

Observation of 3D-Ising Exponents in Micellar Solutions

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We report measurements of the osmotic susceptibility χ and long-range correlation length ξ of binary mixtures of the nonionic surfactant *n*-dodecyl octaoxyethylene glycol monoether with H₂O and D₂O, near the lower consolute temperature. Regardless of which solvent is used, we find 3D-Ising exponent values for both γ and ν , the exponents which describe the divergences of χ and ξ , respectively.

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Considerable attention has been focused lately on the problem of critical phenomena in binary mixtures of water and nonionic surfactants. Surfactants of the type $\text{CH}_3(\text{CH}_2)_{i-1}\text{O}(\text{CH}_2\text{CH}_2\text{O})_j\text{H}$, referred to as C_iE_j , have been studied extensively by means of dynamic and static light scattering.¹⁻⁸ In a pioneering series of papers,¹⁻⁴ Corti, Degiorgio, and co-workers demonstrated that many phenomena previously thought to be the result of growth in the size of spontaneously formed aggregates of the surfactant molecules (micelles) were in fact the manifestations of a true binary-liquid phase transition corresponding to separation into surfactant-rich and surfactant-poor phases. In particular, they have established that both the intensity of scattered light and the correlation length ξ of the fluctuations responsible for the scattering diverge as the temperature is increased toward the lower critical consolution temperature. However, their work,¹⁻⁴ and that of others,⁵⁻⁷ showed that the values of the critical exponents γ and ν describing the divergences of the osmotic susceptibility χ and correlation length ξ , respectively, were strongly dependent on the surfactant used. Corti, Minero, and Degiorgio² found $\gamma=1.25 \pm 0.03$, $\nu=0.63 \pm 0.03$ for C_6E_3 in H₂O. For $C_{12}E_8$ Corti and Degiorgio¹ measured $\gamma=0.88 \pm 0.03$, $\nu=0.44 \pm 0.03$ in H₂O, $\gamma=1.20 \pm 0.03$, $\nu=0.59 \pm 0.03$ in D₂O, and intermediate values in mixtures of H₂O+D₂O. Subsequently, Wilcoxon and Kalor⁸ have studied $C_{12}E_6$ in H₂O obtaining $\gamma=1.2 \pm 0.1$ and $\nu=0.60 \pm 0.03$, whereas Corti and Degiorgio³ had obtained $\gamma=0.97 \pm 0.05$, $\nu=0.53 \pm 0.05$ for this system.

The observation of continuously variable exponents for $C_{12}E_8$ binary mixtures, which are solvent dependent and may assume values below mean-field values ($\gamma=1$, $\nu=0.5$), has elicited intense theoretical interest, and suggests that these systems do not belong to the 3D-Ising universality class, for which $\gamma=1.24$, $\nu=0.63$. A number of attempts have been made to incorporate these findings within the accepted framework of critical phenomena. Fisher⁹ has shown that crossover phenomena could, in principle, produce decades of apparent power-law behavior, even described by effective exponents below mean-field values. Bagnuls and Bervillier¹⁰ showed that within the framework of ϕ^4 theory, such crossover

could yield apparent power-law behavior over several decades in reduced temperature, but that the crossover was monotonic from mean-field behavior to Ising-type behavior, unless very strong transients due to higher-order terms are present. Reatto¹¹ has argued that the observed behavior could be due to what he termed "quasi-marginalism," i.e., behavior akin to that manifested by certain 2D models which contain marginal interaction terms in their Hamiltonians and have asymptotic exponents dependent on a parameter. The hallmark of quasimarginalism would be power-law behavior with parameter-dependent exponents obeying certain scaling laws, which would be observed in a preasymptotic regime, crossing over to an asymptotic regime characterized by 3D-Ising exponents, possibly only very close to T_c . Finally, Shnidman¹² has, in fact, proposed that the observed dependence of exponents on solvent and surfactant is the result of true marginalism, i.e., that the observed exponents are asymptotic, but parameter dependent.

Since one clear hallmark of all crossover phenomena, including quasimarginalism, would be systematic deviations of data from pure power-law behavior, we originally set out either to observe such deviations, or at least to limit strongly their possible amplitude. We were very surprised then to discover in our initial experimental runs with $C_{12}E_8$ in H₂O, where previous experiment¹ had yielded values for γ and ν which were below mean-field values, that we saw values indistinguishable from those observed in binary mixtures of small molecules. We then repeated the measurements using D₂O as the solvent, and obtained the same results.

