_5OH} = 0{,}7890\ \text{g/cm}^3$