Scaling of the shear viscosity of the system nitrobenzene – n-heptane in the critical region

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Abstract. The temperature dependence of shear viscosity of the system nitrobenzene-n-heptane has been studied near the critical concentration. The critical exponent of the shear viscosity Φ was calculated from the empirical formula $\eta = \eta_{id}\varepsilon_{sp}{}^{-\Phi}$ and compared with the theoretical and experimental results obtained for other critical systems. The shear viscosity satisfies scaling law relations similar to those previously established for equilibrium properties.

1. Introduction

On approaching the critical point of liquid mixtures many of the physical quantities exhibit a characteristic behaviour which may be described as follows (Sengers and Sengers 1978; Kumar *et al* 1983):

$$L = L_B + L_C = L_B + A|\varepsilon|^{-\lambda}\left(1 + \sum a_i\varepsilon^{\Delta_i} + \cdots\right), \tag{1}$$

where L_B is the 'background effect', which describes the part of the quantity L that does not show critical effects, $\varepsilon = (T - T_c)/T_c$, A is the amplitude, λ the critical exponent, a_i and Δ_i are the amplitudes and exponents describing the corrections to the scaling.

According to the recent theory of critical phenomena (Sengers and Sengers 1978; Pfeuty and Toulouse 1978) all systems that belong to a given universality class (d, n) where d is the dimension of the space and n the dimension of the order parameter, are characterized by the same values of the universal parameters (that is critical exponents). The renormalization group technique enables the determination of the accurate values of critical exponents for each universality class (d, n). The values thus obtained have been unified experimentally.

Dynamic renormalization group theory (Halperin *et al* 1974; Siggia *et al* 1976; Hohenberg and Halperin 1977; Bhattacharjee and Ferrell 1983) and mode–mode coupling theory (Kawasaki 1976; Kawasaki and Gunton 1978) provide the following relation describing the shear viscosity in the vicinity of the critical point:

$$\eta = \hat{\eta}\cdot(\xi_t\cdot\Lambda)^{z_\bullet} = \hat{\eta}\cdot(\xi_0\cdot\Lambda)^{z_\bullet}\varepsilon^{-\Phi_\bullet}, \tag{2}$$

where $\xi_t = \xi_0 \cdot \varepsilon^{-\nu}$ – correlation length, ν is the critical exponent, $\nu = 0.63$ for the universality class $(3, 1)$, Λ is the microscopic cut off wave number, and $\hat{\eta}$ the critical amplitude (noncritical background). The critical exponent Φ_η found on the grounds of the mode–mode coupling theory is 0.033 (Kawasaki and Gunton 1978) whereas the renormalization group theory predicts $\Phi_\eta = 0.033$ in the ε expansion to first order (Halperin *et al* 1974) and 0.040 in the ε expansion to second order for the dimensionality $d = 3$ (Siggia *et al* 1976).

The viscosity of a binary mixture close to the consolute point is a function of a number of parameters. Concentrating only on the dependence of the critical part we write:

$$\eta = \eta(\xi_t, k, X, \omega). \tag{3}$$

The wave vector k denotes the nonlocal or spatial dependence of the viscosity and ω is a frequency variable. When oscillating viscometers are used, the viscosity becomes frequency dependent. At low frequencies in noncritical fluids this dependence is unimportant, but as the critical point is approached the frequency effect, even for low frequencies, becomes large. Due to the nature of viscosity measurement the fluid is sheared. Here the shear rate dependence is denoted as X. Noncritical fluids become non-Newtonian only when the shear rate becomes sufficiently large. However as the critical point is approached small shear rates have large effects.

Using the published data, a systematic and consistent study has been performed in which corrections due to shear gradients and frequency effects are included and the effect of the functional form for the background viscosity is critically examined (Nieuwoudt and Sengers 1989; Berg and Moldover 1988).

On the other hand, the experimental data may also be satisfactorily well described by the empirical relation proposed by Debye and coworkers (Debye *et al* 1963):

$$\eta = \eta_{id}\varepsilon^{-\Phi}, \tag{4}$$

where Φ is the critical exponent of the shear viscosity, η the macroscopic shear viscosity, η_{id} the ideal viscosity (noncritical) e.g. as expressed by an Arrhenius-type relation, and $\varepsilon = (T - T_c)/T_c$.

This paper is aimed at calculating the critical exponent of the shear viscosity, Φ. The studies were started with determining the phase coexistence curve (binodal), the critical point and the critical exponent β, which characterizes the shape of the phase coexistence curve in the vicinity of the critical point (Dega-Dalkowska 1980). Then, the pseudospinodal of the studied system was determined followed by the critical exponent β^+ of the pseudospinodal, and the amplitude ratio of pseudospinodal and binodal (Dega-Dalkowska 1988).

