

Pressure dependence of the critical temperature of microemulsions near a critical end point

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Experimental data for the pressure dependence of the critical temperature (dT_c/dP) are reported for several microemulsions of *n*-dodecane, water, *n*-pentanol, and sodium dodecylsulfate, with critical points along a critical line ending at a critical end point (CEP). Negative dT_c/dP values, substantially decreasing near the CEP, are obtained for all the microemulsions investigated. Using two-scale-factor universality and combining dT_c/dP with correlation-length critical-amplitude ξ_0 values, we also find that a density anomaly is very likely unobservable experimentally. From the negative sign of dT_c/dP it can also be concluded that if there is any critical contribution of the density anomaly to the refractive index *n*, it must be *opposite* to the anomaly recently reported for *n* by Rebbouh and Lalanne [J. Chem. Phys. **90**, 1175 (1989)].

I. INTRODUCTION

Considerable experimental effort has recently been devoted to studying the thermal transport properties,¹ Rayleigh scattering,^{2,3} and refractive index^{4,5} of microemulsions. Although two-component and three-component microemulsion systems belong to the Ising universality class, it does not seem to be the case for some four-component microemulsion systems^{1,3,5} with large correlation-length amplitudes ξ_0 . These microemulsions symbolized as (A), (B), (C), and (D) are composed of *n*-dodecane, water, *n*-pentanol, and sodium dodecylsulfate (SDS), and have critical points on a critical line ending in a critical end point (CEP). Along the critical line, the effective exponents such as the order-parameter susceptibility exponent γ and the correlation-length exponent ν vary continuously from the Ising values ($\gamma_I=1.24$ and $\nu_I=0.63$) to values as low as 0.40 for γ and 0.21 for ν as the composition is varied. The four-component microemulsion systems [symbolized by (A), (C), and (D)], recently investigated by Rebbouh and Lalanne,⁵ showed a substantial critical anomaly in the refractive index. This anomaly could not be characterized in a satisfactory way in terms of power-law expressions and is not well understood at the present time. The purpose of this paper is to investigate whether the refractive-index anomaly in these microemulsion systems is caused by an anomaly in the density or has a different origin. We have carried out extensive measurements of dT_c/dP , for four different compositions of the same microemulsion system composed of *n*-dodecane, water, *n*-pentanol, and SDS. The results for

dT_c/dP could possibly allow a link, via two-scale-factor universality, with the amplitude of the heat-capacity anomaly.

II. THEORETICAL BACKGROUND

The large fluctuations which develop in the microemulsion near the critical point affect the thermodynamic properties including the refractive index *n* and the dielectric constant ϵ . Recent theory of critical phenomena predicts that the mass density ρ and the refractive index *n* in the one phase region near a critical demixing point can be represented by the following expression:^{6,7}

$$\rho = R_1 + R_2 t + R_3 t^{1-\alpha} + R_4 t^{1-\alpha+\Delta} + R_5 t^{1-\alpha+2\Delta} + \dots, \quad (2.1)$$

$$n = N_1 + N_2 t + N_3 t^{1-\alpha} + N_4 t^{1-\alpha+\Delta} + N_5 t^{1-\alpha+2\Delta} + \dots, \quad (2.2)$$

where for a lower critical point (as in our case), *t* is the reduced temperature difference $(T_c - T)/T_c$ with the critical temperature T_c . The critical exponent α characterizes also the divergence of the heat capacity, $C_{p,x}$, at constant pressure *P* and concentration *x*. Δ is the first correction-to-scaling exponent. The recent calculations⁸ based on the renormalization group give $\alpha=0.11$ and $\Delta=0.50$ for systems belonging to the Ising universality class. From Eqs. (2.1) and (2.2), one gets $R_1=\rho_c$ and $N_1=n_c$, where ρ_c and n_c are, respectively, the density and refractive index at the critical point. The heat capa-

city $C_{p,x}$ can be written as^{6,9}

$$C_{p,x} = C_1 + C_2 t + C_3 t^{-\alpha} + C_4 t^{-\alpha+\Delta} + C_5 t^{-\alpha+2\Delta} + \dots \quad (2.3)$$

Asymptotically, close to the critical point, the singular parts of $C_{p,x}$ and of the thermal expansion at constant pressure and composition $\alpha_{p,x} = -\rho^{-1}(\partial\rho/\partial T)_{p,x}$ are related to the slope dT_c/dp of the critical line. Combining Eqs. (2.1), (2.2), and (2.3) we get

$$R_3 = \frac{\rho_c^2 C_3}{1-\alpha} \frac{dT_c}{dP} \quad (2.4)$$

If two-scale-factor universality¹⁰ holds, one can also relate, as in the case of ordinary binary mixtures, the critical heat-capacity amplitude A_v (per unit volume) to the correlation-length amplitude ξ_0 via the universal constant

$$X_c \equiv \frac{A_v \xi_0^3}{\alpha k_B} \quad (2.5)$$

with k_B the Boltzmann constant.

