Critical phenomena in a polymer–solvent system: slow neutron transmission technique

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The slow neutron transmission technique was used to study the shape of the coexistence curves for polystyrene–deuterocyclohexane solution in the fluctuation region of the critical mixing point. Critical indices and amplitudes of the scaled equation for the coexistence curve were determined. From the data obtained, one can conclude that the system belongs to the same universality class as the Ising model. It is shown that the use of different order parameters did not change the numerical values of critical indices of the coexistence curve and caused only the renormalization of amplitudes. Near the critical mixing point the gravity effect was observed, its temperature range being in agreement with theoretical predictions.

(Keywords: universality class; critical indices; polymer solutions; slow neutron transmission; gravity effect)

INTRODUCTION

Critical phenomena produced by the interaction of drastically growing order parameter fluctuations determine the singularities of thermodynamical properties of real systems near phase transitions and critical points. In the critical region the details of intermolecular interaction become insignificant and the behaviour of physical objects of different natures acquires universal features dependent only on the dimensions of the order parameter (n) and space (d). According to the hypothesis of critical phenomena universality[1,2], systems belonging to the same universality class (n,d) possess an identical set of critical indices and their behaviour should be described by similar equations of state. Recently, the universal behaviour of ordinary solutions near the critical liquid–gas and liquid–liquid points has been established. It has been demonstrated[3,4] that they belong to the same universality class as the Ising model[1,3]. Polymer solutions having highly asymmetric coexistence curves shifted considerably to lower polymer concentrations are interesting from a viewpoint of universality.

In the present work the shape of the coexistence curve for polystyrene–deuterocyclohexane (PS–DCH) solution, plotted as weight concentration (c) against temperature (T), is studied. The measurements were performed in the critical mixing region, taking into account the gravity effect, i.e. macroscopic spatial concentration gradients which can appear in the natural gravitational field due to anomalous growth of osmotic compressibility of a solution when the critical point is approached[5]. The variation of PS concentration in the coexisting phases as a function of temperature was examined for two solutions with PS of different molecular weights by the slow neutron transmission technique, which has been used for studying critical liquid–gas phenomena[6]. Since neutrons are scattered by molecular nuclei of solution components rather than by concentration fluctuation during light scattering and since the coherent component of neutron cross-sections approaching the critical point grows insignificantly[7,8], the above technique can be used for obtaining direct information on coexistence curve shapes, taking into account the gravity effect in the critical region.

From these data, the critical indices and amplitudes of the scaled equation for the coexistence curve were calculated:

$$c^{\pm} = c^{c}(1 \pm B_{c}|\tau|^{\beta_{c}} + B_{c}{}^{1}|\tau|^{\beta_{c}^{1}}) \qquad (1)$$

where c^{+} and c^{-} are the weight PS concentrations in the coexisting phases of the solution, one of which is PS-enriched (+), the other DCH-enriched (−); C^{c} is the critical PS concentration; $\tau = (T - T^{c})/T^{c}$ is the reduced deviation of temperature from the critical temperature T^{c}. The calculated values of β_{c}, β_{c}^{1}, B_{c}, B_{c}^{1} are compared with the corresponding parameters of the equation for the coexistence curve plotted in the volume concentration–temperature diagram obtained in references 9 and 10. The object of the present work is to examine the universality of critical indices and the renormalization of amplitudes, with the weight or volume concentration of polymer solution components taken as an order parameter.

THEORY

Any method for determining the total number of particles present in an equilibrium solution is based on the measurement of some physical parameter dependent on the number of molecules of a given species. Each particle should contribute to the observed parameter with its particular intensity factor[11] determining an error of concentration measurements. For example, the molar extinction coefficient is the intensity factor of spectrophotometry, and the distribution coefficient is that of gas chromatography. The slow neutron transmission technique measures the transmission P, which is a physical parameter dependent on the concentration of particles in a solution and is expressed as a ratio of the intensity I of the neutron beam passed through the cell to the intensity I_0 of the incident beam. In this technique the intensity factor is proportional to the ratio σ_1/σ_2 of bulk cross-sections of slow neutrons

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interacting with the molecules of the first and second solution components.

