

CRITICAL EXPONENT DOUBLING IN MICROEMULSION SYSTEMS

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Recent experimental results on the power-law divergence with temperature of the correlation length near the critical points of microemulsion systems are examined. It is shown that some of these results with unusually large critical exponents, ν , may be explained in terms of an approach to a double critical point where the oil-phase/water-phase immiscibility loops disappear.

There have been a number of recent studies of phase transitions in microemulsion systems which have demonstrated the existence of critical phenomena [1–5]. These studies have used light or neutron scattering to measure the correlation length and diffusivity of critical fluctuations. The correlation length, ξ , has been found to diverge with a power-law dependence on temperature similar to the behavior seen in the more extensively studied binary liquid and liquid–gas systems [6]. In some cases the critical exponent, ν , of the correlation length was approximately equal to that found in binary and liquid–gas systems [2,3] whereas in other cases it was not [1,2,5]. This is contrary to the expectations of the hypothesis of universality and hence deserves further consideration. In this note, I hope to demonstrate that the results of Nicoli et al. [1,2], who found a rather large exponent value of $\nu \approx 1.13$, can be made to fall in line with universality by recognizing that the approach to the critical point followed by Nicoli et al. was parallel to the coexistence curve and may have been approaching a double critical point.

The correlation length data of Nicoli et al. have been extracted from their published graphs and plotted here in fig. 1. The correlation length data from ref. [1] were obtained from the mutual diffusion constant measured using dynamic light-scattering techniques with the assumptions that the viscosity of the emulsion was that of water. This assumption probably led to some error but should be serviceable. On the other hand, the data from ref. [2] were obtained from light-

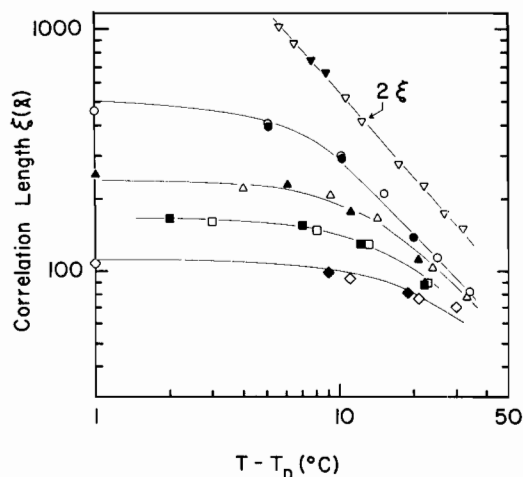


Fig. 1. Correlation length versus the temperature difference from the double critical point temperature, T_D . Symbols for data, NaBr concentration and T_D are: \diamond , 1.3%, 31°C; \square , 1.5%, 33°C; \triangle , 1.6%, 34°C; \circ , 1.7%, 35°C all from ref. [1]; ∇ , 1.77%, 38°C, from ref. [2]. For clarity the 1.77% correlation lengths have been multiplied by two. Open symbols are for $T < T_D$, closed symbols are for $T > T_D$. Curves represent fits to eq. (1) in the text except for the 1.77% data which is the fit given in ref. [2].

scattering asymmetry measurements which involved no assumptions and should be accurate. The two data sets correlate with each other but with some systematic difference and hence had to be plotted on different scales in fig. 1. Fig. 1 plots ξ versus $T - T_D$, where T_D is the temperature at which ξ exhibits a maximum.

Three characteristics of the data are seen. First, for large $T - T_D$ all the data for the different NaBr concentrations approach roughly the same line with slope equal to -1.15 . Second for small $T - T_D$, ξ levels off. Third, one sees symmetry of the data relative to T_D . These three characteristics have also been seen in correlation length and viscosity measurements near the double critical point of pseudo-binary mixtures [7-9]. Hence it is reasonable to propose that analogous double critical point phenomena were being observed in the microemulsion system.

The geometric picture of phase transitions developed by Griffiths and Wheeler [10] may be used to explain exponent doubling. If the approach to the coexistence curve is parallel to the curve, the relevant distance to the critical line becomes, to second order, quadratically dependent on the approach parameter, in this case the temperature difference $T - T_D$. This quadratic dependence doubles the normal exponent. As fig. 3 of ref. [1] shows the approach taken was parallel to the critical coexistence curve of this mixture.

