

## THE PARTICULARITIES OF BINARY MIXTURE COMPONENT MOVEMENT NEAR THE EXFOLIATION CRITICAL POINT

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Previously the process of equilibrium establishment in inhomogeneous individual substances and binary mixtures near the liquids critical point was studied. The temperature dependence of equilibrium establishment time in such systems was founded to be nonmonotonical in presence of gravitational field. In the context of fluctuation theory of phase transitions the connection between this time and the velocity of centre mass movement for inhomogeneous substance was revealed. In this report centre mass movement of binary mixture methanol-hexane near the exfoliation critical point in gravitational field was experimentally studied. The component movement velocity dependences on temperature was researched and some particularities of such process was analyzed. Viscosity of mixture was estimated and analyzed as well.

The aim of this work is experimental studying of binary mixture methanol-hexane component velocities of mass transfer near the exfoliation critical temperature (mass concentration of methanol in given mixture was critical:  $x \approx 0.33$ ). This velocity of mass transfer was calculated by formula:

$$v = \Delta z_{0n} \theta_E^{-1}, \quad (1)$$

where  $\Delta z_{0n} = z_0 - z_n$ , ( $n=1,2$ ) - is the value of displacement of components centre mass vertical coordinate: methanol ( $n=1$ ) and hexane ( $n=2$ ), as system goes to the equilibrium state. These coordinates were evaluated by formula:  $z_n = \int_0^L \rho_n(z) z dz / \rho_{Cn} L$ . Here  $\rho_n(z)$  is the height distribution of components numerical density near the exfoliation critical temperature. This characteristic of nonhomogeneous mixture was found from gravitational effect experimental data with help of refractometrical method [1] using Lorenz-Lorentz formula [2]:  $\rho^{-1} (n^2 - 1) / (n^2 + 1) = x r_1 + (1 - x) r_2$  in assumption of components specific volume additivity.

On figure 1 the temperature dependence of component centre mass coordinates is indicated. The values of coordinates are counted from the bottom of a cell.

As it was previously shown for mixture methanol-hexane [1], the temperature dependence of equilibrium establishment time in inhomogeneous mixture under gravity is nonmonotonical [3] (figure 2). As near liquid-gas critical point [4] maximum equilibrium establishment time corresponds not

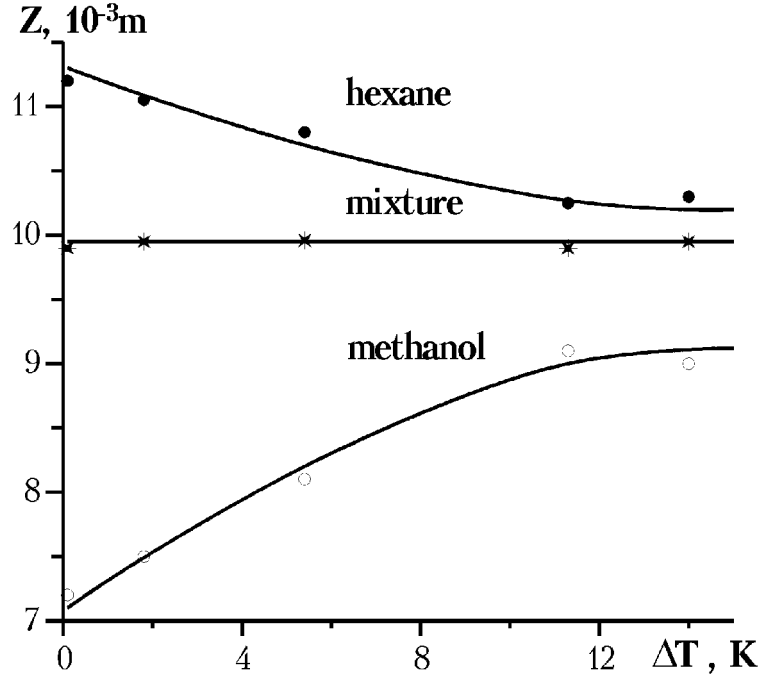


Figure 1. Temperature dependence of component centre mass coordinates.

to critical temperature ( $\Delta T = T - T_C = 0$ ), but temperature  $\Delta T \leq 10K$ . In accordance to [3], temperature dependence  $\theta_E(\Delta T)$  is described by relation:

$$\theta_E(\Delta T) \sim \Delta M(\Delta T) \tau(\Delta T) \Delta z(\Delta T). \quad (2)$$