A parallel beam of monochromatic neutrons with intensity I_0 passing perpendicularly through the cell with solution thickness l is attenuated to intensity I (ref. 12):

$$\frac{dI}{dl}=\kappa I_0 \tag{2}$$

Equation (2) is valid assuming that the neutron beam is not attenuated by the cell walls. The coefficient κ in this equation is dependent on the neutron wavelengths, temperature and concentration chosen. Integrating (2) for a binary solution, we get

$$\ln P=-\kappa l=-N_1\sigma_1 l-N_2\sigma_2 l \tag{3}$$

where N_1, N_2 are the number of particles of species 1 and 2 per unit volume.

Below the critical mixing temperature the binary solution is separated into two phases divided by a meniscus. Each of the phases is a solution containing components of certain concentration varying both with temperature and, if the gravity effect does exist, with height h. The concentration of components in the coexisting phases at different temperatures and heights can be calculated by solving the following set of equations:

$$\begin{gathered}\ln\pi=-\Sigma L\\ \ln P^0=-N_2^0\sigma_2 l-\Sigma L\\ \ln P^1=-N_1^1\sigma_1 l-N_2^1\sigma_2 l-\Sigma L\\ \ln P^i=-N_1^i\sigma_1 l-N_2^i\sigma_2 l-\Sigma L\\ \ln P^{\pm}(h,T)=-N_1^{\pm}(h,T)\sigma_1 l-N_2^{\pm}(h,T)\sigma_2 l-\Sigma L\end{gathered} \tag{4}$$

Here π is the ratio of neutron beam intensities after the cell and ahead of it (empty cell transmission), normalized to monitor indications; P^0 is the transmission of the cell containing a pure solvent (DCH) with an average number of particles per unit volume N_2^0; P^1 is the transmission of the first isotropic calibration PS solution in DCH (determined at $T>T^c$) with an average number of particles of components per unit volume N_1^1, N_2^1; P^i is the transmission of an ith calibration solution; $P^{\pm}(h,T)$ is the transmission of the coexisting phases at $T<T^c$, one being PS-enriched (+), the other DCH-enriched (−); Σ is the macroscopic cross-section[12] of slow neutrons interacting with the cell walls of total thickness L; l is the inside cell thickness (solution thickness).

Assuming an ideal solution approximation, it is easy to get from equation (4)

$$\ln P^i=a+bc^i \tag{5}$$

where $c^i=m_1^i/(m_1^i+m_2^i)$ is the weight PS concentration in an ith calibration solution (m_1, m_2 are the weights of solution components); $a=\ln\pi+[\ln(P^0/\pi)]^{-1}$, $b=(\sigma_1/\sigma_2)[\ln(P^0/\pi)]^{-1}$ are constants for a given experiment. Thus, within the above approximation, the logarithm of solution transmission appears to be directly proportional to the weight PS concentration. To eliminate the unknown value σ_1/σ_2 from the expression for the parameter b, it is necessary to obtain experimentally the calibration plot $\ln P^i\sim c^i$. Then σ_1/σ_2 can be found from the equation

$$\frac{\sigma_1}{\sigma_2}=\frac{1}{n}\sum_{i=1}^{n}\frac{1}{c^i}\frac{\ln(p^i/p^0)}{\ln(p^0/\pi)} \tag{6}$$

where n is the number of calibration solutions. Thus the equation for PS concentration at different temperatures and heights takes on the form

$$c^{\pm}(h,T)=n\frac{\ln[P^{\pm}(h,T)/P^0]}{\sum\limits_{i=1}^{n}\frac{1}{c^i}\ln(P^i/P^0)} \tag{7}$$

To calibrate the experimental unit and to examine the linearity of equation (5), we obtained the plots $\ln P^i=f(c^i)$ in a concentration range $0\leqslant c\leqslant 0.3$ for cells with an inside thickness of $1\leqslant l\leqslant 4$ mm. The calibration measurements showed that in accord with equation (5) the plots of transmission logarithm *versus* PS concentration for the PS–DCH solutions in the above range of concentrations are straight lines with the slope of the lines increasing with l.

