

Turbidity measurements of critical solutions of *n*-alkanes in nitrobenzene

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A series of turbidity measurements have been made for the critical solutions of *n*-decane, *n*-dodecane, and *n*-tetradecane in nitrobenzene at various wavelengths and temperatures. The turbidity data have been fitted to the Ornstein–Zernike equation to obtain the correlation lengths ζ and the osmotic compressibility χ as functions of reduced temperature t [$t = (T - T_c)/T_c$], and the corresponding critical exponents ν and γ . The values of ν and γ are consistent with the theoretical predictions of 1.241 and 0.63 within experimental uncertainties. The experimental results have also been analyzed to determine the corresponding critical amplitudes ζ_0 and χ_0 when γ and ν are fixed at their theoretical values. Combining our earlier experimental results for systems of *n*-octane and *n*-hexadecane in nitrobenzene, we have determined M exponents f and g , which characterize the power-law dependence of ζ_0 and χ_0 on molar mass of *n*-alkane. The values of f and g are, respectively, 0.21 ± 0.04 and -0.12 ± 0.09 , and are in good agreement with that observed from polymer solutions, which indicates that they are universal for chain molecule solutions of both small molecules and polymers. These universal values support the Landau–Ginsburg–Wilson type model we proposed recently.

Polymer solutions near their critical points are well known to exhibit power-law dependence on both the temperature T and the number N of monomer units or molar mass M of the polymer.^{1–6} Any thermodynamic property of polymer solutions near their critical points may be characterized by two exponents: one is related to T , and the other to M . Recently, we showed that this power-law dependence is applicable for chain-molecule solutions of both polymers and small molecules. From a Landau–Ginsburg–Wilson type model, the following general forms for the power-law dependence have been derived:⁷

$$\Delta\phi = B|t|^\beta \propto \phi_c^{1.865} M^{-b} |t|^\beta, \quad b = 0.29 \quad (1)$$

$$\zeta = \zeta_0 |t|^{-\nu} \propto \phi_c^{-0.85} M^f |t|^{-\nu}, \quad f = 0.18 \quad (2)$$

$$\chi = \chi_0 |t|^{-\gamma} \propto \phi_c^{1.20} M^g |t|^{-\gamma}, \quad g = -0.06 \quad (3)$$

with reduced temperature

$$t = (T - T_c)/T_c \quad (4)$$

where $\Delta\phi$, ζ , and χ are the difference of volume fractions of two coexisting phases, correlation length, and osmotic compressibility (or known as the susceptibility), ϕ_c is the critical volume fraction of the non-chain-molecule component, T_c is the critical temperature, β , ν , and γ are t exponents. The coefficients B , ζ_0 and χ_0 in eqn. (1)–(3) are defined as the amplitudes that are M dependent. This M dependence may be characterized by M exponents b , f , and g .

The value of B in eqn. (1) may be obtained from a coexistence curve of a binary solution,^{8,9} and the amplitudes ζ_0 and χ_0 in eqn. (2) and (3) may be extracted from turbidity measurements.^{10,11} Eqn. (1)–(3) were tested using reported experimental results of polystyrene in methylcyclohexane, polymethylmethacrylate in 3-octanone, and *n*-alkane in *N,N*-dimethylacetamide.^{7,12} The latter is a small chain-molecule system. The values of the exponents M , b , f and g from the theory and above experiments are in good agreement. A series of binary solutions of *n*-alkane in nitrobenzene is another small chain-molecule system, which has a larger difference in refractive indexes between two components and a larger index derivative with respect to the volume fraction ϕ than the

system of *n*-alkane in *N,N*-dimethylacetamide. Thus higher precision in measurements of the coexistence curve and turbidity for the system of *n*-alkane in nitrobenzene may be expected. Therefore this system is a better choice for precise determination of the M exponents and tests of eqn. (1)–(3). A series of determinations of coexistence curves by measurements of refractive index for various *n*-alkanes in nitrobenzene have been reported.^{13–16} A value of 0.28 for b has been obtained, which is in excellent agreement with the theoretical prediction of 0.29. In addition, the measurements of refractive indexes n for this system gave the dependence of n on ϕ and T , and the derivative of n with respect to ϕ , which are necessary for analysis of turbidity data to deduce the critical amplitudes ζ_0 and χ_0 .