When  $L^* = \frac{\rho_C g L}{p_C} \gg t^{\beta\delta} = \left(\frac{\Delta T}{T_C}\right)^{\beta\delta}$  in equation (2)  $\Delta M(\Delta T) \sim \Delta T$  [4] - is mass of substance, moving in vertical direction as system tend to an equilibrium state;  $L$  - is cell's height;  $\tau(\Delta T) \sim \Delta T^{-\nu}$  - is relaxation time at the critical density level with;  $\Delta z \sim \Delta T^{\beta\delta}$  [5] is width of the layer where  $\rho = \rho_C$  (here  $\nu = 2/3$ ,  $\beta = 1/3$ ,  $\delta \simeq 5$  - are critical indices [6]). Then in this case, relying equation (2), we obtain:

$$\theta_E(\Delta T) \sim \Delta T^{\beta\delta+1-\nu} \quad (\beta\delta + 1 - \nu > 0), \quad (3)$$

i.e. equilibrium establishment time increases as temperature goes away from critical value. This fact was corroborated experimentally (figure 2).

In case when  $L^* \ll t^{\beta\delta}$ , mass  $\Delta M \sim L = const$ ,  $\tau(\Delta T) \sim \Delta T^\nu$ ,  $\Delta z \approx L$  [4]. Then from equation (2) we obtain:

$$\theta_E(\Delta T) \sim \Delta T^{-\nu} \quad (4)$$

i.e. equilibrium establishment time in system decreases, that was corroborated experimentally as well (figure 2).

Using obtained data of  $\Delta z(\Delta T)$  and  $\theta_E(\Delta T)$  (figures 1, 2) on the basis of (1) temperature dependence of component mass transfer velocities

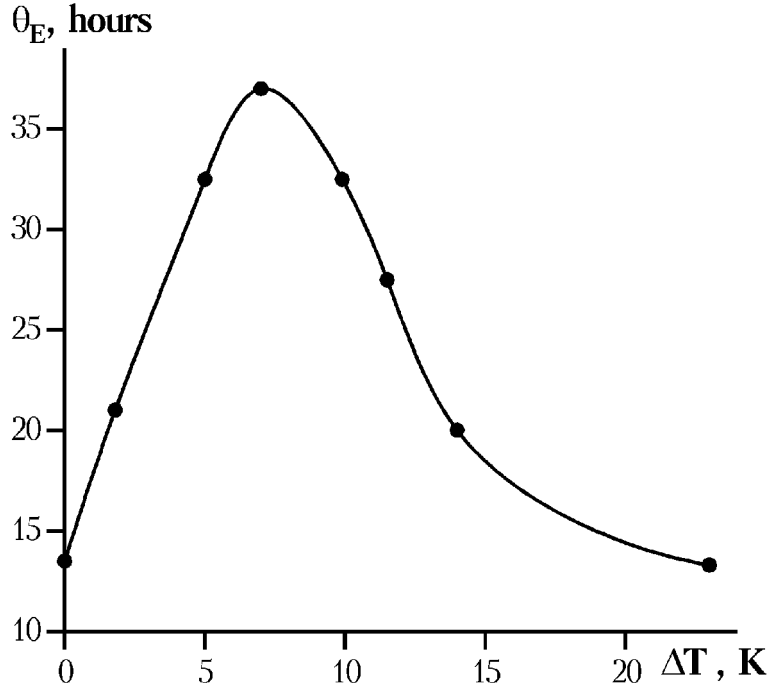


Figure 2. Temperature dependence of equilibrium establishment time.

near exfoliation critical temperature was calculated. Results are shown on figure 3.

Obtained temperature dependencies for  $v(\Delta T)$  were compared with its on theoretical calculation in [7] in the framework of fluctuation theory of phase transitions [6] and gravitational effect theory [5]. In accordance to [7] in temperature range where  $L^* \gg t^{\beta\delta}$  the temperature dependence of velocity of substance transfer near critical point is described by relation:

$$v = K_1 \Delta T^{1+\nu-\beta\delta}. \quad (5)$$

Here  $K_1$  is constant value for given substance and depends on critical parameters  $T_C, p_C, \rho_C$ , cell's height  $L$  and critical indices  $\nu, \beta, \delta$ . This dependence  $v(\Delta T)$  in (7) is very slight because the power exponent  $1 + \nu - \beta\delta \geq 0$  in equation (5) is almost zero. As indicated by figure 3, the theoretical result in temperature range  $\Delta T \leq 4K$  is confirmed experimentally.