An absolute error of concentration measurements at a given l can be determined from the equation $\Delta c=b^{-1}\delta P$, where b is the slope of the calibration line, $\delta P=N^{1/2}/N$ is the statistical error of slow neutron transmission measurements, N is the number of neutrons indicated by the counter during the exposure time t. In our experiment the intensity of neutron beam passed through the cell was 2×10^5 pulses min^{-1}, i.e. $\delta P=0.001$ at the experimental exposure time $t=5$ min. Due to a small error in P measurements and a relatively high contrast of bulk neutron cross-sections of component molecules (the use of the deuterated solvent results in $\sigma_1/\sigma_2\approx 7$), the error in PS concentration measurements was as low as $\Delta c=1.4\times10^{-3}$ for the cell with $l=4$ mm.

EXPERIMENTAL

Samples

The shape of the coexistence curves was studied for two PS–DCH solutions with PS of different molecular weights at the critical component concentrations. To prepare samples, we used PS (Pressure Chemical Co., Pittsburgh) with $M_w=2.3\times10^5$ and 1.3×10^5, $M_w/M_n\lesssim 1.06$ (M_w, M_n are the weight and number average molecular weights), examined on a Du Pont 88 000 Chromatograph, and DCH (Isotope Production Association, Leningrad) with a purity of 99.7% and a degree of deuteration of 99.3% (specification data). Proceeding from a narrow molecular weight distribution of PS, these solutions can roughly be considered as binary solutions.

The critical concentrations of PS–DCH solutions with PS of the above M_w were determined from the literature data by interpolating the plot of critical PS concentration *versus* its molecular weight (*Figure 1*). As can be seen in *Figure 1*, this log–log plot yields a straight line given by the equation

$$\ln\varphi^c=2.04-0.385\ln M_w \tag{8}$$

where φ^c is the critical volume PS concentration, and the numerical values of parameters are calculated by the method of least-squares. The values of φ^c obtained from (8) are converted into weight fractions by

$$c=\frac{\varphi}{\varphi+(1-\varphi)r} \tag{9}$$

where $r=\rho_2/\rho_1$, with ρ_1, ρ_2 being the PS and DCH densities. Thus, $c^c=0.0872$ and $c^c=0.1076$ were chosen as average concentrations of PS–DCH solutions with $M_w(\mathrm{PS})=2.3\times10^5$ and 1.3×10^5.

Procedure and results

The experimental investigations were performed on a research VR-M reactor at the Nuclear Research Institute, Academy of Sciences, Kiev. The variation of PS concentration in the coexisting phases as a function of temperature was studied in the range of reduced temperature $3\times10^{-5}\leqslant|\tau|\leqslant9\times10^{-3}$. To take into account the gravity effect, the concentration was measured as a function of height at each fixed temperature. The PS concentration was calculated by comparing the transmission of the coexisting phases and that of pure DCH by the procedure described above.

