Temperature dependence of the viscosity of binary solutions near the critical solution temperature

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The experimental data on viscosity near the critical mixing temperature of various binary systems is approximated by a function of the form $\eta = A + B\tau^\epsilon$, which follows from the theory of second-order phase transitions. The coefficients A and B in the approximation function are chosen by the least-squares method, and ϵ and T_C are themselves varied in such a way as to determine those values of them which yield the minimum error in the approximation. On the basis of the approximation, it is shown that the probable values of ϵ lie within the range 0.1—0.45. Thus, for these system, it is not the viscosity but rather its derivative with respect to the temperature which becomes infinite.

Information obtained in the reduction of experimental data on the viscosity near the critical mixing point is useful for a comparison of the existing dynamical theories of second-order phase transitions[1-7].

In our previous paper,[8] on the basis of experiments on the shear viscosity of the methanol-cyclohexane system, it was shown that the temperature dependence of the viscosity of this system is approximated with the minimum rms error by the function

$$\eta = A + B\tau^\epsilon, \tag{1}$$

where A > 0 and B < 0 are constants, ϵ is the exponent and is equal to 0.43 and $\tau = (T - T_C)/T_C$. It is of interest to test the suitability of the approximation of the function (1) for known experimental data on the shear viscosity of other systems.

In connection with the possible non-uniqueness of measurements of the viscosity near the critical point, it should be emphasized that the data considered here were obtained with apparatus having characteristic dimensions much greater than the correlation radius. Thus, the depth of the damping, in the case of an oscillating disk and the radius in the case of a capillary are much greater than the correlation radius (10^{-4} cm) at attainable approaches to the critical point.[9]

The suitability of the function (1) for the approximation was tested with the results of the measurement of the viscosity of the binary solutions triethylamine-water and nitrobenzene-hexane[10], isobutyric acid-water[11,12], and aniline-cyclohexane.[15] In the analysis we encountered the difficulty that there were no tabulated values of the data in[12,13], and the results were given only in the form of graphs. Assuming that these graphs are similar to the operating graphs, we established the numerical data by means of a measuring microscope. The numerical values of the viscosity, from which the coefficients of the approximating functions are chosen, are given in Table I. The coefficients A and B of the approximating function (1), the exponent ϵ, and the critical temperature were chosen for a best fit with the experimental data. The coefficients A and B for given ϵ and T_C were obtained by least squares, and ϵ and T_C were themselves varied to obtain values at which the approximation errors would be minimal. The limits of variation of ϵ were chosen to be −1 and +1, and thus the values of ϵ for which the approximating function η either goes to infinity or has a finite

value as $\tau \to 0$ were included. A Minsk-22M computer was used.

Usually the critical mixing temperature is determined visually from many experiments on the onset of stratification upon cooling of a homogeneous solution with critical concentration. In this way the critical temperature can be determined with a error of less than several thousandths of a degree. Therefore, when choosing T_C for the best approximation, we must take such values which differ from the temperature observations by an amount no larger than the error of the visual measurements. In the case of the systems methanol-cyclohexane and isobutyric acid-water,[11] the error in the determination of the critical temperature is not large; therefore the choice of the exponent ϵ can be made rather reliably. In the case of the data of[11], the minimum error of the approximation (see Fig. 1) when T_C and ϵ are varied occurs just at the temperature corresponding to the visually observed stratification.

