The special points in the curves of the phase equilibrium for the system 39.5% (weight) H_2O - 27.89% n-C_6H_{14} - 32.61% n-C_3H_7OH

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ABSTRACT

The investigations of the isochoric heat capacity of the 39.5% (weight) -H_2O - 27.89% n-C_6H_{14} - 32.61% n-C_3H_7OH ternary system were made at the constant composition in the range of temperatures 314-590 K and specific volumes (2.222-5.224)$\cdot 10^{-3}$ m^3/kg with the adiabatic calorimeter. The curves of the phase equilibrium liquid-liquid and liquid-gas were defined from jumps of the isochoric heat capacity. The forms of coexistence curves of phases allow to allocate some special points. In the interval of densities 406.5-191.3 kg/m^3 both lines of phase equilibrium have the form of parabolas. Therefore the special points are points of a maximum, which give the possibility to evaluate the form of the left-hand and right boundary curves.

The following special points are the point of intersection of curves phase equilibria liquid - liquid and liquid - gas, where occurs the duplication of the isochoric heat capacity jump on a isochore and the point at ρ=406.5 kg / m^3 and T=496.15 K, in which we observe the sharp change of the components solubility character.

Keywords: adiabatic calorimeter, heat capacity, mixture, curve of phase equilibrium.

INTRODUCTION

In the previous works [1-3] we carried out the researches of $C_{v,x1,x2}$, P, V,T -properties (x1- the concentration of water and x2- the concentration of n-hexane) of the water - n-hexane binary system. In this work we present the results of experimental measurements of the isochoric heat capacity and P-V-T properties of the water - n-hexane - n-propanol ternary system of a constant composition in the interval of specific volumes $2.222 \cdot 10^{-3}$ m^3/kg - $5.224 \cdot 10^{-3}$ m^3/kg , temperatures 314-590 K, and pressures up to 15 MPa. As a matter of fact, owing to good solubility of n-propanol in n-hexane and water [4,5] a binary system was investigated. The experiment covers the area of a three-phase, two-phase and homogeneous states and transitions from one state to other were precisely fixed. The analysis of curves of the liquid - liquid and liquid - gas phase equilibria for the mixture of 39.5 % (weight) H_2O - 27.89 % n-C_6H_{14} - 32.61 % C_3H_7OH has allowed to allocate some special points on these curves.

EXPERIMENTAL

The experimental researches of the isochoric heat capacity and P, V, T -properties were carried out on the same adiabatic calorimeter, where the measurements of $C_{v,x}$, P, V, T - properties of the water - n-hexane system were made with the same error [3]. The scheme of the adiabatic calorimeter and devices for measure of pressure are presented in the work [3]. For research a double distilled water was used and n-hexane and n-propanol were of 99.87% purity. The calorimeter was filled by the studied mixture under vacuum.

The weighting of components was executed on analytical scales WLT-1 with an error of 0.01%. For each isochore new filling was made.The error in definition of a composition for each isochore was not more than 0.2 % (weight). The filling of the calorimeter by components of a researched mixture was executed in a following sequence: in the beginning n-hexane has been filled, then n-propanol and water.

The investigation of the isochoric heat capacity is carried out for values of specific volume v=const (in units 10^{-3} m^3/kg):

2.222 (composition of 39.45 % H_2O - 28.05 % n-C_6H_{14} - 32.50 % C_3H_7OH);

2.454 (composition of 39.39 % H_2O - 28.05 % n-C_6H_{14} - 32.56 % C_3H_7OH);

2.483 (composition of 39.42 % H_2O - 28.04 % n-C_6H_{14} - 32.54 % C_3H_7OH);

3.253 (composition of 39.52 % H_2O - 27.85 % n-C_6H_{14} - 32.63 % C_3H_7OH);

3.827 (composition of 39.50 % H_2O - 27.89 % n-C_6H_{14} - 32.61 % C_3H_7OH);

5.224 (composition of 39.40 % H_2O - 28.05 % n-C_6H_{14} - 32.55 % C_3H_7OH);

Along isochores v (in units 10^3 m^3/kg):

2.700 (composition of 39.55 % H_2O - 27.79 % n-C_6H_{14} - 32.66 % C_3H_7OH);

