

# SOLUBILITY OF METHYLIC STEARATE IN SUPERCRITICAL CARBON DIOXIDE.

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## Abstract

Within the framework of study of a possibility and expediency of usage of supercritical fluid extragents for the purposes of separation of the reaction mixture received at transesterification of triglycerides of fatty acids (deriving of solar oil), research of solubility of methylic stearate in supercritical carbon dioxide on isotherms 318,15 K and 338,15 K with the pressures range from 10,0 up to 350,0 MPA was carried out.

Measurements of solubility are carried out on a pilot unit represented in a figure 1, implementing the static schema.

The given pilot unit will consist of a system of building and tonometry, the count system and temperature control, an extractor, a knot of a rocking and an analytical part.

The system of building and tonometry will consist of a balloon with CO<sub>2</sub> (1), a thermocompressor (2), a cooler (4), an electric heater (11), and model manometers (20) and (21).

Pressure in the autoclave (3) is framed by a thermocompressor (2) due to isochoric heat of gas. For this purpose the thermocompressor (2) is located in thermostatic tank (4) which is completed by antifreeze. There the working part of a refrigerating unit (9) and an electric heater (11) which ensure refrigerating and heat of a thermocompressor (2) is submersed. For intensification of the given processes in thermostatic tank (4) the agitator (12) is located.

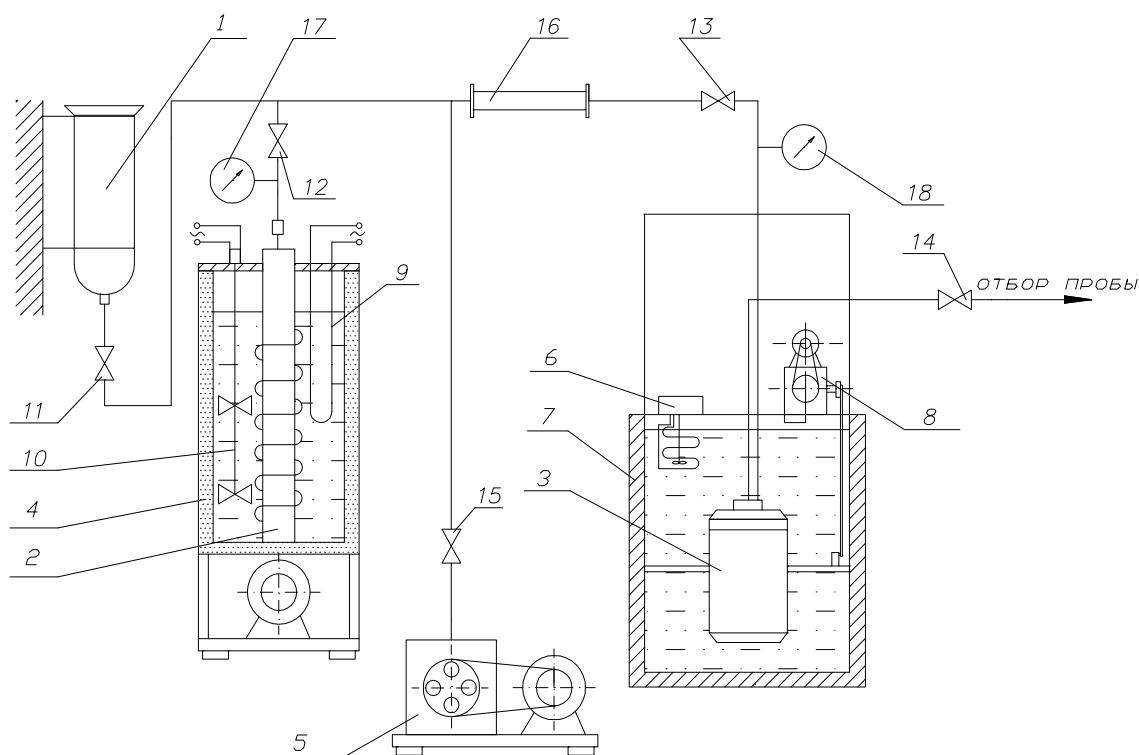
In the beginning, the system is vacuumized by a vacuum pump (5) up to pressure 1,33 Pa at which reaching valves (15) are occluded, (16) and (17). Further the valve (13) for filling by fluid phase CO<sub>2</sub>, from a balloon (1), beforehand refrigerated up to temperature 238 To, a thermocompressor (2) is unclosed. After filling a thermocompressor (2) fluid dioxide of Carboneum, the valve (13) is occluded and included an electric heater (11). At heating a thermocompressor (2) pressure of gas valves (14) and (15) increase, unclosed. Gas moves in the autoclave (3). At reaching necessary value of pressure in the autoclave (3), valves (14) and (15) are occluded. Producing pressure in the autoclave (3) model manometer (21) classes of an exactitude 0,15 is measured. If pressure in the autoclave (3) appears less than necessary value in a system of building of pressure the new ration of gas from a balloon (1) is started, and compression is retried.

