BEHAVIOR OF THE VISCOSITY OF LIQUID SYSTEMS NEAR THE CRITICAL TEMPERATURE OF STRATIFICATION

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We present the results of experimental studies of the temperature dependence of the dynamical viscosity $\eta(t)$ for a wide class of liquid systems near the critical temperature (CT) of stratification. The analysis of those data is performed on the basis of the equation of viscosity of the dynamical theory of critical phenomena and a semiempiric equation which accounts the spatial dispersion of the system near CT. By the data on $\eta(t)$, we have calculated a number of parameters which characterize the fluctuation part of the viscosity of various liquid systems near CT: the amplitudes and the critical indices of correlation length and viscosity, and a finite value of viscosity at the critical point.

The experimental and theoretical studies of individual liquids and double solutions near their critical states, especially the kinetic properties of liquid systems, continue to be actual in the physics of condensed matter [1, 2].

According to the modern dynamical theory of critical phenomena [3–5], the general equation of viscosity near CT, which accounts both the regular part of the viscosity and the fluctuation one, can be presented in the form

$$\eta(T) = \eta_r(T) + \eta_f(T)$$

$$\eta(T) = \eta_r(T)(qR_c)^{Z_\eta} = A \exp \frac{B}{T} (r_0 q)^{Z_\eta} t^{-\nu Z_\eta}, \qquad (1)$$

where $\eta_r(T) = A \exp \frac{B}{T}$ - the regular part of the viscosity which does not account fluctuations of the density or concentration in a liquid system; η_f - the singular or fluctuation part of the viscosity [3–5]; $R_c = r_0 t^{-\nu}$ - the correlation length of fluctuations of the concentration; ν - the critical index of correlation length; z_{η} - the critical index of viscosity; q - the parameter which has the dimension of a wave vector; $t = (T - T_c)/T_c$, and T_c - the critical temperature.

According to [3-5] and (1), the viscosity of a substance grows infinitely, while approaching CT. At the same time, as seen from (1), the temperature region,

where this equation is valid, is bounded: the equation cannot be used in the hydrodynamical region, where $qR_c \ll 1$; in addition, the temperature region of its validity is not specifically determined as $t \rightarrow 0$. As distinct from those theoretical calculations, the analysis of many up-to-date experimental data [6–16] testifies, nevertheless, to the finiteness of the viscosity at the critical point.

The same conclusion can be also drawn from the Fixman's integral equation of critical viscosity [17] which accounts the spatial dispersion of the system near the critical point. Unfortunately, the complicated integral form of this equation hampers its practical application to the analysis of available experimental data on $\eta(T)$.

At the same time, it was shown in [17] on the simplified solution of the equation, by taking the wave vector $q \rightarrow 0$, that the viscosity of the system $\eta(t)$ is related to the compressibility $\beta(t)$ and the correlation length of the system $(\eta_f(t) \sim \beta^{1/2} \sim R_c \sim t^{-1/2} \Rightarrow \infty)$. That is, the shear viscosity $\eta_f(t)$ tends to infinity, according to [17], only as $q \Rightarrow 0$.

Unfortunately, this old work [17] has not been considered and analyzed in the modern analysis of the equations of critical viscosity [3–5].

In view of this fact, we propose here, by basing on the Fixman's scientific position, a semiempiric equation for the critical part of viscosity which accounts, in a simplified manner, the spatial dispersion of the system:

$$\eta_f = \left[\frac{\left(AR_c\right)^2}{1 + \left(qR_c\right)^2}\right]^{1/2} = \left[\frac{\left(\Delta\eta_0 t^{-\nu}\right)^2}{1 + \left(qr_0 t^{-\nu}\right)^2}\right]^{1/2},\tag{2}$$

where $\Delta \eta_0$ – the amplitude of the singular part of viscosity. This formula agrees qualitatively with the Fixman's equation [17] and ensures the finiteness of viscosity at the critical point.

