

Osmotic compressibility and correlation range of a macromolecular solution near its critical mixing point

N. Kuwahara, J. Kojima, and M. Kaneko

Department of Polymer Science, Hokkaido University, Sapporo, Japan

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From the angular distribution of the scattered-light intensity for polystyrene in cyclohexane near its critical mixing point, we have measured $I_{c,0}/T$ ($I_{c,0}$ being the extrapolated zero-angle scattering intensity), which is directly proportional to the osmotic isothermal compressibility χ_T , and the long-range correlation length ξ . We find $(I_{c,0}/T)^{-1} = B(T/T_{sp} - 1)^{1.24 \pm 0.01}$ and $\xi = (5.83 \pm 0.20)(T/T_{sp} - 1)^{-0.62 \pm 0.02}$ Å along the isochore very near the critical concentration, and $(I_{c,0}/T)^{-1} = (2.3 \pm 0.1)B(1 - T/T_c)^{1.21 \pm 0.02}$ and $\xi = (2.40 \pm 0.12)(1 - T/T_c)^{-0.65 \pm 0.03}$ Å along the concentrated phase and $(I_{c,0}/T)^{-1} = (5.9 \pm 0.3)B(1 - T/T_c)^{1.25 \pm 0.03}$ along the dilute phase of the coexistence curve. In addition, we have determined the value of the critical exponent ($\delta \approx 4.4$) which describes the concentration dependence of the chemical potential μ along the critical isotherm.

I. INTRODUCTION

In early work on macromolecular solutions¹ in the vicinity of their critical mixing points, as well as other critical binary mixtures,² the Ornstein-Zernike³ and Debye⁴ theory (sometimes referred to as the OZD theory) was taken to be an excellent representation of the experimental intensity data where the reciprocal scattered intensity obeys a simple K^2 dependence, in which $K = (4\pi n/\lambda_0)\sin\frac{1}{2}\theta$ with n , λ_0 , and θ being the refractive index of the mixture, the incident wavelength in vacuum, and the scattering angle, respectively. However, recent experiments have shown that plots of the inverse scattered intensity versus K^2 are not represented by straight lines but rather by curves that are a little convex upward, in the very immediate neighborhood of the critical point.⁵ Fisher⁶ proposed a more general scattering formula in order to explain this slightly downward turn of the isotherms for small K . For instance, the scattered intensity I_c due to concentration fluctuations within a critical binary mixture is approximated by the relations

$$\begin{aligned} I_c/T &= A_0 \chi_T (1 + K^2 \xi^2)^{\eta/2 - 1}, \\ I_{c,0}/T &= A_0 \chi_T, \end{aligned} \quad (1)$$

with a small positive critical exponent η whose magnitude indicates deviation from the OZD theory. A_0 includes λ_0^4 , $(\partial n/\partial C)_{P,T}^2$ (C being the concentration expressed in g/cm³), Boltzmann's constant k_B , etc., and is treated as a constant parameter. $I_{c,0}$ is the extrapolated zero-angle (i.e., $K \rightarrow 0$) scattered intensity, and $I_{c,0}/T$ is directly proportional to the osmotic isothermal compressibility χ_T . Furthermore, such a linear relation between $(I_{c,0}/T)^{-1}$ and

$|T - T_c|$ or the long-range correlation length ξ and $|T - T_c|^{1/2}$, as expected from the OZD theory, is not found for the critical mixtures.^{7,8} Then we can write, in terms of the critical exponent concept,

$$\begin{aligned} (I_{c,0}/T)^{-1} &= B(T/T_c - 1)^\gamma, \\ \xi &= \xi_0 (T/T_c - 1)^{-\nu} \end{aligned} \quad (2)$$

along the critical isochore above the critical mixing temperature T_c , and

$$\begin{aligned} (I_{c,0}/T)^{-1} &= \begin{cases} B' (1 - T/T_c)^{\gamma'} \\ B'' (1 - T/T_c)^{\gamma''} \end{cases}, \\ \xi &= \begin{cases} \xi_0' (1 - T/T_c)^{-\nu'} \\ \xi_0'' (1 - T/T_c)^{-\nu''} \end{cases} \end{aligned} \quad (3)$$