The regulating system and measurements of temperature will consist of a housing of the thermostat (7) charged on 4/5 volumes with water, and the block of a thermostat (6) UTU-4.

The temperature in the autoclave (3), is sustained with the help of thermostatic fluid and the block of a thermostat (6), by dipping the autoclave (3) in thermostatic fluid. Fluid for thermostatic control chooses water as requirements of experience do not demand heating an extractor above 100<sup>0</sup> C. Deviation of maintenance of an operating temperature is in limens ±0,05 K. The bias of temperature estimates in limens ±0,05 K.

For deriving a saturated solution and reaching of equilibrium in an autoclave, at the given pressure and temperature of experience, it is necessary to carry out intensive agitating of both

phases. Agitating is effected by a rocking of the autoclave by means of the rolling device (10). After that, assay is taken from the autoclave (1) (fig. 2) in the analytical part (2) representing a thin-walled rubber flask. Weight of an analytical part ( $\approx 1$  g) is defined beforehand on analytical balance of ADV 200. That at a sampling unmixing has taken place in an analytical part, instead of earlier in communications, the sampler (3) has the throttling device located on a yield of assay in an analytical part (2). The analytical part is in water 318,15 K. Water heated to temperature is filled in a thermostat (4) up to the inferior ridge of hole (5). Heat and thermostatic control of water is effected with the help of the block of a thermostat (6). Smoothing of temperature of water in a thermostat (4) is effected by the electrically-actuated blender {stirrer} (7). Error of maintenance of temperature of water is in limens  $\pm 0,05$  K. The bias of temperature estimates in limens  $\pm 0,05$  K. The volume of taken assay corresponds {meets} to volume (9) waters superseded in a volumetric flask.



**Figure 1.** A static pilot unit.

For examinations utilised methylic stearate by cleanliness of 97,0 %, and dioxide of Carboneum of the mark {grade} "Alimentary".