To elaborate on the data further, one must know the degree which the approach with temperature is, or is not, parallel to the critical coexistence curve. This can be measured by the temperature difference, $T_U - T_L$ of the upper and lower phase separation temperatures for a given NaBr concentration. If the system does not phase separate, an effective $T_U - T_L$ can be determined by assuming that the NaBr concentration is as much greater than the double critical point concentration, $x_D \approx 1.77\%$ NaBr, as it is less. Using fig. 3 of ref. [1], I have estimated these effective temperature differences and tabulated them in table 1.

Table 1

The effective upper and lower critical point temperature difference, $\Delta T = T_U - T_L$, and ξ_0 from the fit of eq. (1) to the data for various NaBr concentrations x_{NaBr} . The value of ξ_0 for the 1.77% was obtained from the fit described in ref. [2]

$x_{\text{NaBr}} (\%)$	$\Delta T (^\circ\text{C})$	$\xi_0 (\text{\AA})$
1.3	51	11.5
1.5	37	11.3
1.6	30	10.2
1.7	16	10.5
1.77	0	6.0

Using the ideas of Griffiths and Wheeler [10] applied to phenomena near a double critical point one can show that the correlation length, ξ , should diverge as [8,9]

$$\xi = \xi_0 (t_D^2 + \frac{1}{4} \Delta t^2)^{-\nu} \quad (1)$$

Here $t_D = |T - T_D|T_D^{-1}$, $\Delta t = |T_U - T_L|T_D^{-1}$, and ν is the critical exponent of ξ . T_D is now the temperature at the double critical point. Setting $\nu = 0.63$, I have fit eq. (1) to the data using the value of ΔT given in table 1 and varying only ξ_0 . The fitting lines are given in fig. 1 and fit the data well. Values for ξ_0 agree well and are included in table 1. Data for $[\text{NaBr}] = 1.77\%$ are shown with the fit given by Dorshow et al. [2] to a simple power law, $\xi = \xi_0 t^{-\nu}$, with $\nu = 1.13$. The value of Δt for this mixture could not be estimated but is near zero, hence by eq. (1) the exponent should appear to double. The value of ξ_0 for this concentration does not agree with the other concentrations probably because of the viscosity assumption in the data analysis mentioned above. Given the nature of the data a more careful fit varying ν is not warranted. The fits to eq. (1), however, are quite good and give consistent values of ξ_0 indicating that the double critical point interpretation is very reasonable.

The analogy to double critical point phenomena suggests that closed-loop coexistence curves in the temperature versus oil-water plane of the phase diagram should appear at a NaBr concentration of 1.77%. These loops would grow with increasing NaBr concentration. Numerous other aqueous systems that rely on the unique hydrogen bonding characteristics of water exhibit closed-loop coexistence curves which may be changes by the salting out effects of ionic salts [11].

In light of these conclusions it would be interesting to examine the phase behavior of the CTAB-water-decane-NaBr system further. In particular, does the system indeed display closed-loop behavior which shrinks to a double critical point with decreasing NaBr concentration? Also, Dorshow et al. [2] reported that the critical line had not a quadratic but rather a 2.4 power dependence with temperature, i.e. $x - x_D \propto (T - T_D)^{2.4}$ where $x = \text{NaBr concentration}$. This would imply $\nu \approx 1.13/2.4 = 0.47$. This value is too small compared to other microemulsion work [4,5] and numerous binary and liquid-gas systems. Hence, a new enigma replaces the old. Perhaps more careful studies with the above suggested possibility of double

critical point phenomena are needed before a conclusion on universality can be reached. Finally, data given in fig. 5 of ref. [1] suggest that the coexistence curves in the temperature versus oil–water plane lack symmetry as indicated by the lack of symmetry in ξ versus oil concentration in this system. Here again one must wait for experimental data on the phase diagram before final conclusions are made. Regardless of these irregularities, it still seems reasonable to conclude that the unusually large values of the critical exponents observed by Nicoli et al. [1,2] in the CTAB–water–decane–NaBr microemulsion systems were due to an approach to a double critical point, and when proper accounting for this approach is made, universality of the exponents will be achieved.

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