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Nonuniversal Critical Behavior of Micellar Solutions

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(Received 5 April 1982)

The critical behavior of two nonionic-amphiphile solutions showing a lower consolution point is investigated by laser-light scattering. The critical exponents γ and ν take the values $\gamma = 1.15$ and $\nu = 0.57$ for the system H_2O-C_8Et_4, and $\gamma = 0.90$ and $\nu = 0.44$ for H_2O-$C_{12}Et_8$. Both sets of values are different from those previously found with the system H_2O-$C_{12}Et_6$. The description of the observed nonuniversality of critical micellar solutions may require three-dimensional models which exhibit continuously varying critical exponents.

PACS numbers: 64.60.Fr, 05.70.Jk, 82.70.Dd, 87.15.Da

There is a growing awareness of the importance of critical phenomena for the description of the thermodynamic and transport properties of micellar solutions[1,2] and microemulsions.[3] A detailed knowledge of the phase-transition mechanism in such systems, besides its intrinsic interest, is strongly relevant for the biochemical applications of nonionic amphiphiles[4] and for the chemical engineering use of microemulsions. The experimental results previously obtained with the critical binary mixture water–*n*-dodecyl hexaoxyethylene glycol monoether ($C_{12}Et_6$) have shown that the solution properties in a temperature region extending 20°C below the lower consolution point are mainly determined by critical concentration fluctuations.[1] An unexpected result reported in Ref. 1 is that the measured critical exponents ($\gamma = 0.97 \pm 0.05$, $\nu = 0.53 \pm 0.05$) were found to disagree with those measured in usual critical binary mixtures and predicted by the three-dimensional Ising model. In order to test the interpretation of the previous results and to gain further information on the critical behavior of micellar solutions, we have studied by light scattering two nonionic amphiphiles similar to $C_{12}Et_6$, but with different monomer lengths, namely, C_8Et_4 and $C_{12}Et_8$. Our data show that the values of the critical exponents depend on the nature of the amphiphile. Clearly this result is not compatible with the Ising model or with the equivalent predictions of Wilson renormalization-group theory.[5]

The compound C_8Et_4 was synthetized and purified by Grabo *et al.*[6] High-purity $C_{12}Et_8$ was obtained from Nikko Chemicals, Tokyo. The sample preparation procedure and the light-scattering apparatus are the same as in Ref. 1. The scattering angles used were 22° and 90°.

The phase diagram of C_8Et_4 in H_2O at atmospheric pressure is shown in Fig. 1. The curve of critical micelle concentration (cmc, the concentration above which micelles are formed; this should not be confused with the concentration c_c

at the critical point) which separates the monomeric phase I from the ordinary micellar phase II was obtained from surface tension measurements. The cmc decreases from 3.8 mg/cm^3 at 6 °C to 1.1 mg/cm^3 at 60 °C. The phase boundary which separates phase II from phase III where two isotropic micellar solutions coexist was determined by observation of the critical opalescence.[2,6] It shows a rather flat minimum at $T_c = 40.3 \pm 0.1$ °C and $c_c \simeq 70$ mg/cm^3. It is very interesting to note that the cmc curve does not cross the phase-separation boundary: The two curves seem to merge at high temperatures. The fact that no phase separation is observed below the critical micelle concentration represents clear evidence that the phase separation process involves interactions among micelles with no role played by the monomers. The phase diagram of $C_{12}Et_8$ is similar to that shown in Fig. 1, but $T_c \simeq 76.1$ °C and $c_c \simeq 15$ mg/cm^3, and the cmc curve is shifted toward much lower concentations.

In order to study the divergence of static and dynamic quantities as the critical point is approached we have performed light scattering measurements along the critical concentration lines, in the temperature range 2–40 °C for C_8Et_4 and 40–76 °C for $C_{12}Et_8$. Along these lines we have also measured the turbidity $\tau = (1/L)\ln(I_0/I_1)$, where L is the path length of the incident laser beam in the scattering cell, and I_0 and I_1 are, respectively, the intensity of the laser beam before and after passing through the cell.