2.910 (composition of 39.51 % H_2O - 27.86 % n-C_6H_{14} - 32.63 % C_3H_7OH);

3.500 (composition of 39.54 % H_2O - 27.87 % n-C_6H_{14} - 32.59 % C_3H_7OH);

3.636 (composition of 39.45 % H_2O - 27.87 % n-C_6H_{14} - 32.68 % C_3H_7OH);

3.937 (composition of 39.51 % H_2O - 27.85 % n-C_6H_{14} - 32.64 % C_3H_7OH);

4.210 (composition of 39.47 % H_2O - 27.95 % n-C_6H_{14} - 32.58 % C_3H_7OH);

4.348 (composition of 39.56 % H_2O - 27.80 % n-C_6H_{14} - 32.64 % C_3H_7OH);

4.706 (composition of 39.49 % H_2O - 27.93 % n-C_6H_{14} - 32.58 % C_3H_7OH),

5.000 (composition of 39.50 % H_2O - 27.88 % n-C_6H_{14} - 32.62 % C_3H_7OH);

the experiment is carried out near the points of transition through curves of the phase equilibrium, and the temperature of transition was determined with the help of a method of thermogram [6]. The isochoric heat capacity measurements were made after preliminary rise of the temperature up to the area of a homogeneous phase (up to temperatures, exceeding the temperature of transition through the curve of the liquid - gas phase equilibrium).

RESULTS

Researches have shown, that, as follows from figs.1-2, the heat capacity at the constant volume depending on temperature for the ternary system does not essentially differ from the same dependences of the water - n-hexane mixture [3].

Two jumps of the heat capacity take place, two, but their geometrical place on the phase diagram

capacity $C_{v,x1,x2}$ on the isochore we identified with the liquid - liquid phase transition at the presence of a gas phase, the second jump - with the liquid - gas transition (except isochores with $v < 2.224 \cdot 10^{-3}$ m^3/kg). We can make such assumption because of the small size of the first jump of the heat capacity $C_{v,x1,x2} \approx 0.6$ kJ / (kg·K) for all investigated isochores (except $v=2.222 \cdot 10^{-3}$ m^3/kg), its weak dependence on density (and temperature), and the unusual dependence of a line of phase transition on the specific volume (see fig. 3). The temperatures of transition through the liquid - liquid (T_{s1}) and liquid - gas (T_{s2}) curves of the phase equilibria are presented in table 1.

Both of curves of the phase equilibrium in the interval of densities 191.4 - 449.6 kg/m^3 have a kind of parabolas.

We could not find critical parameters for an investigated system from literary sources. But it is possible to evaluate the form of curves of the liquid - liquid and liquid - gas phase equilibrium considering the points of a maximum.

For the approximation of tabulated values the following expression was used. [7]

$$\Delta\rho = (\rho - \rho_m)/\rho_m = \pm B \left| \tau \right|^{\beta} \qquad (1)$$

where $\tau=(T-T_m)/T_m$, ρ_m and T_m are the density and the temperature in a point of a maximum; β and B are the index and amplitude. To omit the subsequent terms in a right part of (1), offered in [8], the values of β and B were calculated in the area of $\tau=10^{-3} \div 10^{-4}$ for the liquid - gas coexistence curve and $\tau=3 \cdot 10^{-2} \div 10^{-3}$ for the liquid - liquid curve.

Results show that, for the liquid - gas curve

$$\Delta\rho = \pm 1.280 \left| \tau \right|^{0.343 \pm 0.010}, \qquad (2)$$

and this, in general, corresponds to values of β and B characteristic for the liquid - gas critical point [6]. In the case of the liquid - liquid phase transition $B \pm 1.085$ and $\beta=0.439.7 \pm 0.015$.