Using Eq. (2.5) and taking into account that $A_v = \rho_c C_3$, one can write the following expression for R_3 :

$$R_3 = \frac{\rho_c k_B X_c}{\alpha(1-\alpha)\xi_0^3} \frac{dT_c}{dP} \quad (2.6)$$

From the above equation it follows that the sign of R_3 is determined by the sign of dT_c/dp .

III. SAMPLE PREPARATION

The microemulsions were made from purified grade *n*-dodecane from Fisher, 99%-pure *n*-pentanol from Aldrich, SDS from Rectapur, and distilled deionized water produced in our laboratory. The microemulsions were prepared by combining the components in the proportions shown in Table I. The prepared microemulsions were left undisturbed overnight. After that, their compositions were adjusted to become critical by carefully adding a drop or two of pentanol or dodecane till the demixing was observed to occur in the middle of the sample. The fact of adding a few drops of one of the components to make the microemulsions critical did not change within the limits of error the initial proportions given in Table I.

IV. MEASUREMENT TECHNIQUE

The experimental study consists in measuring the change of the critical temperature as a function of pressure for four-component microemulsion systems composed of *n*-dodecane, water, *n*-pentanol, and sodium dodecylsulfate, designated, as (A), (B), (C), and (D), containing different ratios X of mass of water to mass of surfactant.

The sample cell used for the dT_c/dP experiment is shown in Fig. 1. The cell is made of Pyrex and is glued at the bottom by epoxy to a stainless-steel Aminco connector. A Teflon ring is placed at the junction of the Pyrex cell and the Aminco connector. A high-pressure tubing originating from the Aminco connector is shaped in a U and then is connected to a compressor for introducing pressures up to 2.0 MPa. The U part of the tubing is filled with mercury to isolate the sample in the cell from the pressurizing fluid. A constant-temperature bath was used to thermostat the sample cell. A calibrated pressure transducer was used to measure pressures while the temperatures were measured with a quartz thermometer (HP model 2801A). Details of the experimental system are shown schematically in Fig. 2.

The precision in the measurement of pressure and temperature is, respectively, $\Delta P = \pm 1$ kPa and $\Delta T = \pm 0.007^\circ\text{C}$. The change in the critical temperature T_c with pressure was noted visually. Following an observation of Clerke *et al.*,¹¹ we used the early appearance of vertical striations and opalescence as an indication that the demixing temperature had been reached. We were careful to always try to identify the same striation pattern in order to avoid as much as possible systematic errors resulting from the measurement procedures. The variation $T_c(P) - T_c(P_0)$, where $P_0 = 1$ atm, is plotted versus $P - P_0$. The slope of the curve gives the value of dT_c/dP .

V. RESULTS AND DISCUSSION

We have measured the change of the critical temperature with applied pressure for several samples of microemulsions. The compositions of the different samples are given in Table I. Several of these microemulsions have the same or nearly the same composition as the ones investigated by Bellocq, Honorat, and Roux,³ Dorion *et al.*,¹ and Rebbouh and Lalanne⁵ with the correspond-

TABLE I. Compositions of the different microemulsion samples, given in weight percent with an uncertainty of ± 0.01 . The ratio $X \equiv [\text{water}]/[\text{SDS}]$ and the observed critical temperature T_c ($\pm 0.007^\circ\text{C}$) are also given.

Sample	<i>n</i> -dodecane	<i>n</i> -pentanol	Water	SDS	X	T_c ($^\circ\text{C}$)
A (sample 1)	58.51	25.80	12.16	3.53	3.445	31.59
A (sample 2)						31.01
B (sample 1)	71.85	15.16	7.89	5.09	1.550	34.50
B (sample 2)						38.40
C	75.75	13.25	6.02	4.98	1.209	33.40
D	78.14	12.07	4.97	4.82	1.031	34.33

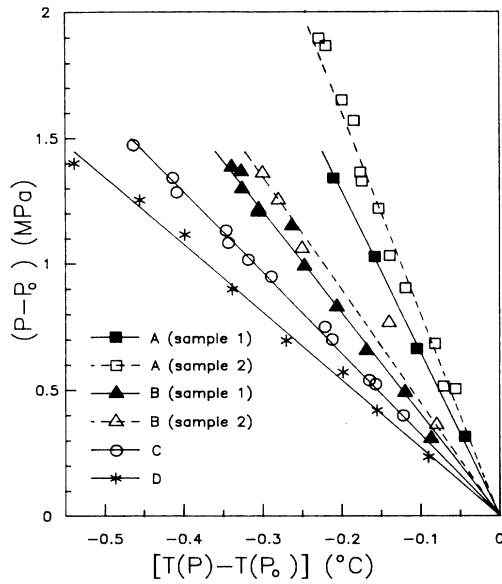


FIG. 3. Variation of the critical temperature T_c with pressure P for several four-component microemulsions of n -dodecane, water, n -pentanol, and sodium dodecylsulfate (SDS). The composition of the different samples is given in Table I. P_0 is a pressure of 1 atm. The slopes of the straight lines through the data correspond with the dT_c/dP values given in Table III.