The results of the shear viscosity measurements were analyzed assuming equation (4) which holds true along the critical isochore. A similar relation holds for noncritical isochores:

$$\eta = \eta_{id}\varepsilon_{sp}^{-\Phi}, \qquad \varepsilon_{sp} = \frac{T - T_{sp}}{T_{sp}} = \frac{T}{T_{sp}} - 1, \tag{5}$$

where T_{sp} is the pseudospinodal temperature found by extrapolation of the properties of a homogeneous solution to the two-phase region. According to (5) the temperature dependence of viscosity along each noncritical isochore is the same as the critical isochore.

2. Experimental

The viscosity coefficients were measured by an Ubbelohde capillary viscometer to an accuracy of $\pm\,0\cdot2\%$. The viscometer was placed in a thermostat vessel. The temperature of the mixture was measured by an iron-constantan thermocouple to an accuracy of $\pm\,0\cdot02$ K. The temperature gradient in the sample volume was insignificant and thus neglected. Viscosity was measured in the homogeneous phase of the solutions for a wide range of concentrations on both sides of the critical point. The accuracy of the concentration determination was 1×10^{-3}. The density of the solutions was determined pycnometrically with an accuracy of $3\cdot \times 10^{-4}\,\text{g/cm}^3$.

Ideal viscosities of the studied solution were determined from the Arrhenius equation:

$$\ln \eta_{id} = (B/T) + C, \tag{6}$$

where B and C are constants and T the temperature. Shear rates was $500\,\text{s}^{-1}$.

3. Results and discussion

Figure 1 presents the plots corresponding to the dependence of $\ln(\eta/\eta_{id})$ on $\ln \varepsilon_{sp}$. Consistent with (5) these dependences make lines of the slope equal to Φ. The value of Φ exponent slightly depends on the concentration. For the concentrations studied
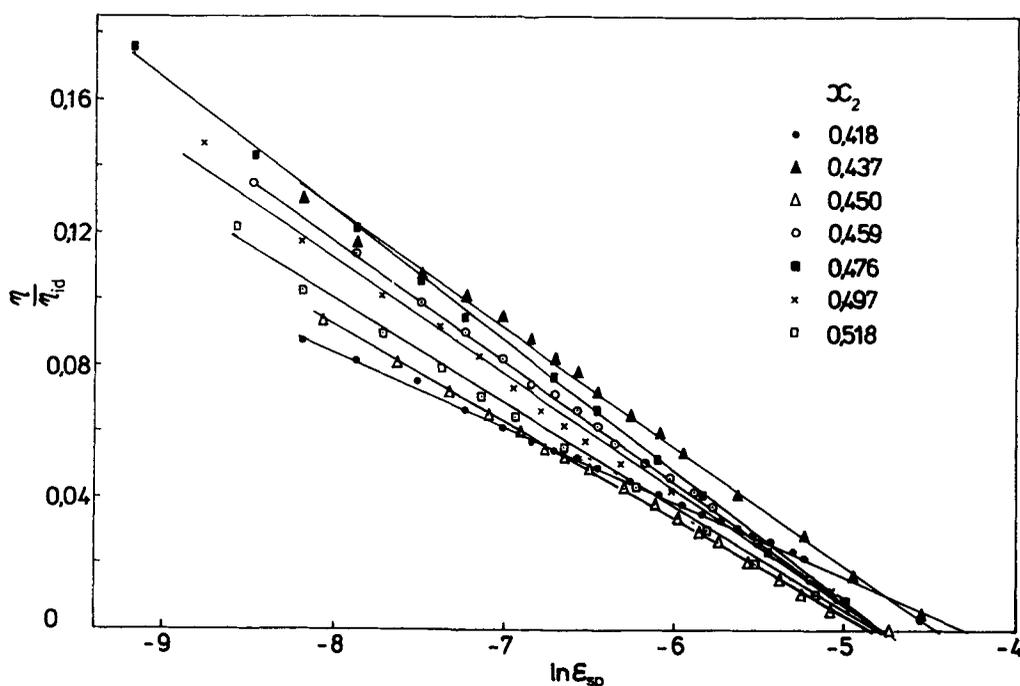

Figure 1. Plot of $\ln(\eta/\eta_{id})$ versus $\ln \varepsilon_{sp}$ for the system of nitrobenzene – n-heptane (x_2-molar fraction of nitrobenzene).