along the concentrated and the dilute phases of the coexistence curve below T_c represented by the superscript primes and double primes, respectively. Although the coexistence curves of binary mixtures (particularly, those of macromolecular solutions) are in general less symmetrical with respect to the critical concentration ϕ_c than those of gas-liquid systems, it should be certainly expected that the critical indices γ' and γ'' or ν' and ν'' become asymptotically equivalent.⁹ According to the homogeneity or scaling hypotheses,^{6,10} the relations among the critical indices γ , ν and η and between γ and γ' (γ'') or ν and ν' (ν'') are represented by the equalities

$$\gamma = (2 - \eta)\nu, \quad \gamma = \gamma' (\gamma''), \quad \nu = \nu' (\nu''), \quad (4)$$

while for the OZD theory, $\gamma(\gamma') = 2\nu(\nu') = 1$ and $\eta = 0$.

The purpose of this work is to determine the temperature dependence of both the extrapolated

zero-angle scattering intensity and the long-range correlation length from measurements on the intensity distribution of the scattered light for polystyrene ($M_w = 1.1 \times 10^5$, $M_w/M_n < 1.02$, with M_w and M_n being the weight- and number-average molecular weights, respectively) in cyclohexane near its critical mixing point. In addition, we report on some considerations concerning the scaling law (Fisher's equality, Widom's equality, etc.) and also information concerning the similarity and dissimilarity in the critical behavior of the macromolecular solution to other critical binary mixtures.

II. EXPERIMENTS

Details of sample preparation have been described elsewhere.⁸ The critical point ($T_c = 21.33_0$ °C, $\phi_c = 0.082_5$) was established by phase-equilibrium measurements.⁸ The light-scattering cells used in our studies were made of Pyrex tubing (6-mm i.d.) and were flame sealed. The temperature of a silicone oil thermostat for the sample cell was controlled to within 0.001 °C. The angular dependence of the scattered-light intensity was measured using a specially designed light-scattering photometer with a He-Ne laser (Nippon Electric Co., Model GLG 2016; >15 mW, $\lambda_0 = 6328$ Å) as a light source.⁸ Since alignment errors in the case of a variable-angle instrument lead to significant errors in critical exponents, particular attention was paid to the alignment of the light-scattering instrument.¹¹ The alignment of the photometer was done using a centrifuged colloidal silica solution in a 6-mm i.d. Pyrex cell. The observed scattered intensity after volume corrections ($\sin\theta$) was found to be constant to within $\pm 0.6\%$ over an angular range of 25–140°. Intensity measurements were carried out along the isochore for six poly-

styrene-cyclohexane samples with different concentrations near the critical point and along the concentrated and the dilute phases of the coexistence curve for the sample having the composition ($\phi = 0.081_3$) very close to the critical point over the angular range typically varying from $\theta = 25^\circ$ to $\theta = 140^\circ$ (approximately 20 different angles for each value of $T - T_c$ or $T_c - T$) at 14 values of $T - T_c$ or $T_c - T$ in the temperature range of $0.07 \leq T - T_c \leq 5.805$ °C or $0.131 \leq T_c - T \leq 2.29$ °C. Intensity data were analyzed according to the procedures described elsewhere.⁸ Intensity readings were corrected for volume, attenuation, and background except for dust, reflection, multiple scattering, etc.

III. RESULTS AND DISCUSSION

From the plot of the reciprocal scattered intensity (after only volume corrections) vs K^2 for the sample ($\phi = 0.081_3$) at fixed temperatures slightly above T_c , downward curvature of the isotherms is observed at small angles in the critical region (i.e., $K\xi > 1$) as shown elsewhere,⁸ and hence it is taken to be experimental evidence of the nonzero critical exponent η for the polystyrene-cyclohexane system.¹² Very recently, it has been shown that the penalty for ignoring η is very large at temperatures very near T_c .¹¹ According to Eq. (1), plots of $(I_c/T)^{1/[(\eta/2)-1]}$ vs K^2 should be straight lines whose intercepts at various temperatures correspond to $(A_0^{-1} \epsilon^\gamma)^{1/[1-(\eta/2)]}$ (ϵ being the dimensionless temperature variable $|T - T_c|/T_c$), and the long-range correlation length could be obtained from the relation