In this paper, we report the turbidity measurements for three critical solutions of *n*-decane, *n*-dodecane, and *n*-tetradecane in nitrobenzene. The experimental results are analysed to determine t exponents ν and γ , and the amplitudes ζ_0 and χ_0 . The dependence of these amplitudes on molar mass M of *n*-alkane are examined to obtain the M exponents f and g and are compared with the Landau–Ginsburg–Wilson type model we proposed recently.⁷

Experimental

The nitrobenzene obtained from the Beijing Chemical Factory (A.R. grade) was dried over calcium chloride for five days and distilled slowly under reduced pressure. The middle part of the distillate was collected and passed through a column of dried chromatographic alumina. The purified nitrobenzene was stored in the dark and over a 0.4 nm molecular sieve. The *n*-alkane (mass fraction 0.99) supplied by the Fluka Co. was dried and stored over a 0.4 nm molecular sieve.

The critical concentrations of nitrobenzene have been reported previously.^{13,15,16} The critical mole fractions are 0.574, 0.630, 0.676; the critical volume fractions are 0.415, 0.434 and 0.452 for *n*-decane, *n*-dodecane, and *n*-tetradecane in nitrobenzene, respectively. Samples with critical compositions were prepared in 10 mm path length rectangular cells provided with Ace-thread connections, which allowed them to be sealed. The sample cell was placed in a cubic metal block

Table 1 Critical parameters ξ_0 , χ_0 , ν and γ in eqn. (2) and (3) for *n*-decane, *n*-dodecane and *n*-tetradecane in nitrobenzene

<i>R</i>	ξ_0/nm	$\chi_0/10^{-9} \text{ M}^3 \text{ J}^{-1}$	ν	γ	χ_v^2
<i>n</i> -decane in nitrobenzene					
0.65	0.157 ± 0.003	2.14 ± 0.12	0.67 ± 0.01	1.29 ± 0.01	0.96
0.67	0.161 ± 0.003	2.11 ± 0.12	0.67 ± 0.01	1.29 ± 0.01	0.94
0.65	0.1692 ± 0.0002	2.687 ± 0.008	(0.63)	(1.241)	0.56
0.67	0.1752 ± 0.0002	2.724 ± 0.008	(0.63)	(1.241)	0.55
<i>n</i> -dodecane in nitrobenzene					
0.65	0.169 ± 0.002	2.77 ± 0.08	0.67 ± 0.01	1.26 ± 0.01	0.32
0.67	0.174 ± 0.002	2.76 ± 0.08	0.66 ± 0.01	1.26 ± 0.01	0.31
0.65	0.1681 ± 0.0003	2.746 ± 0.012	(0.63)	(1.241)	1.13
0.67	0.1742 ± 0.0002	2.791 ± 0.008	(0.63)	(1.241)	1.01
<i>n</i> -tetradecane in nitrobenzene					
0.65	0.168 ± 0.003	2.76 ± 0.12	0.66 ± 0.01	1.26 ± 0.01	0.48
0.67	0.173 ± 0.003	2.73 ± 0.12	0.66 ± 0.01	1.26 ± 0.01	0.47
0.65	0.1687 ± 0.0002	2.771 ± 0.008	(0.63)	(1.241)	1.08
0.67	0.1749 ± 0.0002	2.814 ± 0.008	(0.63)	(1.241)	0.97