Table 1. Critical exponent of the shear viscosity Φ of the system nitrobenzene – *n*-heptane.

x_2	Φ
0·408	0·023
0·418	0·022
0·437	0·031
0·450	0·030
0·459	0·035
0·470 (crit.)	0·038
0·476	0·038
0·497	0·035
0·518	0·031
0·546	0·023

we collected the values of the critical exponent of the shear viscosity Φ describing the temperature changes in η/η_{id} (table 1).

The critical exponent values obtained experimentally by other authors for other systems are $\Phi = 0·038$ for the system of isobutyric acid-water (Izumi and Miyake 1977) and $\Phi = 0·029$ for polystyrene-cyclohexane (Izumi *et al* 1984).

Theoretical predictions are $\Phi = 0·036$ (Ohta 1977) and 0·040 (Siggia *et al* 1976). Table 1 shows that the value of Φ is not constant but becomes higher for the concentrations in the vicinity of the critical point. Analyzing the results of pseudospinodal determination on the grounds of measurements of different physical quantities, we can distinguish two situations: one when the critical exponent describing the temperature dependence of a given physical quantity is constant (Izumi and Miyake 1977; Izumi *et al* 1984), and the other when the critical exponent decreases when we move away from the critical one (Chu *et al* 1969; Pozharskaya *et al* 1984a, b, 1985); Chrapec *et al* 1987; Dega-Dalkowska 1989).

In order to study the influence of concentration on the ratio η/η_{id} isothermal measurements were carried out for $T_c + 0·05$ K, $T_c + 0·10$ K, $T_c + 0·50$ K, $T_c + 1·00$ K and $T_c + 3·00$ K. The results are presented in figure 2. It is seen that the ratio η/η_{id} increases dramatically for the concentrations in the vicinity of the critical one. The figure also illustrates a great influence of temperature.

The influence of concentration on η/η_{id} for the critical isotherm can be described by the following formula (Izumi and Miyake 1977):

$$(\eta/\eta_{id}) \sim (x_2 - x_{2c})^{-\Phi/\beta}, \quad T = T_c \tag{7}$$

where x_{2c} is the critical concentration, Φ and β the critical exponents describing the changes in viscosity and ordering parameter, respectively.

Figure 3 shows the changes in η/η_{id} versus concentration on a ln–ln scale. The exponent Φ/β obtained from the slope of the line presented in figure 3 is 0·083, and using the Φ values from table 1 (taking the average over the four concentrations closest to the critical one) and the earlier determined value of β (Dega-Dalkowska 1980) we obtain $\Phi/\beta = 0·089$. Within the experimental error this value may be accepted as satisfactory.
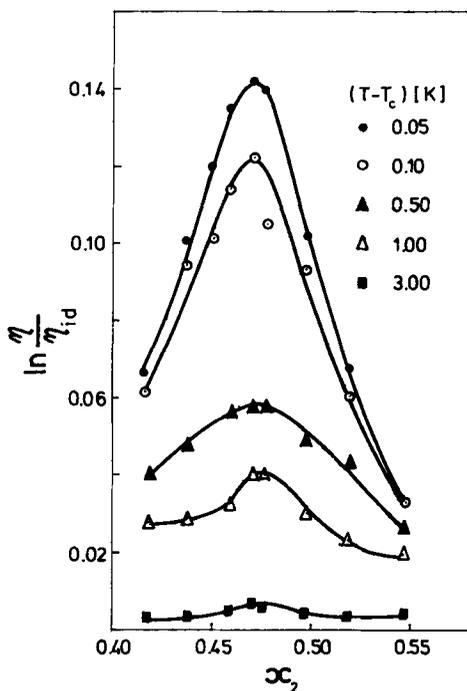
Figure 2. Concentration dependences of η/η_{id} for several isotherms.
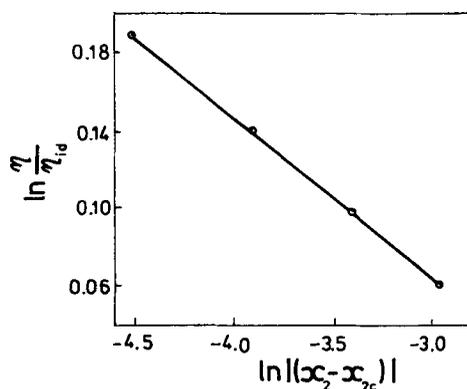

Figure 3. The changes in η/η_{id} versus $|x_2 - x_{2c}|$ on a ln–ln scale for $T = T_c$ isotherm; $x_2 < x_{2c}$.

The value of the critical exponent of the shear viscosity Φ is consistent with the values determined for other binary systems as well as with those predicted by the mode–mode coupling theory and the dynamic renormalization group theory.

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