The extrapolated scattered intensity at zero scattering angle I_{s0} is related to the osmotic compressibility $(\partial\Pi/\partial c)_{T,p}{}^{-1}$ by the expression

$$I_{s0} = Ac\left(\frac{dn}{dc}\right)^2 k_B T\left(\frac{\partial\Pi}{\partial c}\right)^{-1}, \qquad (1)$$

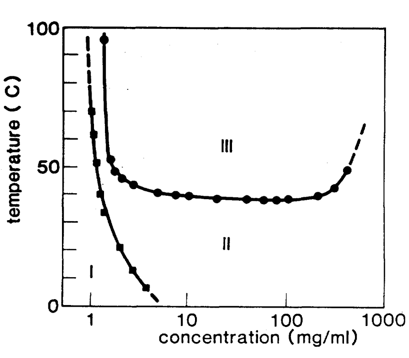

FIG. 1. Phase diagram of C_8Et_4 in H_2O at atomspheric pressure. Region I: monomeric amphiphile in water; region II: micellar solution; region III: two coexisting micellar solutions.

where A is an instrumental constant, dn/dc the refractive index increment, k_B the Boltzmann constant, T the absolute temperature, c the amphiphile concentration in grams per milliliter, and Π the osmotic pressure. The expression for the turbidity τ is obtained by integrating over all angles the light scattering intensity under the assumption that the angular dependence of I_s follows the Ornstein-Zernike relation.[7]

We show in Fig. 2 the behavior of $(\partial c/\partial\Pi)_{T,p}$ measured as a function of $\epsilon = (T_c - T)/T_c$ at the critical concentration c_c for the two solutions. We have also obtained an absolute calibration for the osmotic compressibility, using the turbidity data and the measured refractive index increment ($dn/dc = 0.128$ cm^3/g for C_8Et_4 solutions and $dn/dc = 0.134$ cm^3/g for $C_{12}Et_8$ solutions). The results are well described by the power law $(\partial\Pi/\partial c)_{T,p}{}^{-1} = B\epsilon^{-\gamma}$ with $T_c = 40.285$ °C, $B = (1.17 \pm 0.1) \times 10^{-3}$ cm^{-2} s^2, and $\gamma = 1.15 \pm 0.02$ for the C_8Et_4 solution, and $T_c = 76.075$ °C, $B = 2.60 \pm 0.3$ cm^{-2} s^2, and $\gamma = 0.90 \pm 0.03$ for the $C_{12}Et_8$ solution. The value of B for the C_8Et_4 solution is about five times smaller than the corresponding value for the $C_{12}Et_6$ solution.

The time-dependent part of the measured intensity-correlation function was exponential within

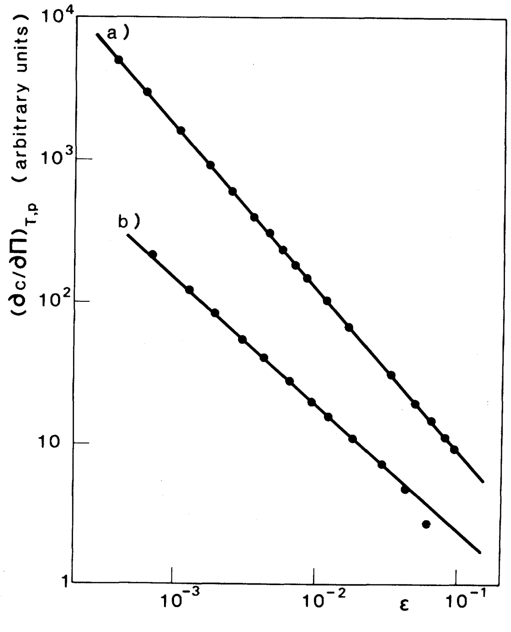

FIG. 2. The osmotic isothermal compressibility of the solution H_2O-C_8Et_4 (curve a) and of the solution H_2O-$C_{12}Et_8$ (curve b) as function of the reduced temperature $\epsilon = (T_c - T)/T_c$ along the critical isoconcentration line.