$$I_c/I_{c,0} = (1 + \xi^2 K^2)^{(\eta/2)-1}. \quad (1')$$

Although a small positive η surely exists for the polystyrene-cyclohexane system,^{8,12} a reliable evaluation of its magnitude is still difficult. Then we choose $\eta = 0.05$ in the $(I_c/T)^{1/[(\eta/2)-1]}$ vs K^2 plots.

Plots of $(I_{c,0}/T)^{-1}$ vs T for the sample ($\phi = 0.081_3$) both along the isochore and along the concentrated and dilute phases of the coexistence curve are shown in Fig. 1. The value obtained from the intercept of the temperature axis, which is extrapolated from T below T_c , corresponds to the critical temperature ($T_c = 21.33_0$ °C) determined by phase-equilibrium measurements. Since $I_{c,0}/T$ (i.e., χ_T) and ξ along the noncritical isochore would diverge on the spinodal curve introduced by Benedek,¹³ the following extension of Eq. (2) are proposed:

$$(I_{c,0}/T)^{-1} = B(T/T_{sp} - 1)^\gamma, \quad (2')$$

$$\xi = \xi_0(T/T_{sp} - 1)^{-\nu}.$$

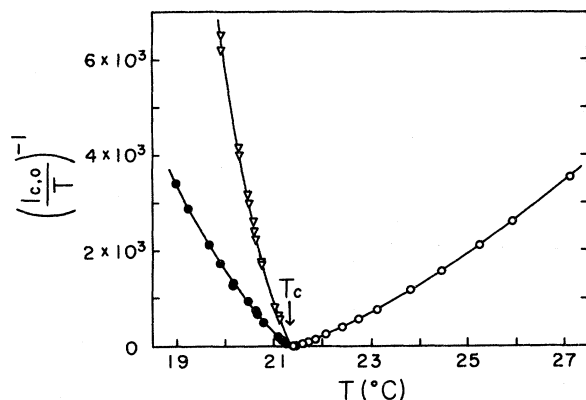


FIG. 1. Plots of $(I_{c,0}/T)^{-1}$ vs T for the sample ($\phi = 0.081_3$). O, isochore; ●, coexistence curve (concentrated phase); ▽, coexistence curve (dilute phase).

Straight lines of slopes γ , $-\nu$, γ' , $-\nu'$, and γ'' in plots of $\log_{10}(I_{c,0}/T)^{-1}$ and $\log_{10}\xi$ as a function of $\log_{10}(T/T_{sp} - 1)$ or $\log_{10}(1 - T/T_c)$ are shown in Fig. 2. These data can be fitted, using $T_{sp} = 21.32_5$ °C and $T_c = 21.33_0$ °C, by the formulas

$$(I_{c,0}/T)^{-1} = (0.437 \pm 0.005) \times 10^6 (T/T_{sp} - 1)^{1.24 \pm 0.01},$$

$$\xi = (5.83 \pm 0.20) (T/T_{sp} - 1)^{-0.62 \pm 0.02} \text{ \AA},$$

along the isochore very near the critical concentration in the temperature range of $0.075 \leq T - T_{sp} \leq 5.81$ °C,

$$(I_{c,0}/T)^{-1} = (1.01 \pm 0.02) \times 10^6 (1 - T/T_c)^{1.21 \pm 0.02},$$

$$\xi = (2.40 \pm 0.12) (1 - T/T_c)^{-0.65 \pm 0.03} \text{ \AA},$$

along the concentrated phase of the coexistence curve in the limited temperature range of $0.131 \leq T_c - T \leq 2.29$ °C, and