Then, in addition to the up-to-date equation of critical viscosity (1), we propose one more equation on

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Fig. 1. Temperature dependence of the fluctuation part of viscosity, a – literature data [10, 11] and b – our experimental data. Solid lines describe the form of Eq. (7), whose parameters a_i and b_i are given in Table 2

the basis of (2):

$$\eta(T) = \eta_r(T) + \eta_f(T) =$$

$$= A \exp\left(\frac{B}{T}\right) + \left[\frac{(\Delta \eta_0 t^{-\nu})^2}{1 + (qr_0 t^{-\nu})^2}\right]^{1/2}.$$
(3)

We will use these equations (1) and (3) simultaneously in the analysis of the experimental data on the temperature dependence of the viscosity $\eta(T)$ of a number of various double liquid systems near CT of stratification: methanol-hexane, methanol-heptane, nitromethane-*n*-pentanol [13, 14], trimethylpyridine-heavy water (3MP-D₂O), and trimethylpyridine+heavy water+sodium chloride (3MP-D₂O+NaCl) [10, 11].

In this case, it is worth noting that the use of only one formula (1) in calculations does not allow one to determine the critical index of viscosity z_{η} which appears in this formula in the form of a product $(\eta_f \sim t^{-Z_{\eta}\nu})$. In order to determine it, we need to find separately the critical index of correlation length of the system ν $(R_c \sim t^{-\nu})$.

In the present work, we calculated the parameters A and B of the regular part of viscosity η_r with the purpose to determine the fluctuation part of the viscosity η_f (2) for the objects under study [13, 14] and to describe the literature data [10, 11] firstly in the supercritical region of temperatures $(t > 10^{-2})$, where $\eta_r \gg \eta_f$ (the results are given in Table 1).

T a b l e 1. Parameters of Eq. (3) which characterize the viscosity of the liquids under study near CT

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$A, \mathrm{mPa}\cdot\mathrm{s}$	<i>B</i> , K	$\Delta \eta_0$, mPa·s	$n \sim \nu$	$\eta_{fc}, \mathrm{mPa} \cdot \mathrm{s}$	(qr_0)
0.2×10^{-1}	878	0.19×10^{-2}	$0.61 {\pm} 0.05$	9.5×10^{-2}	0.02
0.2×10^{-1}	900	0.18×10^{-2}	$0.63 {\pm} 0.05$	6.4×10^{-2}	0.028
0.65×10^{-3}	2180	0.45×10^{-2}	$0.64{\pm}0.05$	0.26	0.017
0.49×10^{-3}	2520	0.75×10^{-2}	$0.60 {\pm} 0.05$	0.50	0.015
0.51×10^{-3}	2530	0.6×10^{-2}	$0.62 {\pm} 0.05$	1.11	0.009
	$\begin{array}{c} A, \text{ mPa} \cdot \text{s} \\ 0.2 \times 10^{-1} \\ 0.2 \times 10^{-1} \\ 0.65 \times 10^{-3} \\ 0.49 \times 10^{-3} \\ 0.51 \times 10^{-3} \end{array}$		A, mPa·s B, K $\Delta\eta_0$, mPa·s 0.2×10^{-1} 878 0.19×10^{-2} 0.2×10^{-1} 900 0.18×10^{-2} 0.65×10^{-3} 2180 0.45×10^{-2} 0.49×10^{-3} 2520 0.75×10^{-2} 0.51×10^{-3} 2530 0.6×10^{-2}	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

T a ble 2. Parameters which define the equation of asymptotics of the fluctuation part of the viscosity of the liquid systems under study

Name of a system	a_0 , mPa·s	b_0 , mPa·s	a_1 , mPa·s	b_1 , mPa·s	ν	(qr_0)
Methanol-hexane	12	500	12000	0.05	0.61	0.024
Methanol-heptane	15	650	15000	0.2	0.63	0.023
Nitromethane-n-pentanol	3	144	7936	0.015	0.6	0.020
$3MP-D_2O$	2	150	5000	0.05	0.64	0.013
$3MP-D_2O+NaCl_2O+NaCl$	2	190	6000	0.0080	0.62	0.010