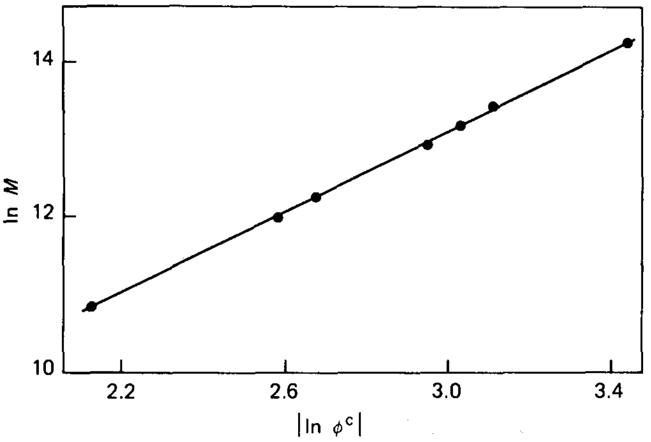

Figure 1 Critical concentration of polystyrene–cyclohexane solution *versus* molecular weight of polystyrene[6,7,25,26]

A schematic diagram of the experimental unit is shown in *Figure 2*. A neutron beam from the active zone of the reactor fell on a biologically shielded monochromator (1). A Pb monocrystal monochromatized a neutron beam with a wavelength of 0.15 nm. A system of collimators (3) formed a narrow neutron beam of small vertical height ($\approx$0.5 mm) which fell on a cell (6) placed in a temperature-controlled container. The intensity of the neutron beam passed through the cell was recorded by a detector counter (7). The intensity of the neutron beam incident on the cell was monitored by a special counter (2). In order to determine the background, motors (4) shut off the incident beam by cadmium shields (5). The temperature-controlled container with thin-walled aluminium cells containing the solutions was placed on a lift, enabling its vertical movement with a minimal spacing of 0.1 mm. A two-stage thermostatting system controlled to ±3 mK was used to maintain the samples at constant temperature over 24 h. The temperature was measured with a platinum resistance thermometer. The temperature gradient along the total height of solution ($H\approx8$ mm) checked by a 16-junction copper–constant thermocouple did not exceed 10^{-4} K.

During the experiment isotherms of solution transmission as a function of height were recorded (*Figure 3*). The time of cell thermostatting necessary for attaining the equilibrium concentration distribution varied from 12 h at $T\ll T^c$ to $\approx$60 h at $T\approx T^c$. The height equilibrium concentration distribution was considered to be attained if repeat measurements of height transmission profiles agreed with the preceding measurements within random errors. As can be seen from *Figure 3*, near the critical mixing temperature ($T^c-T\lesssim0.15$) height distribution of transmission and, consequently, concentration is observed. The critical mixing temperatures determined by the disappearance of transmission jump at the meniscus are $T^c=301.10\pm0.01$ K ($M_w=2.3\times10^5$) and $T^c=297.18\pm0.01$ K ($M_w=1.3\times10^5$). The PS concentration in the coexisting phases for the region with substantial effects of spatial concentration inhomogeneity was calculated from the data on neutron transmission by solution layers immediately adjacent to the meniscus.