$$(I_{c,0}/T)^{-1} = (2.62 \pm 0.06) \times 10^6 (1 - T/T_c)^{1.25 \pm 0.03}$$

along the dilute phase of the coexistence curve in the limited temperature range of $0.205 \leq T_c - T \leq 1.42$ °C. The present results are summarized by $\gamma = 1.24 \pm 0.01$, $\gamma' = 1.21 \pm 0.02$, $\gamma'' = 1.25 \pm 0.03$, $\nu = 0.62 \pm 0.02$, and $\nu' = 0.65 \pm 0.03$. The ratios of the critical constant are given by $B'/B = 2.3 \pm 0.1$ and $B''/B = 5.9 \pm 0.3$ [e.g., $(B' + B'')/2B = 4.1 \pm 0.2$]. According to the Van der Waals equation, the ratio of $B'(B'')/B$ is equal to 2.0, while the experimental result of xenon near its critical region is given by $B'(B'')/B = 4.1 \pm 0.2$.¹⁴

For the behavior of physical quantities where the order parameter participates as a variable, the asymmetric features with respect to the critical concentration are particularly emphasized in macromolecular solutions.⁹ The temperature and concentration of the dilute phase come a little closer to the critical point along the coexistence curve for a change in temperature as compared with the concentrated phase.⁹ Although γ' is slightly different from γ'' in the limited temperature range because of asymmetry of the coexistence curve with respect to the critical concentration, it is expected that γ' and γ'' become asymptotically equivalent in the very immediate neighborhood of the critical point. The present values of γ , γ' (γ''), ν and ν' (ν'') are in excellent agreement with the corresponding values reported for one- and two-component systems, as shown elsewhere,⁵ and consequently these exponents show that the critical-exponent concept and pseudospinodal generalization are equally applicable even to the macromolecule-solvent systems. In our case, the resultant estimated exponents γ , γ' (γ''), ν , ν' , and η are approximately satisfied by the relations $\gamma = (2 - \eta)\nu$,

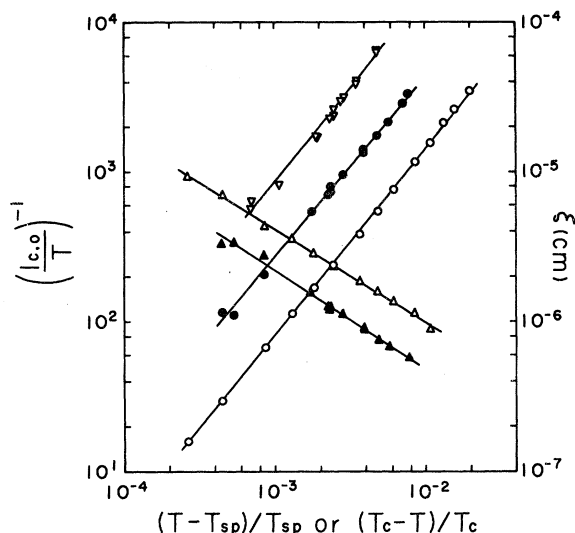


FIG. 2. Log-log plots of $(I_{c,0}/T)^{-1}$ and ξ vs $|1 - T/T_c|$ (or T_{sp}) for the sample ($\phi = 0.081_3$). \circ and Δ , isochore; \bullet and \blacktriangle , coexistence curve (concentrated phase); ∇ , coexistence curve (dilute phase).

$\gamma = \gamma'$ (γ''), and $\nu = \nu'$, derived by the scaling law. However, we feel that further work is still necessary for settlement of these scaling relations for macromolecular solutions.

It is of particular interest to determine the critical exponent δ which describes the concentration dependence of the chemical potential μ at the critical isotherm $T = T_c$. For binary mixtures, in Griffiths's formulation,¹⁵ using quantities made dimensionless by appropriate combinations of critical parameters, the chemical potential $\Delta\mu = \mu(\phi, T_c) - \mu(\phi_c, T_c)$ is an asymmetric function of $\phi - \phi_c$ at the critical temperature and can be expressed as follows:

$$\Delta\mu \propto (\phi^{(+)} - \phi^{(-)})^\delta \text{sgn}(\phi_c - \phi), \quad (5)$$