Then, by using the values of the parameters Aand B, we separated and analyzed the temperature dependence of the fluctuation part of viscosity (2) $\eta_f(T) = \eta(T) - \eta_r(T)$. These data are presented in Fig. 1, a, b. As seen from this figure, while approaching CT $(t \rightarrow 0)$, the reciprocal quantities η_f^{-1} tend to a constant value $\eta_f^{-1}(t = 0) = \eta_{fc}^{-1}$ (see Figs. 1,*a*,*b* and 2,*a*,*b*), which confirms the form of Eq. (2) at t = 0 $(\eta_{fc}^{-1} =$ $\frac{qr_0}{\Delta\eta_0}$). Its values for the studied objects are presented in Table 1. In order to determine the temperature behavior of the fluctuation part of viscosity, we analyzed the temperature dependence of the difference $(\eta_f^{-1} - \eta_{fc}^{-1}) =$ $\Delta \eta_f^{-1} \sim t^n$ on the double logarithmic scale. It is established that, for all the studied objects, the index $n = 0.61 \pm 0.03$ and is close, in the limits of the experimental error, to the critical index of correlation length $\nu = 0.63$ [1].

The values of the index n, amplitude $\Delta \eta_0$, and product (qr_0) for all the studied objects are presented in Table 1.

Thus, this experimental result, $(n \approx \nu)$, confirms both the conclusion made in [17] on the linear connection of the fluctuation part of viscosity with the correlation length of the system $(\eta_f(t, q = 0) \sim R_c(t))$ and the proposed form of the equation of critical viscosity (2).

In what follows, these data (Fig. 1) are used for the determination of the critical index of viscosity z_{η} $(\eta(t) \sim t^{Z_{\eta} \cdot \nu})$ [3,4]. To this end, by analyzing the temperature dependence of the ratio $\frac{\eta(t)}{\eta_{F}(t)} \approx t^{Z_{\eta} \cdot \nu}$ for all the systems [10, 11, 13, 14], we will determine, at first, the product $z_{\eta}\nu = 0.04\pm 0.005$. Then, with regard for the value of the index $n \cong \nu = 0.62\pm 0.03$ obtained earlier, we found the critical index of viscosity $z_{\eta} = 0.065\pm 0.01$ (Table 1). This result is corroborated by the analysis of the data of other experimental studies of the viscosity near CT [6–9, 15, 16].

Our experimental results on $\eta_f(t)$ [13, 14] and the literature data [10, 11] (Fig. 1) allow us to verify the form of the asymptotics of the above-proposed equation (2) in various limiting cases.

In the critical region $(t \rightarrow 0, qR_c \rightarrow \infty)$, Eq. (2) yields

$$\eta_f^{-1} = \frac{qr_0}{\Delta\eta_0} \left[1 + \frac{1}{2} \left(\frac{t^{\nu}}{qr_0} \right)^2 \right] = a_0 + a_1 t^{2\nu},$$

$$a_0 = \frac{qr_0}{\Delta\eta_0}, \quad a_1 = \frac{1}{2(qr_0)\Delta\eta_0}.$$
 (4)

It is seen from (4) that, at the critical temperature (t = 0), the viscosity takes a finite value $\eta_{fc} = \frac{\Delta \eta_0}{r_0 q}$. While

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Fig. 2. Behavior of the viscosity $\eta(t)_f^{-1}$ of the systems under study in the close vicinity of the critical temperature $(qR_c \gg 1)$: $\eta_f^{-1} = a_0 + a_1 t^{2\nu}$: a – our experimental data; b and c – the literature data [10, 11]

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Fig. 3. Behavior of the viscosity $\eta(t)_f^{-1}$ of the systems under study in the hydrodynamical region of temperatures $(qR_c \ll 1)$: $\eta(t)_f^{-1} = b_0 t^{\nu} + b_1 t^{-\nu}$, a) our experimental data; b) the literature data [10, 11]

moving off CT, the reciprocal quantity η_f^{-1} varies by the square law $\eta_f^{-1} = \text{const} + a_1(t^{\nu})^2$.