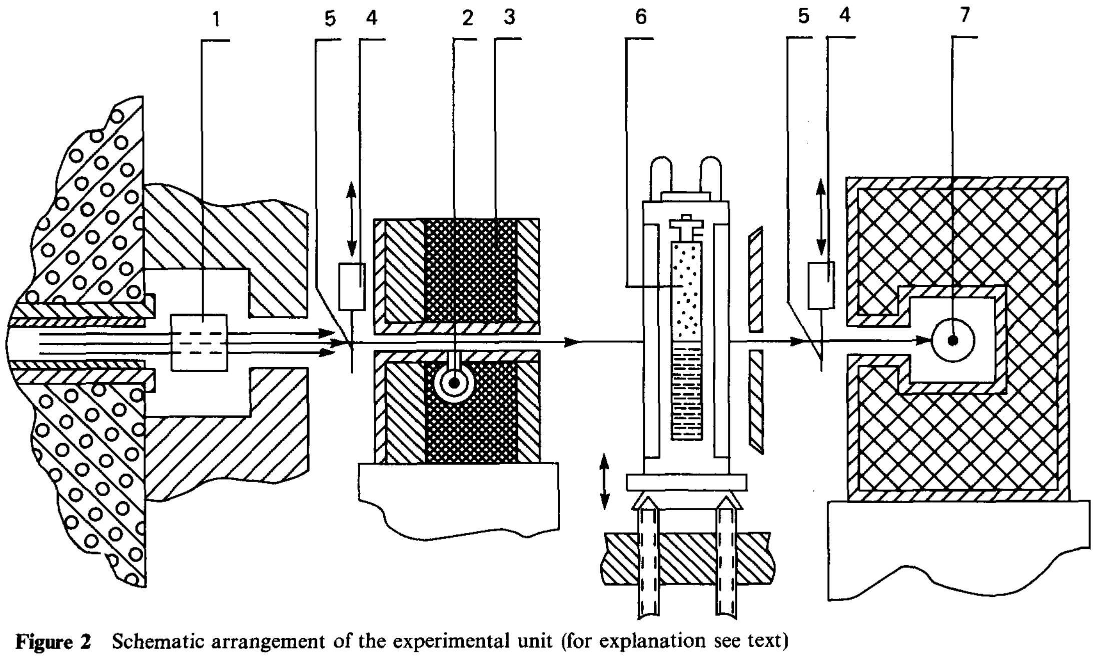

Figure 2 Schematic arrangement of the experimental unit (for explanation see text)

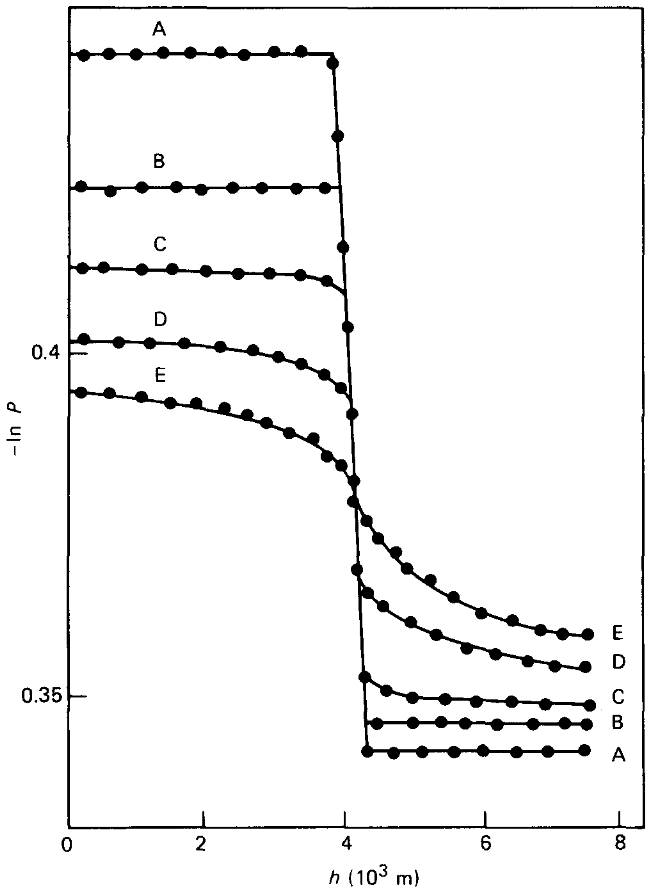

Figure 3 Transmission of PS–DCH solution (M_w(PS)$=2.3\times10^5$) as a function of height at temperature T (K)= : curve A, 298.381; curve B, 300.020; curve C, 300.511; curve D, 300.950; curve E, 301.074

Plots of PS concentration in the coexisting phases as a function of temperature are given in *Figure 4*.

In the temperature range investigated, data for $c^{\pm}=F(\tau)$ were fitted by the relations for the order parameter difference in the coexisting phases:

$$\Delta_c=\frac{(c^{+}-c^{-})}{2c^{c}}=B_c|\tau|^{\beta_c} \tag{10}$$

and for the coexistence curve diameter:

$$D_c=\frac{(c^{+}+c^{-})}{2c^{c}}=1+B_c^1|\tau|^{\beta_c^1} \tag{11}$$

immediately following from equation (1).