TABLE I. Viscosity from the data of various authors

η/η_1	t	η/η_1	t	η	t	η	t	η	t
Methanol-cyclohexane [8]				Triethylamine-water [10]		2.344	27.850	Aniline-cyclohexane [15]	
		1.100	45.52			2.152	29.825		
		1.103	45.47			1.980	32.260		
		1.095	45.45	4.123	18.025			1.879	29.855
1.008	17.02	1.110	45.43	4.192	18.10	Isobutyric acid-water [12]		1.809	29.888
1.000	47.01	1.118	45.42	4.181	18.13			1.795	29.894
1.000	46.93	1.115	45.42	4.264	18.17			1.783	29.900
1.010	46.99	1.134	45.39	4.238	18.19	2.910	26.340	1.727	29.962
1.000	46.97	1.120	45.39	4.354	18.22	2.909	26.344	1.693	30.042
1.002	46.80	1.109	45.38	4.389	18.24	2.908	26.350	1.676	30.103
1.011	46.62	1.110	45.39	4.413	18.25	2.900	26.360	1.653	30.165
1.020	46.56	1.132	45.37	4.475	18.27	2.869	26.388	1.606	30.457
1.013	46.49	1.150	45.37			2.841	26.423	1.586	30.599
1.010	46.48	1.119	45.36	Nitrobenzene-hexane [10]		2.803	26.449	1.570	30.732
1.021	46.37	1.139	45.36			2.768	26.478	1.551	30.930
1.040	46.27	1.135	45.37	0.790	18.10	2.718	26.500	1.528	31.189
1.035	46.18	1.145	45.36	0.832	15.75	2.689	26.584	1.512	31.435
1.047	46.11	1.135	45.34	0.890	14.70	2.619	26.730	1.490	31.836
1.039	46.04	1.160	45.34	0.900	14.20	2.564	26.939	1.474	32.084
1.050	45.97	1.158	45.32	0.933	13.90	2.485	27.311	1.440	32.719
1.049	45.95	1.170	45.33	0.954	13.75	2.416	27.835	1.418	33.196
1.018	45.92	1.145	45.33	0.978	13.67	2.345	28.295	1.388	33.917
1.050	45.87	1.141	45.33	0.992	13.64	2.232	29.332	1.359	34.660
1.065	45.74			1.005	13.61	2.132	30.305	1.318	35.910
1.078	45.69					2.066	31.314	1.285	37.113
1.065	45.65			Isobutyric acid-water [11]		1.991	32.530	1.254	38.188
1.060	45.63					1.913	33.871	1.232	39.031
1.075	45.57			2.776	26.315	1.802	35.077		
				2.726	26.355				
				2.647	26.460				
				2.533	26.755				

<u>Note</u>: The values of η are given in centipoise, the temperature in °C; for the system methanol—cyclohexane, the values of the viscosity are given in relative units, η, are the values of the viscosity at 47°C. The numerical data of [12,13] were taken from graphs of the published papers.

TABLE II

System	A	B	T_c'', °C	T_c', °C	σ_0	ε
Methanol—cyclohexane	1.165	—1.297	45.330	45.330	0.0097	0.35—0.45
Isobutyric acid—water [12]	3.120	—3.917	26.315	—	0.0160	0.25—0.40
Isobutyric acid—water [11]	2.862	—4.048	26.300	26.30	0.0046	0.35—0.42
Triethylamine—water [10]	4.689	—5.863	18.281	—	0.0218	—0.5—0.5
Nitrobenzene—hexane [10]	1.023	—1.061	13.609	—	0.0072	0.1—0.35
Aniline—cyclohexane [13]	1 936	—1.853	29.854	—	0.0074	0.15—0.25
Helium (He⁴), λ point [16]	—	—	—	—	—	0.75

Note: The constants ε, A, B, and T_c'' determine the function (1), T' is the critical temperature from visual observation, $\sigma_0 = [\Sigma\sigma_i^2/(n-1)]^{1/2}$ is the least approximation error per experimental point. The values of A and B are given in relative units for methanol—cyclohexane, (see [8],) and n centipoise for the remaining systems.
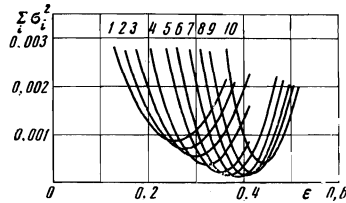

FIG. 1. Approximation error of the function (1) in the reduction of the data of [11], as a function of ε and T_c. Each curve corresponds to a definite temperature T_c: 1—26.200; 2—26.220; 3—26.240; 4—26.260; 5—26.280; 6—26.290; 7—26.300; 8—26.306; 9—26.310; 10—26.314°C.
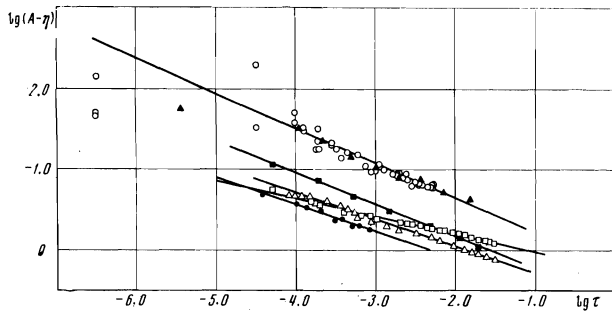

FIG. 2. Representation of the experimental data by the function $\eta = A + B\tau^\varepsilon$: O—methanol—cyclohexane; ▲—nitrobenzene—hexane; ■—isobutyric acid—water, [11] △—isobutyric acid—wter; [12] □—aniline—cyclohexane; ●—triethylamine—water.

