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CRITICAL EXPONENT β FOR THE SYSTEMS: NITROBENZENE–*n*-HEXANE AND NITROBENZENE–*n*-HEPTANE*

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The critical exponent β is determined by analysis of the phase coexistence curve in the plane (x_2, T_S) for the systems nitrobenzene–*n*-hexane and nitrobenzene–*n*-heptane by measurement of the viscosity coefficient. This points to yet another method for the determination of the phase separation temperature of solutions with restricted mutual miscibility. Detailed analysis of the data shows that the differences in composition of coexisting liquid phases are proportional to $\left(\frac{T_c - T_s}{T_c}\right)^{\beta}$, with $\beta = 0.39 \pm 0.04$ for nitrobenzene–*n*-hexane and $\beta = 0.38 \pm 0.04$ for nitrobenzene–*n*-heptane.

1. *Introduction*

The shape of the phase coexistence curve of two-component liquid systems near the critical point has been studied repeatedly with care in recent years [1–9].

In studies of critical phenomena, priority is given to the numerical determination of critical exponents, describing the behaviour of various physical properties near the critical point.

For liquid binary solutions, the critical exponent is

$$\beta = \lim_{\varepsilon \to 0} \frac{\log (x' - x'')}{\log (-\varepsilon)}, \tag{1}$$

where $(x' - x'')$ is the difference in concentrations of the components at equilibrium in molar fractions and $\varepsilon = \frac{T_s - T_c}{T_c}$ the "relative difference" between the phase separation temperature T_s and critical temperature T_c. The difference $(x' - x'')$ is the ordering parameter for the critical point of liquid solutions. Critical exponents are often determined by

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having recourse to measurements of the slope of the logarithmic curves obtained from the experimental data, since de l'Hospital's rule and Eq. (1) lead to

$$\beta = \frac{d[\log (x'-x'')]}{d[\log (-\varepsilon)]} . \tag{2}$$

The systems nitrobenzene–n-hexane and nitrobenzene–n-heptane are critical solutions with an upper critical temperature of miscibility. Studies of fundamental physical quantities such as viscosity [10–14], heat diffusivity [15], specific heat [16], diffusion [17], thermal diffusion [18], ultrasonic wave dispersion [19] as well as ultrasonic absorption and velocity [24] versus temperature and concentration give special attention to the critical region of the systems studied. The present paper is aimed at determining the critical exponent β from the phase coefficient curve. We obtained the latter by measuring the viscosity coefficient of the systems. The values of β for the systems studied by us are compared with those for other liquid two-component mixtures.

2. *Experimental results*

Nitrobenzene of purity grade, from VEB Jenapharm Laborchemie Apolda (GDR) was twice distilled under lowered pressure and dried with chromatographic aluminium trioxide. N-hexane of purity grade, from Reakhim, USSR, was distilled twice under normal pressure N-heptane for IR spectrography, produced in Belgium, was distilled once under normal pressure.

The method of viscosity coefficient measurement was used to determine the phase coexistence curve in the (x_2, T_s)-plane, it being our aim to obtain the critical parameters x_c and T_c and thus to calculate the critical coefficients β for the mixtures.

This coefficient, characterizing the temperature-dependence of the order parameter for mixtures with restricted miscibility of the components is to be determined from Eq. (2) once the phase coexistence curve in the (x_2, T_s)-plane is available. The phase separation temperature for each concentration was determined as that corresponding to the viscosity coefficient maximum on the temperature hysteresis of the viscosity.