The values of critical indices and amplitudes can be calculated from the experimental data by least squares according to (10) and (11): $\beta_c=0.330\pm0.005$, $\beta_c^1=0.89\pm0.06$, $B_c=6.0\pm0.2$, $B_c^1=33\pm4$ ($M_w=2.3\times10^5$); $\beta_c=0.329\pm0.004$, $\beta_c^1=0.90\pm0.06$, $B_c=5.8\pm0.2$, $B_c^1=28\pm4$ ($M_w=1.3\times10^5$). Analysis of residuals exhibited no systematic deviations of calculations from the experimental data, which shows that the data are well fitted by $c^{\pm}=F(\tau)$, taking into account only two terms given by equation (1).

DISCUSSION

Critical indices and amplitudes

To compare the shapes of the coexistence curves in the (c,T) and (φ,T) diagrams, we will use the relations[13] between the critical indices and amplitudes of the equations for the coexistence curves in terms of different order parameters. If, for the order parameter in terms of volume fractions, $\Delta_\varphi(\tau)$ and $D_\varphi(\tau)$ are

$$\Delta_\varphi=\frac{\varphi^{+}-\varphi^{-}}{2\varphi^{c}}=B_\varphi|\tau|^{\beta_\varphi} \tag{12}$$

$$D_\varphi=\frac{\varphi^{+}+\varphi^{-}}{2\varphi^{c}}=1+B_\varphi^1|\tau|^{\beta_\varphi^1} \tag{13}$$

then with the change-over to the new order parameter c related to φ by equation (9)

$$\Delta_c=zB_\varphi|\tau|^{\beta_\varphi} \tag{14}$$

$$\begin{aligned}D_c&=1+zB_\varphi^1|\tau|^{\beta_\varphi^1}-z(1-z)(B_\varphi)^2|\tau|^{2\beta_\varphi}\\&\equiv1+B^{*}|\tau|^{\beta_\varphi^1}-B^{**}|\tau|^{2\beta_\varphi}\end{aligned} \tag{15}$$

should be satisfied, where $z=rc^{c}/\varphi^{c}=r/[\varphi^{c}+(1-\varphi^{c})r]$ (reference 13). But, as mentioned above, the coexistence