The data processing of the isochoric heat capacity $C_{v,x1,x2}$ depending on temperature at $v=3.827 \cdot 10^{-3}$ m^3/kg shows, that close to T_m on the side of the two-phase area a renormalization of the

The next special point is a point of intersection of the liquid - liquid and liquid - gas phase equilibria curves. The character of phase changes on various isochores are demonstrated in fig.4. In the three-phase area the existence of liquid phases of n-propanol solutions in a water and in n-hexane and of the gas phase, consisting of vapour of all three components, takes place. With the rise of the temperature for specific volumes $v < 2.224 \cdot 10^{-3}$ m^3/kg in the beginning the liquid - gas phase transition occurs, and then the liquid - liquid phase transition follows. For isochores $v > 2.224 \cdot 10^{-3}$ m^3/kg , on the contrary, in the beginning the liquid - liquid phase transition occurs at the presence of a gas phase, and then the liquid - gas phase transition follows. Researches of the isochoric heat capacity on the isochore $v = 2.224 \cdot 10^{-3}$ m^3/kg , where the intersection of curves of phase equilibrium occurs, were not managed to carry out by us, but on isochore close to $v = 2.222 \cdot 10^{-3}$ m^3/kg , the dependence $C_{v,x1,x2}$ on temperature is presented in fig. 1.

The experiment permits to make the conclusion, that on isochore $v= 2.224 \cdot 10^{-3}$ m^3/kg will take place the merge of both jumps of the heat capacity. The system will behave as one-component substance, and the point A represents, probably, a point of azeotrope (see Fig.3.)

In the point B the sharp break of the line of the liquid - liquid phase equilibrium occurs. In this point the significant change of the character of the solubility of components of the water - n-hexane - n-propanol system takes place. The linear site of this curve at $\rho > 406.5$ kg/m^3 abruptly displaces to the side of high pressures and temperatures.

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Table 1. The temperatures of the liquid-liquid (T_{s1}) and liquid-gas (T_{s2}) phase transition for the system 39.5% (weight) H_2O - 27.89% n-C_6H_{14} - 32.61% n-C_3H_7OH.

v, 10^{-3} m^3/kg	T_{s1}, K	T_{s2}, K	v, 10^{-3} m^3/kg	T_{s1}, K	T_{s2}, K
2.222	561.25	552.62	3.827	500.38	569.71
2.234	510.18	555.32	3.937	500.38	569.71
2.454	469.23	-	4.210	498.55	569.60
2.483	472.93	559.85	4.348	497.15	569.40
2.700	478.02	562.95	4.706	492.55	568.95
2.910	484.55	565.50	5.000	488.05	568.55
3.253	493.54	568.02	5.224	483.97	567.66
3.500	498.15	569.25			
3.636	499.45	569.55			