a very good approximation. The mass-diffusion coefficient D was derived from the time constant τ_c of the exponential as $D=(2k^2\tau_c)^{-1}$ where k is the modulus of the scattering vector. In the range of our dynamic measurements no angular dependence of D was observed. We have measured, by an Ubbelohde flow viscometer, the shear viscosity η, and we have calculated from the experimental data the quantity $\xi'=k_BT/(6\pi\eta D)$. We have plotted in Fig. 3 the behavior of ξ' as a function of ϵ along the critical concentration line of the C_8Et_4 solution. The length ξ' follows a power-law behavior, $\xi'=\xi_0'\epsilon^{-\nu}$, with the best-fit values of the two constants $\xi_0'=0.54\pm0.03$ nm and $\nu=0.57\pm0.03$. The $C_{12}Et_8$ data, not shown in Fig. 3, are of similar quality, and yield $\xi_0'=1.75\pm0.05$ nm and $\nu=0.44\pm0.04$.

In the hydrodynamic regime the correlation range ξ is predicted by the mode-mode coupling theory to be proportional to ξ', $\xi=h\xi'$, with a proportionality constant $h\simeq1$.[8] It was previously found that $h=1.1$ for $C_{12}Et_6$.[1] In this experiment we did not accurately measure ξ. Nevertheless we could obtain h through a fit of the turbidity data by taking the experimental values of $(\partial\Pi/\partial c)_{T,p}^{-1}$ and ξ' and assuming $\xi=h\xi'$, h being the only free parameter in the fit. We obtain $h=1.11\pm0.04$ for both systems. The best-fit curve describes the turbidity data remarkably well, as shown in Fig. 3 for C_8Et_4 solutions, indicating a very good consistency of static data with dynamic light scattering and viscosity data.

The most striking feature of our results is the finding that the values of the critical exponents γ and ν for the H_2O-C_8Et_4 system are different from those measured with the H_2O-$C_{12}Et_8$. Both sets of values are different from those previously reported for the system H_2O-$C_{12}Et_6$.[1] The C_8Et_4 exponents are intermediate between the mean-field theory (MFT) ($\gamma=1$ and $\nu=0.5$) and the three-dimensional Ising model (IM) ($\gamma=1.24$ and $\nu=0.63$) predictions.[9] Since the $C_{12}Et_6$ exponents were found to be close to MFT predictions, there was mentioned in Ref. 1 the possibility that the investigated temperature range was still out of the asymptotic region to which IM applies. Following this line of thought, if the investigated temperature range includes the crossover region between MFT and IM one could perhaps expect to see over a limited temperature interval a power-law behavior with intermediate exponents. Clearly this explanation cannot be applied to the $C_{12}Et_8$ data. Concerning the C_8Et_4 results, we judge very unlikely that the transition from MFT to IM could be so smooth as to give a power-law behavior extending over almost three decades as shown in Fig. 2.

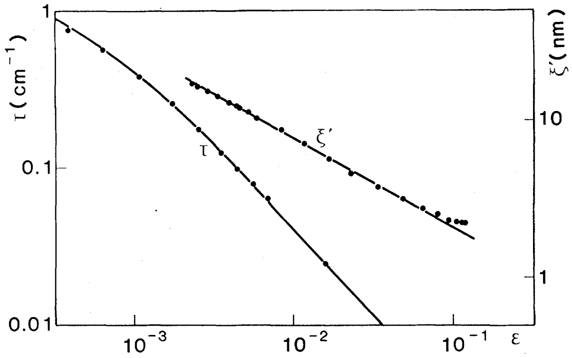

FIG. 3. The turbidity τ and the correlation length ξ' as functions of ϵ along the critical isoconcentration line of the system H_2O-C_8Et_4.