used as a precisely temperature-controlled thermostat. The temperature fluctuation and the temperature difference in the cell were less than 0.003 K. There was a light-pass tunnel passing through the middle of the sample cell. The block was sat in a spectrometer (Backman DU-7), by which the absorbency A of the sample was measured at various wavelengths. The total turbidity τ_T was then calculated by $\tau_T = -A/L$, where L is the light path length in the sample cell. The accuracy in determination of τ_T was estimated to be *ca.* 0.005 cm^{-1} . The precision in measurements of wavelength is better than 1

nm. The critical temperatures of the samples were determined by observations of the phase-separation points through the tunnel, which were 296.0, 300.4 and 305.0 K for *n*-decane, *n*-dodecane, and *n*-tetradecane in nitrobenzene, respectively. The accuracy in measurement of the temperature difference ($T - T_c$) was about ± 0.005 K.

Besides the contribution to the turbidity from the critical concentration fluctuation τ , the total turbidity τ_T experimentally determined for various wavelengths in this work would include the background contributions τ_b , such as absorption of a solution and the cell windows, the effects of the reflections from the cell windows and the scattering from the dust in the sample, and the contribution of density fluctuation of the fluids. The contribution from the critical concentration fluctuation to turbidity may be expressed by:^{10,11}

$$\tau = \tau_T - \tau_b \quad (5)$$

When the temperature is far from the critical solution point, the contribution from concentration fluctuation to the total turbidity may be negligible. We made a series of turbidity measurements at various temperatures for each sample and found that the total turbidity decreased as the temperature increased and almost remained unchanged when the temperature was 10 K above the critical solution points. The unchanged values of turbidity then were taken as τ_b , and were used to calculate τ using eqn. (5). The turbidity τ , the correlation length, and the osmotic compressibility are related by an integrated form of the Ornstein–Zernike equation^{10,17,18}

$$\tau = (\pi^3/\lambda_0^4)(\partial n^2/\partial \phi)^2 k_b T \chi f(\alpha) \quad (6)$$

where λ_0 is the wavelength of light in a vacuum, k_b is the Boltzmann constant, n and ϕ are, respectively, the refractive index and the volume fraction of the solution. The correlation length enters through the function $f(\alpha)$:

$$f(\alpha) = (2\alpha^2 + 2\alpha + 1)[\ln(1 + 2\alpha)]/\alpha^3 - 2(1 + \alpha)/\alpha^2 \quad (7)$$

with $\alpha = 2(2n\pi\xi/\lambda_0)^2$. From eqn. (2), (3), (6) and (7), the t critical exponents ν and γ , and the critical amplitudes ξ_0 and χ_0 may be extracted by proper non-linear least-squares fittings.

Results and Discussion

The turbidity measurements at various temperatures and wavelengths in the one-phase region of the critical solution

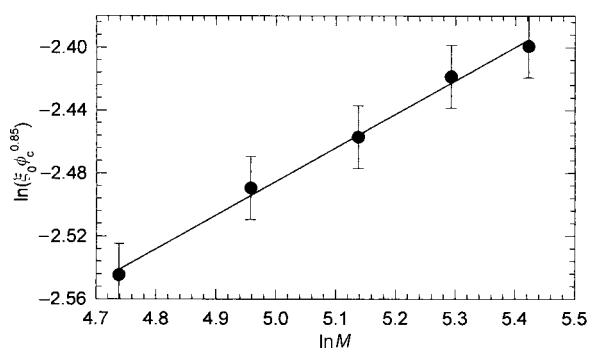


Fig. 1 Ln–ln plot of $(\xi_0 \phi_c^{0.85})$ against M for *n*-alkane in nitrobenzene. (●) Experimental values, and (—) fit of eqn. $\ln(\xi_0 \phi_c^{0.85}) \propto \ln M$.