The $C_{12}E_8$ was purchased from Nikko Chemicals Co., Ltd. (lot No. 6015), and used without further purification. Distilled water which had been fed through a Milli-Q ion-exchange system (Millipore Co.), or D₂O (Aldrich 99.8 at.% D), was boiled for 20 min to degas it. The sample cells, and all glassware used in our preparation of samples, were cleaned by soaking in Chem-Solv (Mallinckrodt) for several hours, rinsed with water, soaked in a 50-vol% ethanol in 1M NaOH solution in water for several hours, followed by soaking and extensive rinsing with water. These precautions were taken to

minimize any possible contamination of the samples by surfactants other than $C_{12}E_8$. All samples were prepared under nitrogen and filtered with previously flushed Millipore Millex MF GS ($0.22 \mu\text{m}$) filters, allowing no contact with air, since oxygen is known to attack these surfactants,¹³ especially at elevated temperatures, breaking the chains and producing a polydisperse mixture of chain lengths. The sample cells were glass, with a 3-mm inner diameter, and were flame sealed, after freezing of the samples in liquid nitrogen.

We determined the critical concentration from measurements of the coexistence curve using a set of samples differing in surfactant concentration in steps of 0.5 wt.%, and found it to be 3.9 ± 0.2 wt.% in H_2O and 3.2 ± 0.2 wt.% in D_2O . Samples prepared at the critical concentration exhibited very little change in their critical temperatures with time ($\lesssim 1$ mK/month) indicating that no significant sample degradation was occurring. We measured the absolute intensity and angular dependence of light (633 nm) scattered from samples dissolved in H_2O and D_2O , as functions of temperature, covering a range from about 20 K below T_c to within 10 mK of T_c . The angular range covered was from 8° to 126° , corresponding to a scattering wave vector q ranging from 1.9×10^4 to $2.4 \times 10^5 \text{ cm}^{-1}$. For data taken within 100 mK of T_c it was clear that in addition to single scattering, multiple scattering was also present, and we corrected for the effect of double scattering using the method of Shanks and Sengers.¹⁴

The quantity we actually measured was the q -dependent Rayleigh factor $R(q)$ which is related to the

osmotic susceptibility $(\partial c/\partial \pi)_T$ and the correlation length ξ by

$$\frac{Kc}{R(q)} = \frac{(\partial c/\partial \pi)_T^{-1}}{N_A k_B T} (1 + q^2 \xi^2), \quad (1)$$

where $K = (4\pi^2 n^2 / N_A \lambda_0^4) (\partial n / \partial c)^2$, with n the refractive index of the solution of concentration c , and λ_0 the vacuum wavelength of the incident light. In the writing of Eq. (1), the Ornstein-Zernike form of the correlation function has been assumed. This assumption is borne out quite well by the experimental results, as shown in Fig. 1 which is a plot of $Kc/R(q)$ vs q^2 , for data taken in D_2O at a reduced temperature $t \equiv (T_c - T)/T_c$ of 2.67×10^{-3} where there was little evidence of multiple scattering. As may be seen, the data are accurately linear in q^2 . This linearity is not observed, however, in data taken sufficiently near T_c , as shown by the data represented as open circles in Fig. 2, which were measured at $t = 4.72 \times 10^{-5}$. This effect is expected to occur, however, whenever double or higher-order scattering processes contribute significantly to the scattered intensity. Shanks and Sengers¹⁴ have recently developed a very tractable method of calculating the ratio of the double-

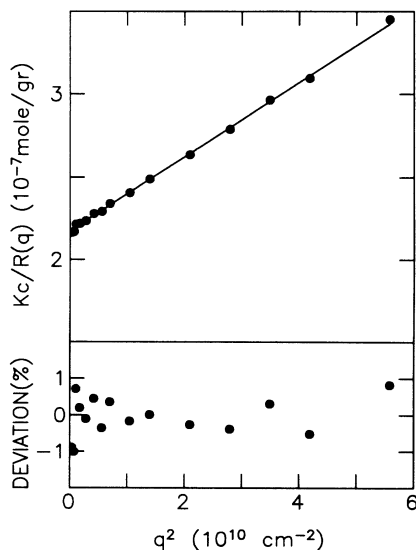


FIG. 1. Plot of the reciprocal Rayleigh factor $Kc/R(q)$ vs the square of the scattering wave vector. Data points were taken at a reduced temperature $t = 2.67 \times 10^{-3}$ for the $C_{12}E_8 + D_2O$ sample. The line is a fit to the data with use of Eq. (1). Deviations of the data from the fitted function are shown in the lower section of the figure.