In opposite case when  $L^* \ll t^{\beta\delta}$  in accordance to [7]:

$$v = K_2 \Delta T^\nu, \quad (6)$$

i.e. dependence  $v(\Delta T)$  is multiplied considerably, that is in agreement with experiment as well (figure 3).

Obtained experimental data of fluctuation cluster transfer velocity in a gravitational field for system going to equilibrium state were used to estimate viscosity of a nonhomogeneous mixture near the exfoliation critical temperature. For this purpose the Stokes method of viscosity determination by formula:

$$f = 6\pi\eta v R \quad (7)$$

was used. Here  $f$  is force of medium resistance, that acts on a probe particle with the radius  $R$  and velocity of movement  $v$ .

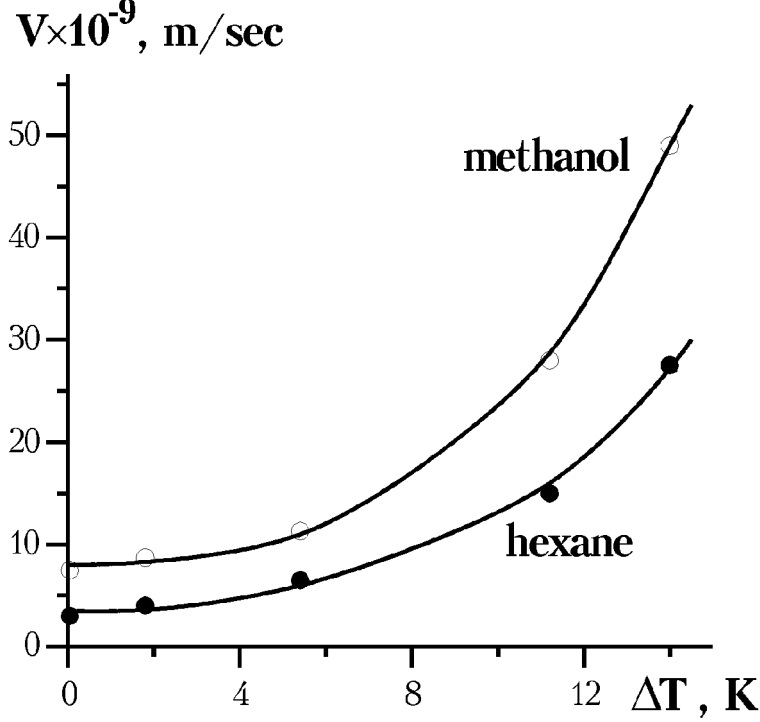


Figure 3. Velocities of transfer of binary mixture component's centre mass.

As applied to an inhomogeneous medium near a critical point, density fluctuation of substance - cluster with radius  $R$  is supposed to be probe particle, moving in vertical direction with velocity  $v \approx \Delta z / \theta_E$ . On the basis of such assumption using equation (7) in framework of fluctuation theory of phase transitions [6] in [8] it was shown that viscosity of substance can be calculated by formula:

$$\eta = \frac{k_B T_C}{6\pi v \Delta z \omega R_C}. \quad (8)$$

Here  $\omega = 1 - \rho_C \rho_{Fl}^{-1}$ ,  $\rho_{Fl}^{-1}$  - is the density of substance inside of density fluctuation. Evaluation of this parameter near liquid-gas critical point demonstrated that  $\rho_{Fl} = (2 \div 3) \rho_C$  [8]. Close to exfoliation critical temperature such a parameter wasn't calculated. But it can be estimated using relation:

$$\frac{\rho_{Fl}}{\rho_C} \leq \frac{\rho_M}{\rho_C}, \quad (9)$$

where  $\rho_M$  is the liquid density near melting temperature. In accordance to experimental data obtained for the mixture methanol-hexane, the value  $\rho_M / \rho_C \approx 1.2$ . Then parameter  $\omega$  in (8) can be estimated as  $\omega \approx 0.2$ . Using obtained experimental data  $\Delta z(\Delta T)$  (figure 1),  $v(\Delta T)$  (figure 3), temperature dependence of correlation radius along critical izohore for given mixture  $R_C = r_0 t^{-\nu}$  ( $r_0 = 0.58 \cdot 10^{-9}$  m,  $\nu = 0.62$ ), in accordance to equation

(8) the temperature dependence of viscosity near exfoliation critical point was calculated. The results are depicted on figure 4. As indicated by this figure, within  $\Delta T$  range from  $14^0$  to  $4^0$  value of binary mixture viscosity increased five times. To check obtained results  $\eta(\Delta T)$  experimental research of shear viscosity  $\eta_S$  of mixture methanol - hexane near exfoliation critical point was performed by means of viscosimetric method. Obtained data are shown on figure 4. As is seen, calculated by equation (8) values of viscosity considerably exceed experimentally obtained values  $\eta_S$  in whole studied range of temperature.