In this way, the viscosity coefficient method was proved to be well adapted to the calculation of the critical coefficient β. The viscosity coefficients of the systems nitrobenzene–n-hexane and nitrobenzene–n-heptane were measured throughout the entire concentration range in the temperature interval from 289.8 K to 299.2 K using an Ubbelohde viscosimeter, placed in a thermastatizing vessel. The accuracy thus achieved amounted to $\pm 0.5\%$. The measurements were performed at constant temperature in steps of 0.5 deg for temperatures far from T_s and of 0.05 deg at temperatures approaching T_s. The temperature was determined with an iron-constantan thermocouple, with an accuracy of ± 0.02 deg. The restricted accuracy of the temperature readings made it possible to approach T_s to within $-\varepsilon = \frac{T_c - T_s}{T_c} > 2 \times 10^{-4}$. Since the solvents used had relatively low boiling points, the accuracy with which the concentrations were determined is evaluated at $\Delta x_2 = \pm 1 \times 10^{-3}$.

The viscosity coefficient versus temperature dependence $\eta(T)$, studied for various concentrations, was found to exhibit anomalies in the region of the phase separation temperature T_s. As temperature decreases in steps of 0.05 deg, η increases, becomes maximal at T_s, and then decreases steeply. The most marked hysteresis of η occurs for solutions of critical concentration. Fig. 1. shows graphs of $\eta(T)$ for three concentrations of nitrobenzene in *n*-heptane. With the phase separation temperature T_s and corresponding concentration x_2 available, we plotted the phase separation curves (Fig. 2). Applying the law

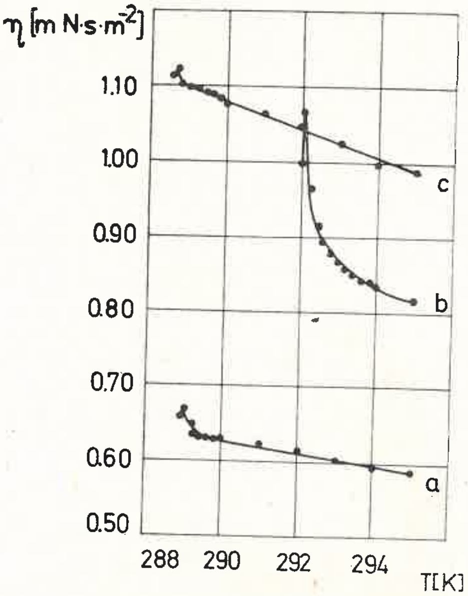
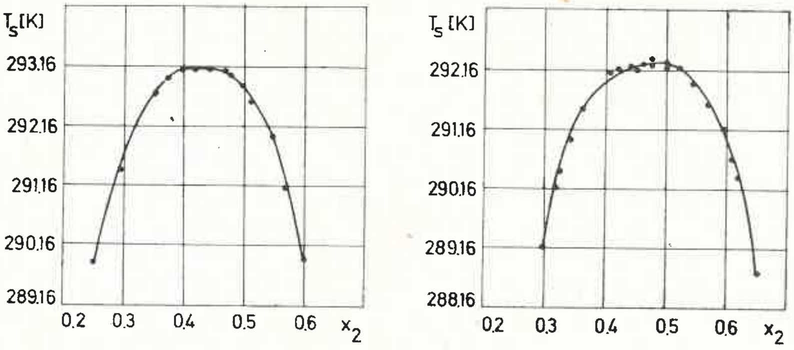


Fig. 1. Viscosity coefficient versus temperature, for selected concentrations of nitrobenzene in *n*-heptane: a – concentration below critical ($f = 0.296$), b – concentration close to critical ($f = 0.476$), c – concentration above critical ($f = 0.649$)



a.

b

Fig. 2. Phase coexistence curve in the plane (x_2, T_s): a – for the system nitrobenzene–*n*-hexane, b – for nitrobenzene–*n*-heptane

of rectilinear diameters of Cailletet and Mathias, we determined the critical concentrations and the critical temperatures corresponding thereto for the two systems. Our results are given in Table I.