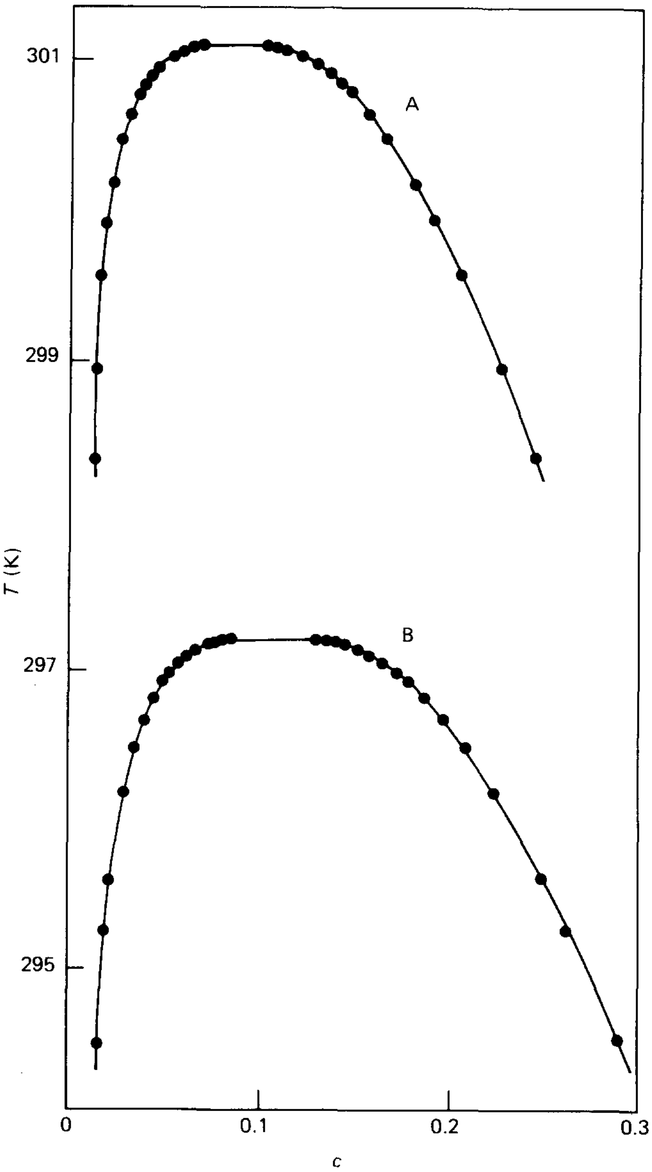

Figure 4 Coexistence curves for PS–DCH solutions: curve A, M_w(PS)$=2.3\times10^5$; curve B, M_w(PS)$=1.3\times10^5$

curves for polymer solutions are highly asymmetric (their ratio B^1_φ/B_φ is an order of magnitude or more greater than that of ordinary solutions). Thus, for a polymer–solvent system the contribution from the first term in equation (15) is predominant, e.g. for PS–CH solution with $M_w = 2 \times 10^5$ we have $B_\varphi \approx 6.6$, $B^1_\varphi \approx 38$ (reference 6) and $z = 0.91$, i.e. in this case $B^*/B^{**} \approx 9 \gg 1$. Thus, in the temperature range investigated, the contribution from the term with the singularity $2\beta_\varphi$ in equation (15) may be neglected. Hence we have

$$D_c = 1 + zB^1_\varphi|\tau|^{\beta^1_\varphi} \tag{16}$$

Therefore it follows from (10), (11), (14) and (16) that the critical indices and amplitudes of the equation for the coexistence curves of polymer solutions in terms of ϕ and c should be related as

$$\beta_c = \beta_\varphi \tag{17}$$

$$B_c = zB_\varphi \tag{18}$$

as well as

$$\beta^1_c = \beta^1_\varphi \tag{19}$$

$$B^1_c = zB^1_\varphi \tag{20}$$

It was shown experimentally in references 6 and 7 that the shape of the coexistence curve for PS–CH solution in the (φ, T) diagram was described by the universal critical index β_φ, its value being in the range 0.327–0.340 and independent of the molecular weight of PS. Within experimental error this value agrees with $\beta_c \approx 0.33$ obtained by us, which confirms equation (17). Using the above experimental values of $B_\varphi, B^1_\varphi, z$ for the PS–CH solution with $M_w(\text{PS}) = 2 \times 10^5$ as well as our values of B_c, B^1_c for the PS–DCH solution with similar $M_w(\text{PS}) = 2.3 \times 10^5$, it is easy to see that relations (18) and (20) are also valid.

Our critical indices β_c are very different from the mean field value of $\beta = 0.5$ and are similar to $\beta = 0.320 \pm 0.15$ obtained by renormalization-group calculations within the Ising model, equations (1) and (3)[14]. From the above and $\beta_c = \beta_\varphi$, we can conclude that the system belongs to the same universality class as the Ising model and that different order parameters chosen for the description of the coexistence curve shape 'do not withdraw' the system from this universality class and cause only the renormalization of amplitudes, which confirms the conclusions of reference 13. The deviation from the law of rectilinear diameter for a given solution confirms the model calculations[15-17] predicting the diameter singularity in the critical region. Within experimental error and in accord with equation (19), the value of $\beta^1_c \approx 0.9$ agrees with $\beta^1_c = 0.92 \pm 0.02$ (reference 7) as well as with the theoretical value of $\beta^1 = 1 - \alpha$, where $\alpha = 1/8$ is the critical index of specific heat.