Table II gives the values of the coefficients A and B and the critical temperature T_c'' of the approximating function (1) for various binary solutions, and the values of the visually determined critical temperature T_c' cited by various authors. The rms errors in the approximation $\sigma_0 = [\Sigma\sigma_i^2/(n-1)]^{1/2}$ are also given, where σ_i is the departure of the experimental values from the approximating curve and n is the number of experimental points. The limits of the range of possible values of the exponent were estimated from the formula

$$\sigma^2 = \sigma_0^2(1 + 1/\sqrt{N-P}),\qquad(2)$$

where σ_0 is the rms error of the approximation, N the number of experimental points, P the number of adjustable parameters, and σ the rms approximation error corresponding to the limiting values of ε.[14]

Figure 2 illustrates the approximation of the experimental data on the viscosity of the various systems by means of the function (1). The authors of[12], to find the approximation functions, plotted their data in the coordinates $\log(\Delta\eta/T)$ and $\log\tau$, and found that the experimental data in the temperature range $T - T_c$
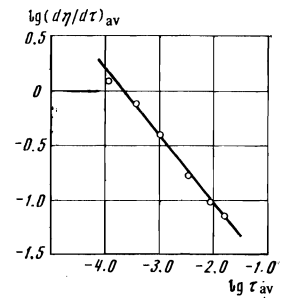

FIG. 3. Dependence of the derivative of the viscosity on the temperature, from the data of [11].

= 0.1—1°K are described by a power law of the form

$$\frac{\Delta\eta}{T} = \frac{\eta - \varphi(\tau)}{T} = A\tau^\varepsilon\qquad(3)$$

with $\varepsilon = -0.65 \pm 0.01$, where $\varphi(\tau) = B + C'\tau + C''\tau^2 + \ldots$ is the function that describes the experimental values of the viscosity far from the critical temperature. Since the right-hand side of Eq. (3) does not vanish even far from the critical point at $\tau = 1$ and $\varepsilon < 0$, such a treatment must be regarded as incorrect. The data of[12] can also be approximated by a relation that follows from the theory of second-order phase transitions:[15]

$$\eta = A\tau^\varepsilon + \varphi_1(\tau),\qquad(4)$$

where $\varphi_1(\tau)$ is a regular function and differs from $\varphi(\tau)$ by the constant A in the case $\varepsilon < 0$. Such an approximate was used in[13].

In the case $\varepsilon > 0$, the regular part can no longer be represented in the form of the series

$$\varphi_1(\tau) = B' + C'\tau + C''\tau^2 + \ldots,$$

inasmuch as a term should appear which damps the growing singular contribution $A\tau^\varepsilon$ as $\tau \to \infty$. Additional parameters are introduced in (4) in comparison with (1). Of course, the function (4) is a better approximation of the experimental data over a wider range of temperatures. However, the accuracy of the determination of ε is lower here and the data can be represented by Eq. (4) with a positive and negative exponent ε with practically the same approximation error. Near the critical point, the function (4) goes over into (1). This also makes it possible, by varying the exponent ε in (1), to conclude that the viscosity is finite at the critical point.

Accurate values of the viscosity were obtained in[11], and we have attempted to determine the temperature dependence of the viscosity by finding the derivative $\partial\eta/\partial\tau$ by numerical differentiation. Figure 3 leaves no doubt as to the positiveness of the exponent ε, since the data are well described by the function $\partial\eta/\partial\tau = A\tau^{-0.6}$ ($\varepsilon = 0.4$), where the exponent ε does not change down to $\tau \sim 10^{-4}$.

The data on the viscosity of He⁴ were considered in[16] from the viewpoint of approximating them with a power-law dependence in the form (1). We have also concluded that the exponent is positive and equal to 0.75, and the viscosity itself has a finite value at the critical point. The fact that the viscosity increases continuously on going through the critical point if we stir the solution indicates that the viscosity is finite at the critical point. This was shown in[8]. Thus, in accord with the calculations of Patashinskiĭ and Cherepanova,[6,7] and without contradicting Swift[4], it is not the viscosity that becomes infinite, but the derivative of the viscosity with respect to the temperature, according to the law $\partial\eta/\partial\tau \sim \tau^{\varepsilon-1}$ with $0 < \varepsilon < 1$.

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