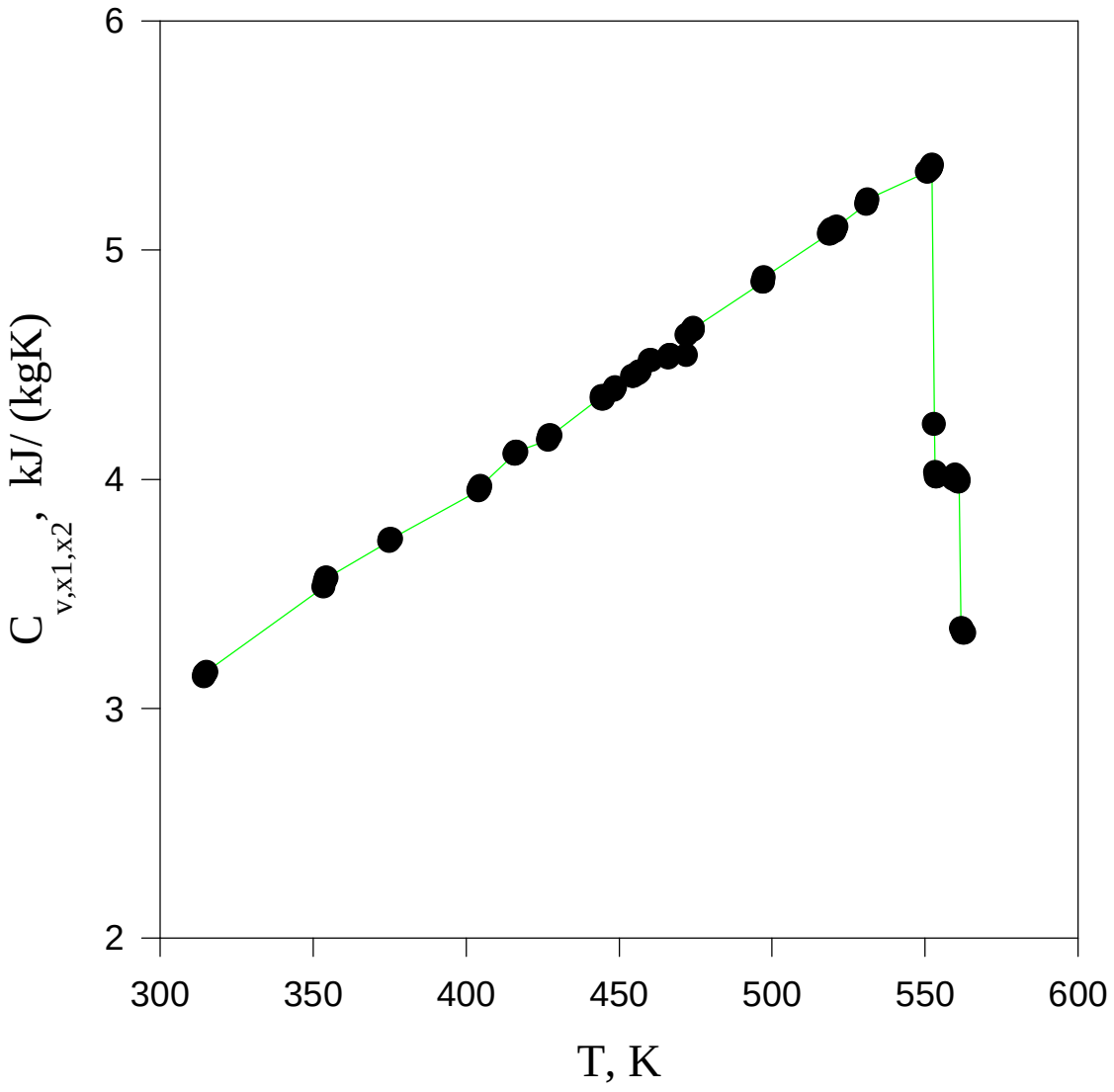

Fig.1. The dependence of the isochoric heat capacity on the temperature for the system

39.45 % H_2O - 28.05 % n-C_6H_{14} - 32.50 % C_3H_7OH at v=2.222 $\cdot 10^{-3}$ m^3/kg