Gravity effect

In the present work we first observed the gravity effect near the critical mixing point for the polymer–solvent system. The temperature range where concentration gradients occur is wide ($|\tau|_g \lesssim 5 \times 10^{-4}$). It should be noted that the literature data on the realization of gravity effect near the critical liquid–liquid point are contradictory. Both the complete isotropy of binary solutions and the vertical gradients of density and concentration in the critical region are reported[18]. To explain those contradictions, it is suggested in references 19 and 20 that the concentration gradients at constant temperature are formed both due to the mutual diffusion of particles of the system components and due to their sedimentation. While mutual diffusion in the critical region is critically slowing down, particle flow caused by sedimentation increases due to the divergence of the Onsager coefficient when the critical point is approached. According to references 19 and 20, the values of sedimentation-induced concentration gradients, the rate of their formation and the temperature range of their realization are dependent on the sedimentation coefficient S proportional to the difference of equilibrium densities of the components ρ_1 and ρ_2. Assuming an ideal solution approximation, the parameters S and $|\tau|_g$ can theoretically be evaluated by the relations[18,21]:

$$S = \frac{x_2 M_1 M_2 (\rho_1 - \rho_2)}{x_1 M_1 \rho_2 + x_2 M_2 \rho_1} \tag{21}$$

$$|\tau|_g = \left[\frac{A}{4B}\frac{SgH}{x_1 x_2 kT^c}\right]^{1/(\beta+\gamma)} \tag{22}$$

where x_1, x_2 are the molar concentrations of solution components; M_1 is the molecular weight of PS monomer, M_2 is the molecular weight of DCH; A is the amplitude in the singular part of the scaled relation for specific heat; g is the gravity constant; k is the Boltzmann constant; H is the total height of solution in a cell; γ is the critical susceptibility index. Estimation by equation (21) results in $S \approx 25$, which is much greater than the corresponding values for most of the systems which have been investigated[18]. The substitution of experimental values of H, x, T^c, B, β, S and theoretical values for the three-dimensional Ising model $\gamma = 5/4$, $A \approx 1$ (reference 21) in equation (22) yields $|\tau|_g \approx 4 \times 10^{-4}$, which is in good agreement with our results. In our opinion, no gravity effects reported in references 6 and 7 are associated with the specific procedure of the experiment (the solutions were thoroughly mixed by a magnetic stirrer at $T > T^c$, then the temperature was quenched to a given temperature $T < T^c$ at which the polymer concentration in the coexisting phases was immediately measured) or with insufficiently long periods of system observation, which did not exceed several hours.

It should be noted that the polymer–solvent system is characterized by an abrupt diffusion slowdown in the critical region, compared to ordinary solutions. For polymer solutions the diffusion coefficient takes on the form[22]

$$D = T/6\pi\eta\xi \tag{23}$$

where η is the solution viscosity, ξ is the correlation length. In the critical mixing region the latter is dependent on temperature as follows:

$$\xi = R_0\left(\frac{\theta - T^c}{T - T^c}\right)^\nu \tag{24}$$

where θ is the Flory temperature[23], ν is the critical index of correlation length. The correlation length proportional to the large factor R_0 corresponding to polymer coil sizes[24] is the only specific 'polymer' value in equation (23). Therefore at $T \to T^c$ a diffusion-induced particle flow in the polymer–solvent system is slowing down far more rapidly than in ordinary solutions. An extremely abrupt slowdown of diffusion characteristic of the polymer–solvent system in the critical region and a free movement of macromolecules relative to each other because of no entanglement effects at temperatures and concentrations near to the critical values[24], enable us to conclude that the gravity effect in the polymer–solvent system develops by the sedimentation mechanism.

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