Provided that the measured critical exponents are true asymptotic exponents, our results demonstrate that the critical properties of micellar solutions depend on the nature of the amphiphile. The nonuniversality of the observed critical behavior suggests that critical phenomena in micellar solutions are not of the simple type described by the Ising model.

It is worth mentioning here that in recent years several authors have discussed two-dimensional models, like the eight-vertex Baxter model, which exhibit critical exponents varying continuously as a function of an appropriately defined coupling parameter.[10] Although it is certainly premature to establish a connection between these models and micellar solutions, it is interesting to note that directional interactions of the type considered in the Baxter model may exist in aqueous solutions of polyoxyethylene amphiphiles since the solubility of polyoxyethylene chains in water seems to be due to hydrogen-bond formation between the ether oxygens of polyoxyethylene and water.[11]

As a final comment, it could be argued that the observed values of the critical exponents may somewhat depend on the fact that the critical concentration line is not a path of constant micelle concentration. Indeed, when the total amphiphile concentration is kept fixed, the micelle concentration can change because both the cmc and the micelle size may depend on T. However, the change in the micelle concentration is certainly small because the cmc is always much smaller than c_c, as shown in Fig. 1, and because the micelle size in the critical region is not considerably dependent on T, as found in a recent neutron-scattering experiment on C_8Et_4 solutions.[2]

We are indebted to J. P. Rosenbusch for the gift of the amphiphile C_8Et_4 and to M. Grabo for the cmc measurements reported in Fig. 1. We also thank M. Giglio and L. Reatto for useful comments. This work was supported by the Consiglio Nazionale delle Ricerche–Centro Informazioni Studi Esperienze Contract No.81.00938.02.

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Calculated Binding Properties of Hydrogen on Nickel Surfaces

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(Received 12 March 1982)

An extremely simple calculational method based on the effective medium theory is developed to describe chemisorption systems. It is tested for hydrogen chemisorbed on Ni(100) and (111). Good agreement with experiment is obtained for all quantities calculated: chemisorption energy, equilibrium position, vibrational frequency, and the energy of the hydrogen-induced level. The results indicate that hydrogen may exist under the first Ni layer of Ni(111), but that the binding here is weaker than outside the surface.

PACS numbers: 68.20.+t

In the present Letter, an extremely simple calculational method is presented which allows the calculation of the full potential-energy surface for an atom interacting with a metal surface. The method is tested for the H/Ni(100) and H/Ni(111) chemisorption systems. Contrary to the proposal of Eberhard, Greuter, and Plummer[1] the results do not show hydrogen under the Ni(111) surface to be more stable than on the surface, but it is suggested that at low temperature both sites can be filled. This can explain both the photoemission[1-3] and the low-energy electron diffraction[4] results, as well as the two peaks observed in electron energy-loss spectroscopy.[5] Similar good agreement with experiment is found for H/Ni(100).

The calculational scheme used is a new version of the effective medium theory.[6,7] The binding energy of an atom (hydrogen) to a host (nickel surface) is written[7]

$$\Delta E = \Delta E^{\mathrm{hom}}(\bar{n}_0) - \alpha_{\mathrm{at}}\bar{n}_0 + \delta\int_{-\infty}^{\epsilon_F}\Delta n(\epsilon)\epsilon\, d\epsilon . \qquad (1)$$

For a full derivation of Eq. (1) the reader is referred to Ref. 7. The starting point is the hydrogen atom in a homogeneous electron gas (the effective medium). ΔE^{hom} is the binding energy here. The electron-gas density $\bar{n}_0$ is chosen as an average of the host electron density $n_0(\vec{r})$ over the atom electrostatic potential.[6,7] The second term is an electrostatic term which has been expressed[7] as a constant α_{at}, only depending on the atom in question, times $\bar{n}_0$. The third term is the difference in the sum of the one-electron energies of the atom-induced states [density of