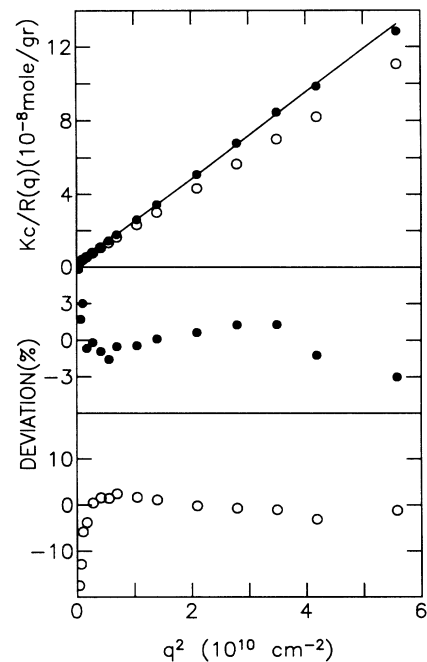


FIG. 2. Same plot as in Fig. 1 for the same sample at a reduced temperature of 4.72×10^{-5} . Filled circles are for data points corrected for double scattering (see text) and open circles are for uncorrected data. The line shown is a fit to the corrected data with use of Eq. (1). The deviations of the data from the fit are shown for the corrected and uncorrected data. The large systematic deviations for the uncorrected data (open circles) are reduced but not eliminated after correction for double scattering (filled circles), indicating the presence of some higher-order scattering.

scattered to the single-scattered intensities (I_D/I_S) for a given total scattering cross section (as determined, e.g., by sample turbidity), assuming the Ornstein-Zernike form of the correlation function. We used this method of calculating I_D/I_S to correct our data iteratively for the effects of double scattering. The steps consisted of the fitting of the raw data by Eq. (1) to determine a rough value of ξ , and the use of this together with the measured sample turbidity to calculate I_D/I_S for each scattering angle. After using these results to correct the raw data, we refitted to determine ξ more accurately, recalculated I_D/I_S , and recorrected and refitted for a third time to obtain the reported values for ξ and $(\partial c/\partial \pi)_T$, which is also determined by the fit. This procedure converged very rapidly; in no case did the second and third values of ξ differ by more than 1%. The results of this correction procedure are shown by the solid circles in Fig. 2. Of course, this procedure cannot correct for the effects of triple and higher-order scattering, and we have no reliable *a priori* method of determining when such processes occur to a significant extent.

Using the procedure described above we measured and corrected our data to obtain the osmotic susceptibility and correlation length as functions of temperature, for $C_{12}E_8$ in both H_2O and D_2O . The results for the susceptibility are shown in Fig. 3, with the uncorrected data

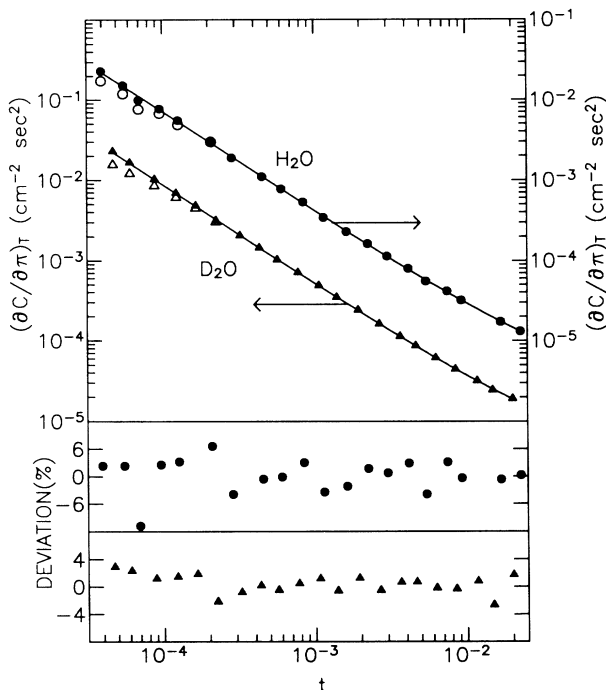


FIG. 3. Osmotic susceptibility $(\partial c/\partial \pi)_T$ vs reduced temperature t . Circles are data for the sample $C_{12}E_8$ in H_2O , triangles for $C_{12}E_8$ in D_2O . Filled symbols are data corrected for double scattering, open symbols are for uncorrected data, and the lines are the result of the fit by Eq. (2). Deviations of the data from the fit are shown in the lower section of the figure.