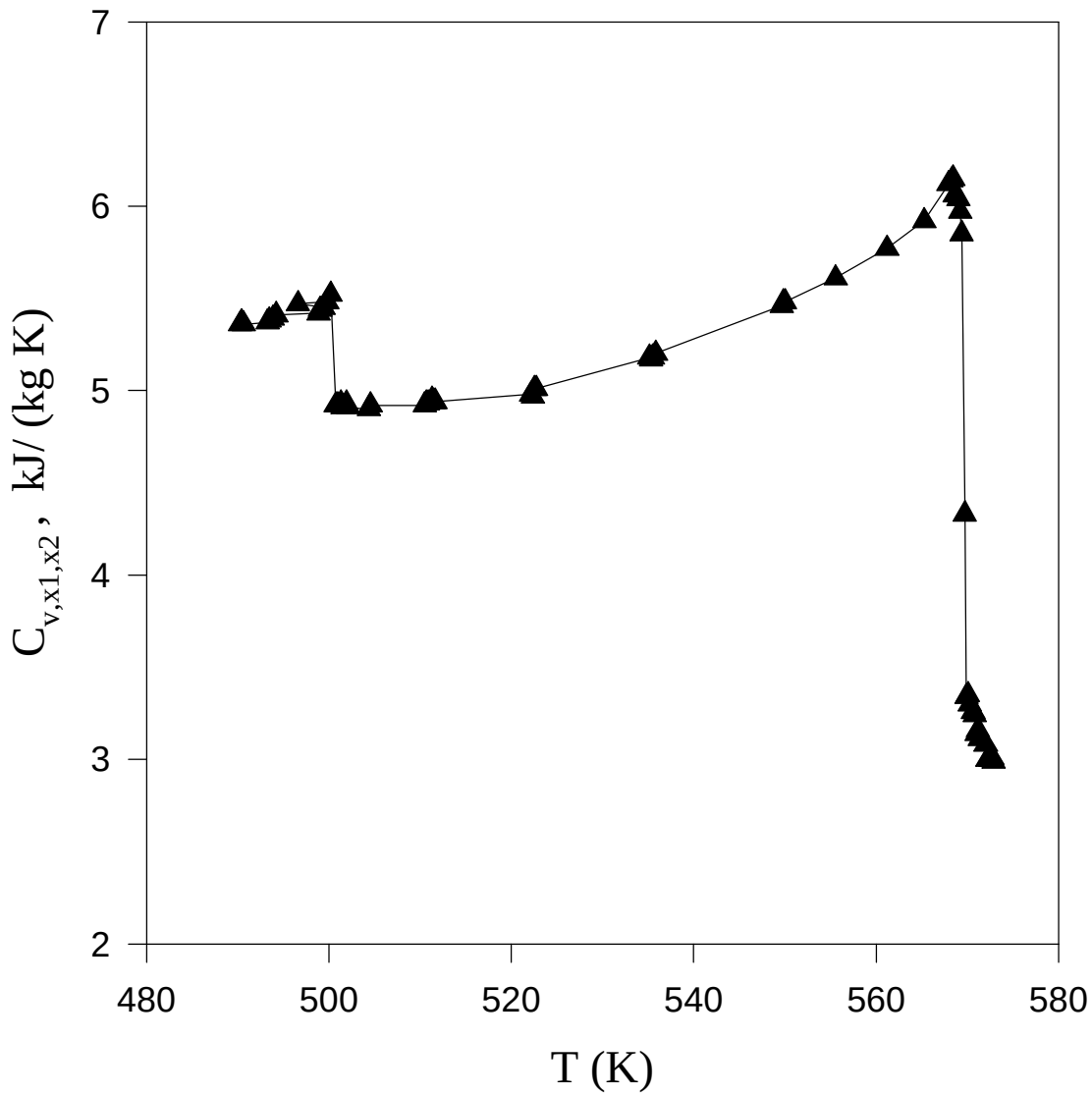

Fig.2. The dependence of the isochoric heat capacity on the temperature for the system

39.50 % H_2O - 27.89 % n-C_6H_{14} - 32.61 % C_3H_7OH at v=3.827 $\cdot 10^{-3}$ m^3/kg