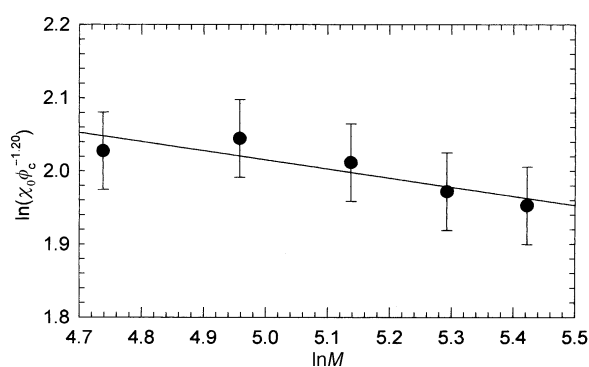


Fig. 2 Ln–ln plot of $(\chi_0 \phi_c^{-1.20})$ against M for *n*-alkane in nitrobenzene. (●) Experimental values, and (—) fit of eqn. $\ln(\chi_0 \phi_c^{-1.20}) \propto \ln M$.

Table 2 The critical amplitudes ξ_0 and χ_0 for *n*-octane and *n*-hexadecane in nitrobenzene^a

<i>R</i>	<i>n</i> -octane in nitrobenzene ^b		<i>n</i> -hexadecane in nitrobenzene ^c	
	ξ_0/nm	$\chi_0/10^{-9} \text{ m}^3 \text{ J}^{-1}$	ξ_0/nm	$\chi_0/10^{-9} \text{ m}^3 \text{ J}^{-1}$
0.65	0.168	2.47	0.168	2.81
0.67	0.174	2.50	0.174	2.85

^a The critical exponents γ and ν were fixed at the theoretical values of 1.241 and 0.63. ^b Ref. 14. ^c Ref. 27.

were conducted for each of the three samples of *n*-decane, *n*-dodecane and *n*-tetradecane in nitrobenzene.[†]

The n and $(\partial n^2/\partial \phi)$ in eqn. (6) are dependent on temperature, volume fraction and wavelength. The dependence of the refractive index on temperature and volume fraction for each of the three samples has been reported.^{13,15,16} Thus the values of n and $(\partial n^2/\partial \phi)$ for any given temperature and volume fraction may be calculated. The dependence of refractive index on wavelength may be expressed as:¹⁹

$$n = a_0 + a_1/\lambda^2 + \dots \quad (8)$$

We assumed that eqn. (8) is valid to solutions with the following relation:

$$a_{1s} = a_{1A}x + a_{1B}(1-x), \quad (9)$$

where, a_{1s} , a_{1A} and a_{1B} are the values of a_1 in eqn. (8) for a solution at given mole fraction x , for $x = 1$, and $x = 0$, respectively. The refractive indices of nitrobenzene and of each *n*-alkane for different wavelengths at given temperatures measured by us and reported by others^{20,21} were used to estimate a_{1s} . The value of n for a solution at a given wavelength was then calculated by eqn. (8) and (9). Finally, the dependence of $(\partial n^2/\partial \phi)$ on wavelength may be estimated by using eqn. (8), (9), and the dependence of the refractive index on volume fraction for a given solution.

In principle, the exponents of f , g , γ and ν in eqn. (2) and (3) may be obtained by fitting the experimental values of turbidity at various temperatures and wavelengths with eqn. (2), (3), (6) and (7). However, in practice, simultaneous determinations of these four exponents are difficult because of the strong correlations between them.^{10,22}

It has been shown that the amplitudes in eqn. (2) and (3) were related by:

$$R = \zeta_0[(B/2)^2/(k_B T_c \chi_0)]^{1/3} \quad (10)$$

with a predicted value^{23,24} of 0.65 from series expansions or 0.67 from ϵ expansions in a renormalization-group setting. With the help of eqn. (10), ζ_0 may be expressed as a function of χ_0 and B . The values of B for each of the three samples were obtained in previous work; they are 1.580, 1.625, 1.636 for *n*-decane,¹³ *n*-dodecane¹⁵ and *n*-tetradecane¹⁶ in nitrobenzene, respectively. The number of optimal parameters then was reduced to 3. A weighted non-linear least-squares programme was used to fit the turbidity data with eqn. (2), (3), (6) and (7) to obtain ν , γ , and ζ_0 . The value of χ_0 was then calculated by eqn. (10). The total uncertainties of τ used in weighting include the uncertainties in measurements of τ_T and τ_b , the standard deviations propagated from measurements of $(T - T_c)$, and the errors in the estimation of the dependence of n and $(\partial n^2/\partial \phi)$ on wavelength. The values of ζ_0 , χ_0 , ν and γ for $R = 0.65$ and $R = 0.67$, respectively, are listed in Table 1. In Table 1, χ_r^2 is the reduced χ -squared²⁵ and the value of χ_v^2 is a measure of the accuracy of the fit and the uncertainties of optimal parameters are the standard errors of fits, including no systematic ones. The total errors including the systematic ones were estimated to be 0.03 and 0.05 for ν and γ , respectively. Thus the optimal values of exponents ν and γ are in good agreement with the theoretical predictions ($\nu = 0.63$, $\gamma = 1.241$)²⁶ within experimental uncertainty and almost no difference for $R = 0.65$ and $R = 0.67$. With the critical exponents ν and γ to be fixed at the theoretical values, the turbidity data were fitted with eqn. (6) and (7) to determine ζ_0 and further to calculate χ_0 by using eqn. (10). The values of ζ_0 and χ_0 are also listed in Table 1. The numbers in the brackets in Table 1 refer to the theoretical predictions. The values of χ_v^2 indicate that the fits with $R = 0.67$ are slightly better than the fits with $R = 0.65$.

[†] Available as supplementary material (SUP 57378; 4 pp.) deposited with the British Library. Details are available from the editorial office.

According to eqn. (2) and (3), \ln - \ln plots of ζ_0 and χ_0 against M may give the M exponents f and g . Recently, we measured the turbidity for *n*-octane¹⁴ and *n*-tetradecane²⁷ in nitrobenzene, and determined the values of ζ_0 and χ_0 when the critical exponents γ and ν were fixed at their theoretical values of 1.241 and 0.63, which are listed in Table 2. Combining these two sets of our earlier experimental results, the values ζ_0 and χ_0 with $R = 0.67$ for five systems then are \ln - \ln plotted against M in Fig. (1) and (2). Least-squares fitting gives $f = 0.21 \pm 0.04$ and $g = -0.12 \pm 0.09$. The same values of f and g were also obtained from the data of ζ_0 and χ_0 with $R = 0.65$ for the five systems. The values of f and g are in good agreement with those observed from polymer solutions,¹² and are consistent with the theoretical predictions⁷ of 0.18 and -0.06 within the experimental uncertainties. It supports the universality of f and g and the Landau–Ginsburg–Wilson type model we proposed recently⁷ for chain-molecule solutions of both small molecules and polymers.

Summary

We have determined the correlation lengths (ξ) and the osmotic compressibilities (χ) for critical solutions of *n*-alkane (with 10, 12 and 14 carbon atoms, respectively) in nitrobenzene within a temperature range of about 2 K from the critical temperature *via* turbidity measurements. The scaling exponents ν and γ of the reduced temperature t were extracted from the experimental results. The average values ν and γ are 0.66 ± 0.03 , and 1.27 ± 0.05 , and are consistent with the theoretical predictions of 0.63 and 1.241. Combining our earlier experimental results for *n*-octane and *n*-hexadecane in nitrobenzene, we determined M exponents f and g , which are 0.21 ± 0.04 , and -0.12 ± 0.09 , respectively. These values are in good agreement with those observed for polymer solutions,¹² indicating that they are universal for chain-molecule solutions of both small molecules and polymers. Thus apart from a system-dependence constant, two universal scaling exponents (those of t and M) fully characterize ξ and χ . It supports the Landau–Ginsburg–Wilson type model we proposed recently.⁷

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