represented by open symbols and the corrected data by solid symbols. As may be seen, the corrected data for both samples show accurate power-law behavior for $t \lesssim 10^{-3}$ and the slopes of the two data sets are the same to within experimental accuracy. We fitted the data for $(\partial c/\partial \pi)_T$ by a single power law of the form $(\partial c/\partial \pi)_T = \Gamma t^{-\gamma}$, over the temperature range $4 \times 10^{-5} \lesssim t \lesssim 6 \times 10^{-3}$, and obtained $\gamma = 1.21 \pm 0.02$ for the sample in D_2O and $\gamma = 1.20 \pm 0.04$ for the sample in H_2O . Both exponents are close to the 3D-Ising value, $\gamma = 1.241$, and to verify consistency with theory, we also fitted the data over the full reduced temperature range $4 \times 10^{-5} \leq t \leq 3 \times 10^{-2}$ using the form

$$(\partial c/\partial \pi)_T = \Gamma t^{-\gamma} (1 + a_1 t^{\Delta_1} + a_2 t^{\Delta_2}) \quad (2)$$

with Δ_1 and Δ_2 fixed at 0.50 and 1.00, respectively. These fits yielded $\gamma = 1.28 \pm 0.09$ for H_2O and $\gamma = 1.20 \pm 0.05$ for D_2O , both of which are consistent with the 3D-Ising value. To demonstrate this consistency as clearly as possible we repeated both fits with γ fixed at 1.241. It is these fits which are shown by the solid lines in Fig. 3. They yielded

$$\Gamma = (7.75 \pm 0.27) \times 10^{-8} \text{ sec}^2/\text{cm}^2,$$

$a_1 = 0.6 \pm 1.0$, and $a_2 = 20.3 \pm 5.5$ for H_2O , and

$$\Gamma = (9.43 \pm 0.18) \times 10^{-8} \text{ sec}^2/\text{cm}^2,$$

$a_1 = 0.9 \pm 0.5$, and $a_2 = 21.3 \pm 2.8$ for D_2O . In our carrying out of these fits the critical temperature was considered to be an adjustable parameter, and the best-fit values were $78.370 \pm 0.002^\circ \text{C}$ for H_2O and $74.728 \pm 0.002^\circ \text{C}$ for D_2O .

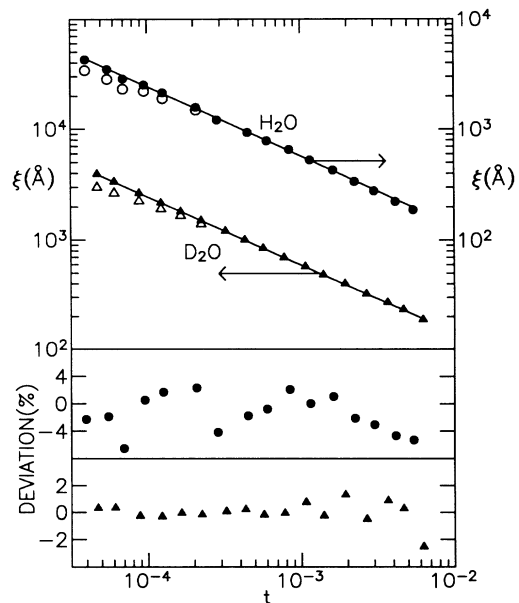


FIG. 4. Correlation length ξ as a function of reduced temperature t . Symbols are as defined for Fig. 3. The lines are the result of the fitting of the data by a single power law.

Our data for the correlation length are shown in Fig. 4, with the uncorrected data being represented by open symbols, and the corrected data by solid symbols. Fits of the corrected data by a simple power law $\xi = \xi_0 t^{-\nu}$ yielded $\xi_0 = 7.5 \pm 0.2 \text{ \AA}$, $\nu = 0.63 \pm 0.01$ for H_2O and $\xi_0 = 8.4 \pm 0.2 \text{ \AA}$, $\nu = 0.62 \pm 0.02$ for D_2O , with the critical temperatures fixed at the values quoted previously. Clearly these results are completely consistent with the 3D-Ising value, $\nu = 0.63$.

On the basis of our data we must conclude that C_{12}E_8 exhibits identical critical behavior in both H_2O and D_2O , and that this behavior is completely consistent with current theory in the form used to understand the behavior of simple fluids and binary mixtures of small molecules. We see no evidence of effects which would make it necessary to invoke the more elaborate theoretical possibilities which have been considered.

Since our results are in such striking contrast to those of Corti and Degiorgio which were obtained on several different samples, we obtained a portion of the C_{12}E_8 sample which they had used most recently, and studied it dissolved in water at the critical concentration they quote. We observed precisely the same precautions as for our own samples and measured ξ as a function of temperature. We obtained results nearly identical to theirs, however. In fact when we fitted the uncorrected data by a simple power law we obtained $\nu = 0.44$, identical to the value they obtained. For the temperature range involved ($6 \times 10^{-5} \leq t \leq 2 \times 10^{-2}$), double scattering, for which they made no correction, has little effect on the measured exponents, and so we believe that

the problem lies in their sample.

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