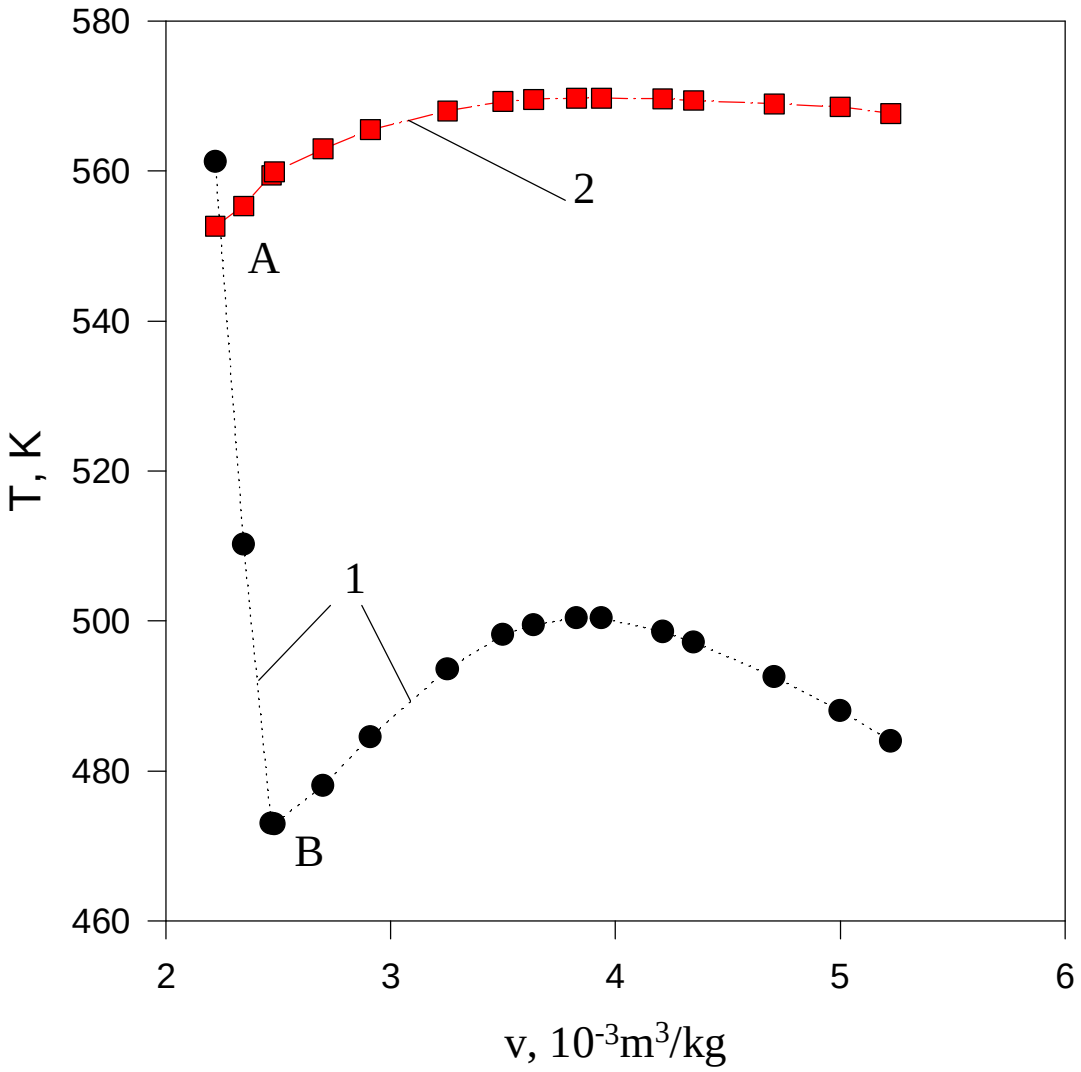

Fig.3. The curves of the liquid-liquid (1) and liquid-gas (2) phase equilibrium for the system 39.50 % (weight) H_2O - 27.89 % n-C_6H_{14} - 32.61 % C_3H_7OH

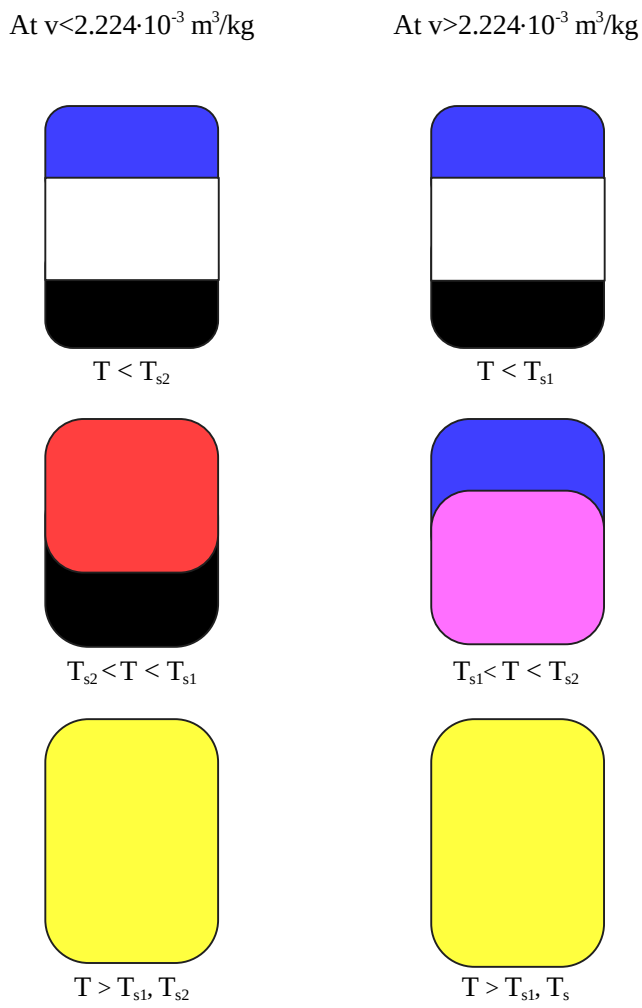

Fig.4. The scheme of the phase changes.

- the gaseous phase
- the solution of the n-propanol in the n-hexane
- the solution of the n-propanol in the water
- the n-propanol + n-hexane liquid mixture
- the liquid mixture of the n-hexane + n-propanol + water
- the gomogeneous phase.