TABLE I

Critical temperatures and critical concentrations

System	T_c [K]	x_c
nitrobenzene–*n*-hexane	293.11	0.426
nitrobenzene–*n*-heptane	292.26	0.470

TABLE II

Critical temperatures and critical concentrations for the system nitrobenzene–*n*-hexane, studied by different methods

T_c [K]	x_c	References, method
292.76	0.428	[23]
292.86	0.412–0.432	[17] diffusion
292.16–294.16	about 0.5	[18] thermal diffusion
293.06	0.428	[14] static and dynamic viscosity
292.76	0.428	[19] ultrasonic wave dispersion
294.16	0.370	[24] ultrasonic absorption and velocity
293.36	0.420	[25]
294.14	0.401	[26]
286.96	0.422	[16] specific heat

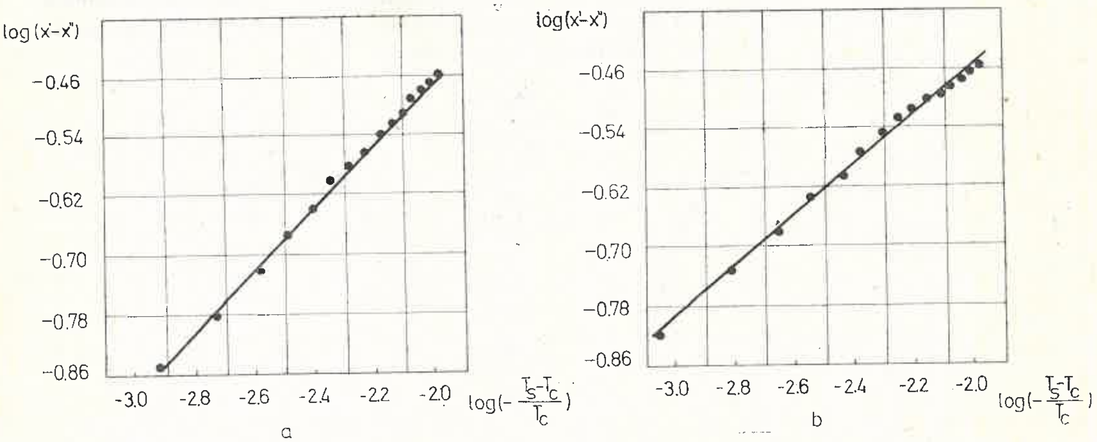


Fig. 3. Curve of log $(x'-x'')$ versus log $\left(-\frac{T_s-T_c}{T_c}\right)$: a — for the system nitrobenzene–*n*-hexane, b — for nitrobenzene–*n*-heptane

From the phase coexistence curve, one can determine the value taken within these limits by β (which defines the temperature-dependence of the ordering parameter $(x'-x'')$) from Eq. (2). Using this dependence, we determined by the least squares method the critical exponents for the two systems, obtaining the following values:

$$\text{nitrobenzene} - n\text{-hexane} \quad \beta = 0.39 \pm 0.04,$$
$$\text{nitrobenzene} - n\text{-heptane} \quad \beta = 0.38 \pm 0.04.$$

Fitting coefficients of the experimental points to formula (2) are equal to $r = 0.995$ and $r = 0.992$ for nitrobenzene – *n*-hexane and nitrobenzene – *n*-heptane respectively. Fig. 3 shows the ordering parameter $(x'-x'')$ as a function of temperature for both systems. Table III gives the critical coefficients β for various critical systems. The values of β obtained by us for the systems nitrobenzene – *n*-hexane and nitrobenzene – *n*-heptane are in good agreement with that derived theoretically on the three-dimensional Ising model and amounting to $\frac{1}{3}$, and are in good agreement with those obtained experimentally by other methods for the critical exponent β of critical liquid solutions.

TABLE III

The values of β exponents for critical systems

System	β
liquids	0.33–0.40 [20, 21]
liquid solutions	0.30–0.38 [3, 4, 8, 20, 21, 22]

The viscosity coefficient method used by us for the determination of the phase separation temperature of solutions with restricted miscibility is appropriate and at the same time, relatively convenient, since the changes in shape of $\eta(T)$ are very easy to observe. We already suggested the possibilities of this method in Ref. [10].

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