tion of dT_c/dP which can have either sign. Thus the sign of the amplitude R_3 of the density anomaly depends on the sign of dT_c/dP , which is negative for all microemulsions considered here. This implies that N_3 in Eq. (2.2) should also be a negative quantity¹² provided the refractive-index anomaly is solely due to a density effect. In an n versus T plot a negative N_3 value results in a reduced negative slope on approaching the critical point. With respect to a straight line through the data away from the critical point a positive deviation would be observed. This is exactly *opposite* to what has been observed in the refractive-index data of Rebbouh and Lalanne.⁵ Thus, regardless of the actual values of R_3 , our negative dT_c/dP values necessarily imply that the observed refractive-index anomaly is not a density effect. Moreover, the actual calculated values of R_3 are so small, because of the large ξ_0 values, that such an anomalous deviation from a "linear background" would probably not be observable with present experimental resolution. Indeed a calculation of R_3/ρ_c in Eq. (2.6), using the Ising values^{8,13} $\alpha=0.11$ and $X_c=1.97 \times 10^{-2}$ and the experimental results $\xi_0=27 \text{ \AA}$ and $dT_c/dP=-15.5 \times 10^{-8} \text{ K/Pa}$ for the microemulsion *A*, gives

$$R_3/\rho_c = 2.19 \times 10^{-5}. \quad (5.1)$$

This value is of the same magnitude as obtained for the microemulsion AOT-water-decane.⁴ For that system it was pointed out that the corresponding $R_3 t^{1-\alpha}$ term in Eq. (2.1) would be more than two orders of magnitude smaller than the corresponding $N_3 t^{1-\alpha}$ term in Eq. (2.2)

TABLE III. Pressure coefficient of the critical temperature for the different microemulsions investigated. The errors correspond to three standard deviations.

Sample	X	$10^8(dT_c/dP)$ (K/Pa)
A (sample 1)	3.445	-15.5 ± 1.1
A (sample 2)	3.445	-12.3 ± 0.4
B (sample 1)	1.550	-24.9 ± 0.5
B (sample 2)	1.550	-22.1 ± 1.2
C	1.209	-31.2 ± 0.9
D	1.031	-37.1 ± 1.2

for the refractive index, where only an anomaly of about 1 part in 10^5 above the linear background was measured. As in the cases of AOT-water-decane⁴ and triethylamine-water,¹⁴ the density anomaly cannot explain the observed anomaly in the refractive index of the four-component microemulsions considered here.

An interesting observation which can be made from the data in Table III is that there is a substantial increase in the quantity $\Delta(dT_c/dP)\Delta x$ on approaching the critical end point. This behavior is similar to the large changes observed by Bellocq, Honorat, and Roux³ for ξ_0 , ν , and γ near the CEP. The anomalous behavior of the microemulsions close to CEP has been suggested by Bellocq, Honorat, and Roux³ as being associated with a "lamellar" L_3 phase existing in the phase diagram of sample *D* in the vicinity of the CEP. Moreover, the role of the vicinity of a second critical point has been noted.¹⁵ Recently, Rebbouh and Lalanne⁵ have developed a microscopic explanation for the observed anomalous decrease of the refractive index n near T_c , by assuming the formation of dynamic clusters. This aggregation can create pretransitional merging, leading to local modifications of the structure, and thereby increasing the volume fraction of the dispersed phase. Such modifications could be at the origin of the important change of dT_c/dP near the CEP. It has already been mentioned by Kim *et al.*¹⁶ that pressure contributes to the attractive force between dispersed entities, which could lead to the lowering of the critical temperature.

VI. CONCLUSION

We have carried out the measurements of dT_c/dP for four different microemulsions with varied compositions of n -dodecane, water, n -pentanol, and sodium dodecylsulfate. The experimental values of dT_c/dP have been obtained as a function of X , the ratio of the mass of water to the mass of the surfactant.

An unexpected increase of the influence of the pressure on the critical temperature near the CEP, probably connected to the modifications of the local structure of the microscopic species occurring near this point, is, for the first time, evidenced. It confirms the previously observed anomalies near the CEP.

On the basis of the sign of our results for dT_c/dP we could arrive at the conclusion that if there is any critical

contribution of the density anomaly to the refractive index, it must be *opposite* to the anomaly experimentally measured by Rebbouh and Lalanne.⁵ Using the two-scale-factor universality relation (2.6) for microemulsion away from the CEP, we predict the size of a possible density anomaly connected to the heat capacity at constant pressure anomaly to be very small and very likely unobservable experimentally.

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