$$(\partial\mu/\partial\phi) \propto \chi_T^{-1} \propto I_{c,0}^{-1} \propto (\phi^{(+)} - \phi^{(-)})^{\delta-1}, \quad (6)$$

where the superscripts (+) and (-) refer to the concentrated and the dilute phases of the curve of $(\partial\mu/\partial\phi)$ vs ϕ with respect to the critical concentration ϕ_c , respectively. Plots of $I_{c,0}^{-1}$ vs ϕ obtained from intensity measurements at six concentrations are represented by the solid curve for the critical isotherm and by the dashed curves for the isotherms above T_c in Fig. 3. According to Eq. (6), a plot of $\log_{10} I_{c,0}^{-1}$ vs $\log_{10}(\phi^{(+)} - \phi^{(-)})$ should be a straight line with the slope of $\delta - 1$. We find $\delta \approx 4.4$ at $T = T_c$, and its value is in good agreement with the corresponding values reported for one-component systems.¹⁶ Furthermore, the resultant estimated exponents δ , γ' , and β (determined by phase-equilibrium measurements)⁸ are approximately satisfied by the Widom equality

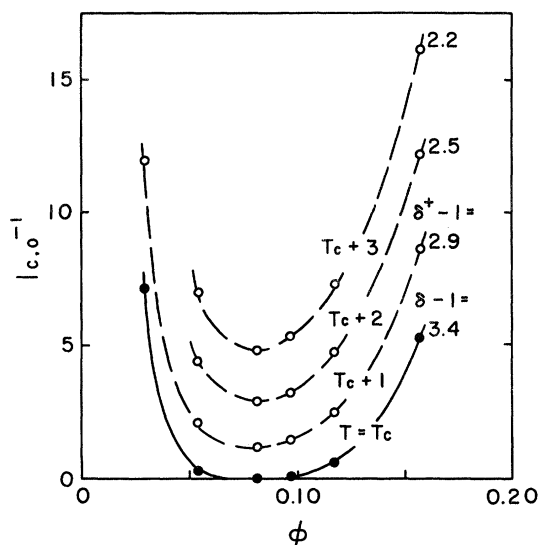


FIG. 3. Plots of $I_{c,0}^{-1}$ [i.e., $(\partial\mu/\partial\phi)$] vs ϕ . The solid curve and the dashed curves represent the critical isotherm ($T=T_c$) and the isotherms above T_c ($T>T_c$), respectively.

$\gamma' = \beta(\delta - 1)$. On the other hand, χ_T at $T=T_c$ obeys the following relation using the critical exponent β^+ which governs the shape of the spinodal curve near its critical mixing point:

$$\chi_T^{-1} \propto I_{c,0}^{-1} \propto (T_c - T_{sp})^{\gamma} \propto (\phi^{(1)} - \phi^{(2)})^{\gamma/\beta^+},$$

where the superscripts (1) and (2) refer to the concentrated and the dilute concentrations on the spinodal curve, respectively. As expected on the

grounds of the homogeneity or scaling hypotheses, the value of $\beta^+ \approx 0.38$ found in the previous work⁸ is essentially the same as the value of $\beta \approx 0.34$, and consequently the following relation is obtained:

$$\gamma/\beta^+ \approx \gamma'/\beta \approx \delta - 1 \approx 3.4.$$

We have determined the exponent δ^+ which describes the concentration dependence of the chemical potential μ at the isotherms above T_c ($T>T_c$). Consequently, it would be expected that the concentration dependence of μ at the isotherms in the high-temperature hydrodynamic region described by $T \gg T_c$ asymptotically coincides with the Van der Waals equation of state (i.e., $\delta^+ = 3$). It should be also noted that the plot of $I_{c,0}^{-1}$ vs ϕ for the critical isotherm is appreciably asymmetric with respect to ϕ_c . Detailed examinations from the viewpoint of the symmetric features will bring to light the asymmetric features found for the behavior of physical quantities described by the order parameter. As macromolecular solutions possess such remarkably asymmetric coexistence, spinodal, and critical isotherm curves, such systems should be very useful in investigating asymmetric features.

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