In the opposite limiting case in the hydrodynamical region $(qR_c \ll 1)$, Eq. (2) yields

$$\eta_f^{-1} = \left(\Delta \eta_0 t^{-\nu}\right)^{-1} + \frac{(qr_0)^2}{2} \left(\Delta \eta_0 t^{\nu}\right)^{-1} = \\ = \left(\Delta \eta_0 t^{-\nu}\right)^{-1} + \frac{\eta_{\Phi K}^{-2}}{2} \Delta \eta_0 t^{-\nu} = b_0 t^{\nu} + b_1 t^{-\nu}, \tag{5}$$

where

$$b_0 = \frac{1}{\Delta \eta_0}, \quad b_1 = \frac{(qr_0)^2}{2\Delta \eta_0} = \frac{b_0(qr_0)^2}{2}$$

Using (4) and (5), we get

$$qr_0 = \frac{a_0}{b_0}.\tag{6}$$

Then, on the basis of (6), Eq. (2) can be also represented as

$$\eta_f = \left[\frac{\left(b_0^{-1}t^{-\nu}\right)^2}{1 + \left(\frac{a_0}{b_0}t^{-\nu}\right)^2}\right]^{1/2}.$$
(7)

The proposed equations of critical viscosity (2), (7) and the form of their asymptotics (4), (5) were verified by the data on the temperature dependence of the viscosity of the objects under study [13,14] and [10, 11] near CT in two limiting cases: $(qR_c)^2 \gg 1$ (Fig. 2) and $(qR_c)^2 \ll 1$ (Fig. 3).

In these figures, the solid lines show asymptotics (4) and (5), whose parameters a_0 , a_1 , b_1 , b_0 , ν , and the product (qr_0) (6) are presented in Table 2.

Using these parameters, we calculated such an important parameter of the fluctuation part of viscosity as (qr_0) with the help of formula (6) (Table 2). As seen, its value coincides, in the limits of the experimental error, with the experimental value (Fig. 1, Table 1).

It is clear that the experimental data on $\eta(t)$ (Fig. 1) represented in the general form and the behavior of $\eta(t)$ in the asymptotics $qR \gg 1$ and $qR \ll 1$ (Figs. 2 and 3) well correspond to the form of Eqs. (2), (7) and asymptotics (4), (5) with the parameters given in Tables 1 and 2.

A similar analysis of the other literature data [6–9, 15, 16] performed by us also corroborates the conclusions drawn above.

In the case, the simultaneous application of the equation of viscosity (1) of the modern dynamical theory of critical phenomena [3, 5] and Eq. (2), which agrees qualitatively with the Fixman's theoretical calculations [17], turns out to be fruitful. This allows us to calculate, by using the data on $\eta(t)$, a number of parameters which characterize the fluctuation part of the viscosity of various liquid systems near CT (the amplitudes and the critical values of correlation length and viscosity) and to determine a finite value of viscosity at the critical point.

Thus, we may conclude on the basis of the performed experimental studies of the temperature dependence of

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the shear viscosity of liquid systems of different nature such as dielectric liquids [13, 14], liquid and ionic systems [10, 11], solutions of polymers [9], metal melts [15, 16], and liquid crystals [12] that the proposed equation for the fluctuation part of viscosity is in agreement with the Fixman's equation [17] and describes adequately the available experimental data on the temperature dependence of the viscosity near the critical point.

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ПОВЕДІНКА В'ЯЗКОСТІ РІДИННИХ СИСТЕМ ПОБЛИЗУ КРИТИЧНОЇ ТЕМПЕРАТУРИ РОЗШАРУВАННЯ

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Резюме

В роботі представлено результати експериментальних досліджень температурної залежності динамічної в'язкості широкого класу рідинних систем поблизу критичної температури розшарування. Аналіз цих даних проведено на основі рівняння в'язкості динамічної теорії критичних явищ і напівемпіричного рівняння, що враховує просторову дисперсію системи поблизу критичної температури. За даними $\eta(t)$ розрахували цілий ряд параметрів, що характеризують флуктуаційну частину в'язкості різноманітних рідинних систем поблизу критичної точки (КТ): амплітуди і критичні показники радіуса кореляції та в'язкості; визначили кінцеве значення в'язкості в критичній точці.