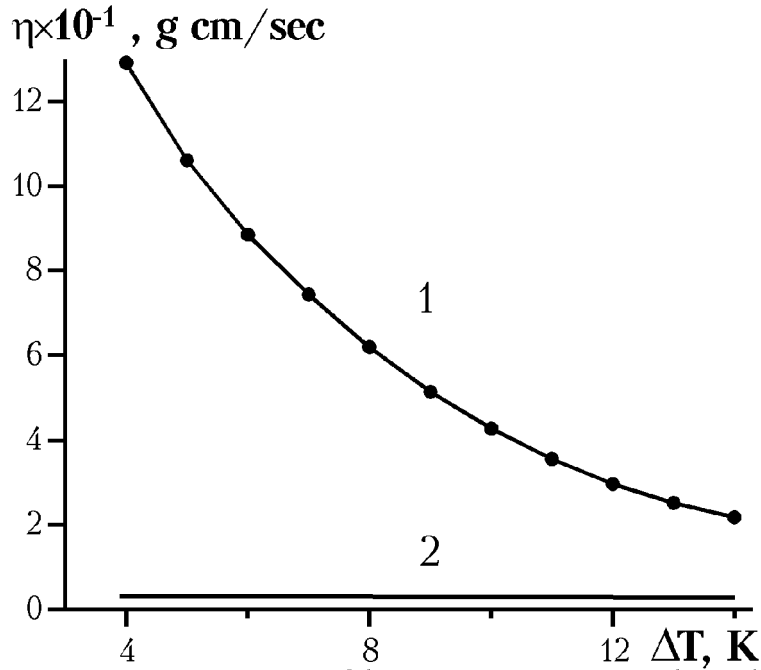


Figure 4. Viscosity of binary mixture methanol-hexane: 1 – results of calculation by equation (8), 2 – viscosimetric experiment.

Gained result ( $\eta(\Delta T) \gg \eta_S(\Delta T)$ ) confirms the assumption done in [8], that the viscosity in equation (8) near the critical point is not shear but the complete viscosity of substance  $\eta = (4/3)\eta_S + \eta_V$ ; here  $\eta_V$  is the volume viscosity. Such assumption is acceptable enough for a medium with very-developed fluctuations of density and concentration of substance. When movement of nonhomogeneous system centre mass realizes in gravitational field, fluctuation clusters under real conditions don't change their positions like whole and undividable formations, that perceive only shear viscous tensions. In fact, thickening of substance inside a fluctuation cluster after certain time interval of life decays and forms again in an other place of a cell. In such fluctuation process of centre mass transfer in inhomogeneous substance the main role has to play volume viscosity of substance  $\eta_V \gg \eta_S$ .

It needs special noting, that calculated by equation (8) values of viscosity are in agreement with experimental data about the relation  $\eta_V/\eta_S$  behaviour obtained by acoustic methods in [9] for *n*-hexane and methanol in the temperature range  $30 \div 50^0C$ . These data lead to the value of  $\eta_V/\eta_S \approx 4$  at the temperature  $T = 40^0C$ .

Analysis made above allows to make a conclusion that suggested method of studying of the centre mass velocity in inhomogeneous system in the gravitational field can be used as well to estimate the volume viscosity of substance near the critical point.

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## ОСОБЛИВОСТІ РУХУ КОМПОНЕНТІВ ПОДВІЙНОГО РОЗЧИНУ ПОБЛИЗУ КРИТИЧНОЇ ТОЧКИ РОЗШАРУВАННЯ

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У попередніх роботах досліджувався процес встановлення рівноваги у неоднорідних індивідуальних рідинах та подвійних розчинах. Було виявлено, що температурна залежність часу встановлення рівноваги в таких системах в гравітаційному полі є немонотонною. В рамках флуктуаційної теорії фазових перетворень було встановлено зв'язок між цим часом та швидкістю руху центру мас неоднорідної речовини. У цій роботі було експериментально досліджено рух центру мас подвійного розчину метанол-гексан у гравітаційному полі поблизу критичної температури розшарування. Було вивчено температурну залежність швидкості руху компонентів та проаналізовано деякі особливості такого процесу.