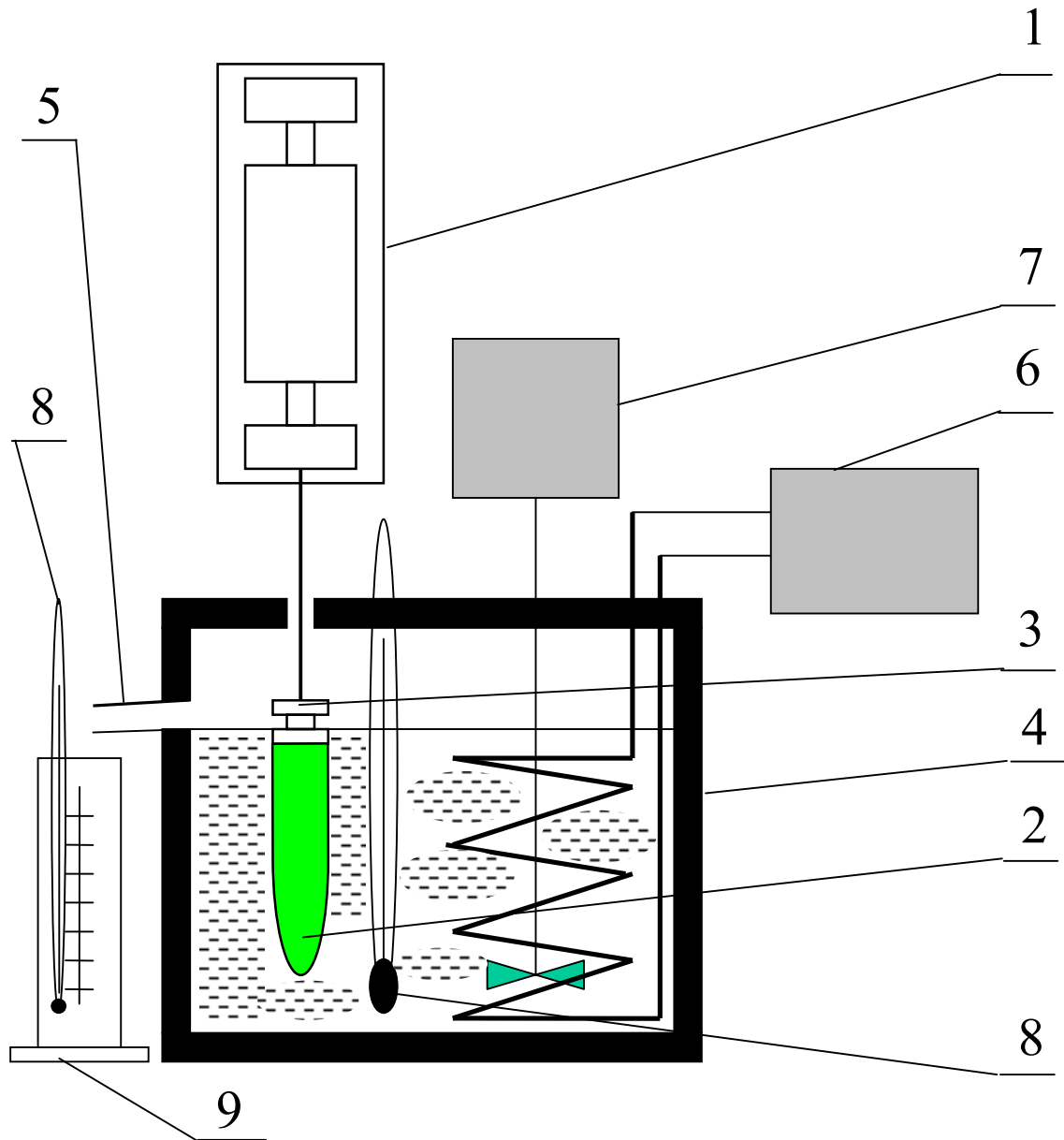


Figure 2. The schema {circuit} of the device samplings.

The exposition of observed datas is carried out with usage of the equation of Peng- Robinson:

$$P = \frac{RT}{v - b} - \frac{a\alpha}{v^2 + 2bv - b^2} \quad (1)$$

Where a and b - parameters of the equation of Peng-Robinsona, defined as follows:

$$a = \sum_i \sum_j y_i y_j a_{ij} \left( \frac{b}{b_{ij}} \right)^{m_{ij}},$$

$$b = \sum_i y_i b_i$$

Here  $y_i$  and  $y_j$  - molecular ratios accordingly i-th and j-th formulation constituents in any of equilibrium phases, and  $m_{ij}$  quotient of binary interaction. Parameters of the equation of Peng-Robinson for clear builders are a combination of bottlenecks:

$$a_i = 0.45724 R_2 T_c^2 a_i(T) / P_c$$

$$b_i = 0.0778 R T_c / P_c$$

$$\alpha(T) = [1 + (0.37464 + 1.54226 \omega_i - 0.26992 \omega_i^2) (1 - \sqrt{T/T_c})]^2,$$

Here  $T_c$ ,  $P_c$  and  $\omega_i$  - critical temperature, pressure and the factor of an acentric factor of i-th component. Thus, the parameter a can be calculated by a method of a thermodynamic similarity as the factor of an acentric factor  $\omega$  is parameter of a similarity. The quotient of binary interaction is defined at the fixed temperature by minimization of function of errors:

$$F = \sum_{i=1}^N \sqrt{\frac{(y^{расч} - y^{эксн})_i^2}{N}} \quad (2)$$

The terminating formula for calculation of a miscibility looks as follows:

$$\ln(y) = \ln(P_0/P) - \ln(\Phi_2) + P \mu v / RT \quad (3)$$

Where y - a miscibility of material {matter} in molecular ratios,  $p_0$  - a saturation pressure of solved material {matter} at the given temperature of a system, P - pressure in a system,  $\mu v$  - volume of 1 mole of clear solved material, R - generalpurpose gas constant.

Critical parameters of methylic stearate have been calculated on a method of the Dohrn [1]. This method allows to calculate  $T_c$ ,  $P_c$  and  $w$  using liquid molar volume  $v_{L20}$  and boiling temperature  $T_b$  as input information. For many two-parameter EOS, the pure-component parameters  $a_c$  and  $b_c$  for the critical temperature can be determined from the conditions at the critical point:

$$a_c / \Omega_a = R^2 T_c^2 / P_c, \quad (4)$$

$$b_c / \Omega_b = R T_c / P_c, \quad (5)$$

where  $\Omega_a$  and  $\Omega_b$  are EOS specific constants, e. g. for the Peng-Robinson EOS  $\Omega_a = 0.45724$  and  $\Omega_b = 0.0778$ . Dohm proposed to calculate  $a_c$  and  $b_c$  from the liquid molar volume  $v_{L20}$  and  $T_b$  as follows:

$$b_c / \Omega_b = b^{(1)} v_{L20} T_b + b^{(2)} \quad (6)$$

$$a_c / \Omega_a = a^{(1)} (b_c T_b / \Omega_b)^{a^{(2)}} \quad (7)$$

were  $b^{(1)}=0.02556188 \text{ K}^{-1}$ ,  $b^{(2)}=0.168721 \text{ m}^3\text{kmol}^{-1}$   $a^{(1)}=21.26924 \text{ kJkmol}^{-1}\text{K}^{-1}$   $a^{(2)}0.913049$  have been determined by correlating the data of 380 fluids. When  $a_c$  and  $b_c$  are known,  $T_c$  and  $P_c$  can be determined:

$$T_c = \frac{a_c \Omega_b}{\Omega_a b_c R} \quad (6)$$

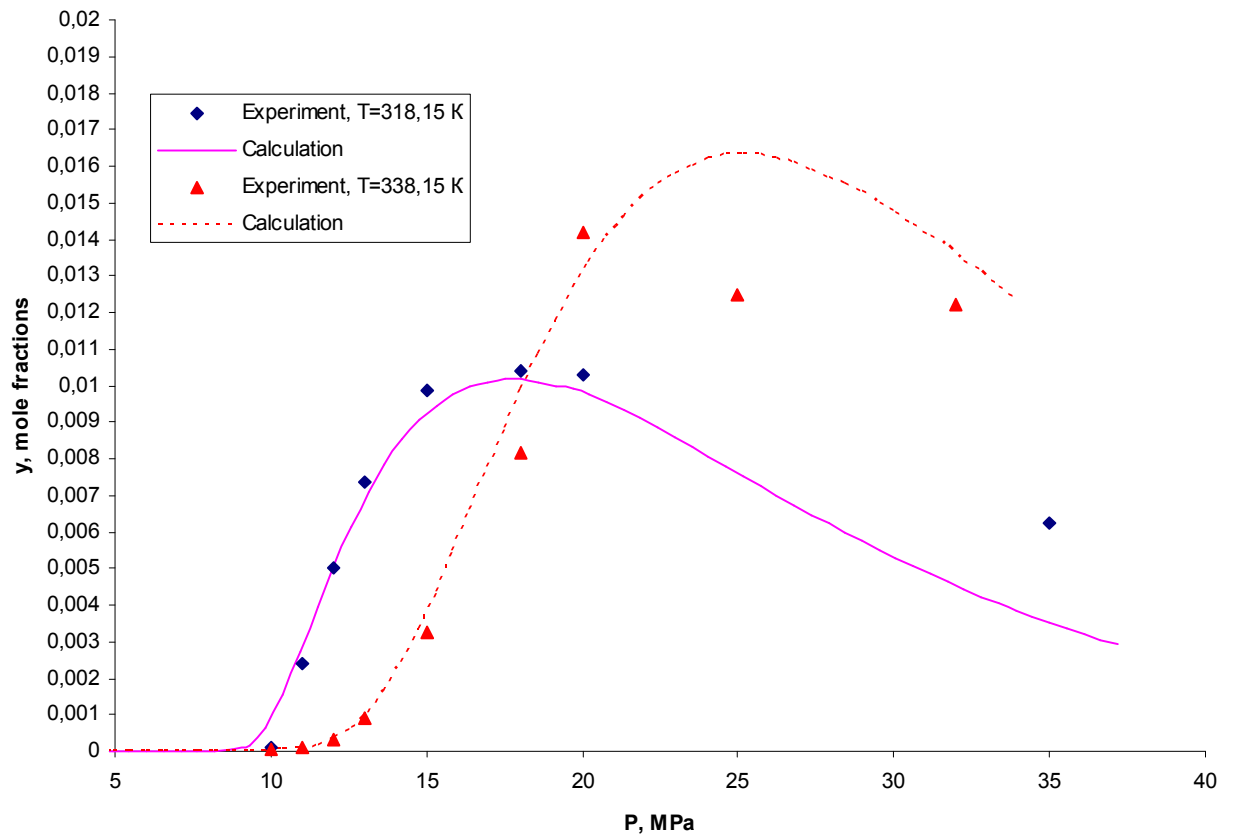
$$P_c = \frac{a_c}{\Omega_a} \left( \frac{\Omega_b}{b_c} \right)^2 \quad (7)$$

Correlation for the acentric factor is following:

$$w = -\frac{3 \lg(101.3kPa / P_c)}{7 (T_c / T_b - 1)} - 1 \quad (8)$$

Parameters are  $T_c=877,37 \text{ To}$ ,  $P_c=1,11 \text{ MPA}$ .

Observed datas and their exposition are given in figure 2.



**Figure 3** Miscibility of methylic stearate In supercritical dioxide of Carbonium.

Quotients of binary interacting presented in the table.

**Table 1.**

Parameter	Temperature, K	
	318,15	338,15
$m_{ij}$	0,796	0,750

**REFERENCES:**

1. R. Dohrn, G. Brunner An estimation method to calculate  $T_b$ ,  $T_c$  and  $w$  from the liquid molar volume and the vapour pressure. p. 241
2. M. Mukhopadhyay, G. V. Raghuram Rao Thermodynamic Modeling for Supercritical Fluid Process Design // Ind. Eng. Chem. Res. 1993, 32, p.922-930
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