A small angle neutron scattering study of density fluctuations at near-critical region and a van der Waals model in a three-component microemulsion

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A small angle neutron scattering investigation near the critical point of D₂O/n-decane/AOT water-in-oil microemulsion was carried out. Although the previous results in literature indicated the Ising behavior, the meanfield behavior for the susceptibility was observed. From the analysis of the susceptibility divergence, binodal point and spinodal point for each composition were given. In order to explain these points, the Gibbs free energy of mixing with the Flory–Huggins interaction parameter is introduced in the framework of the van der Waals model.

I. INTRODUCTION

An oil rich mixture of AOT (2-ethylhexylsulfosuccinate), water, and n-decane is known to form a “water-in-oil” microemulsion, i.e., water droplets coated with AOT film dispersed in n-decane solvent. The droplet size is determined by the water to AOT ratio and is found to be rather constant and monodisperse. This system is homogeneous at room temperature. As the temperature is increased, a miscibility gap appears and the system decomposes into droplet rich and droplet poor domains. At low temperature in the one phase region, density fluctuation of the droplets occurs and becomes stronger at higher temperatures. It determines the critical phenomena near the critical temperature $T_c$. In scattering experiments one measures the correlation length and susceptibility (osmotic compressibility) of the fluctuations which according to $\xi = \xi_0 e^{-\gamma}$ and $\chi = \chi_0 e^{-\gamma}$ become infinite at $T_c$, where $\gamma$ is the reduced temperature and $\gamma$, $\nu$ are critical exponents, which are known for various universality classes such as meanfield approximation ($\gamma = 1$, $\nu = 0.5$) and 3D-Ising model ($\gamma = 1.24$, $\nu = 0.63$). Several authors investigated this phenomenon with small angle neutron scattering (SANS) and with static and dynamic light scattering. As summarized by Rouch et al., the trend of interpretation of the observed critical exponents for the susceptibility and the correlation length is 3D-Ising. However, the critical exponents are somewhat different from the expected values of 3D-Ising, for example, $\gamma = 1.30$ and $\nu = 0.76$ (Honorat et al.).

One has to take into account that the meanfield theory might be plausible in a “near-critical region” for a certain temperature region and that a fluctuation of an order parameter starts to increase exponentially but is not large enough as compared with the order parameter itself. It is expected that the crossover from the mean-field to a non-mean-field behavior is observed when a temperature of a system approaches from the “near-critical region” to the critical region. Schwahn et al. verified the crossover from the mean-field to Ising behavior for PVME/d-PS [poly(vinylmethylether) and deuterated polystyrene] polymer blend system and Bates et al. for PI/PEP [polyisoprene and poly(ethylene-propylene)] system. In micellar systems, there were some experimental results supporting the mean-field behavior. Corti et al. showed the mean-field values of the critical exponents for $CE_j$ and water system. Hamano et al. observed the similar result for the PEGDE (pentaethylene glycol mono n-dodecyl ether) and water system. Note that some results of Corti et al. were refuted by other authors.

From these points of view, we believe that the problem of the critical behavior of the microemulsion system has not yet been solved. We have studied the critical behavior of the three-component microemulsion system in the near-critical region with SANS at RISØ National Laboratory. As a result, the mean-field behavior has been observed for the critical exponent of the susceptibility corresponding to the density fluctuation of droplets. Binodal points and spinodal points have been determined for four compositions near the critical concentration. In order to explain the observed phase diagram including spinodal and binodal points, a phenomenological Gibbs' free energy with the generalized Flory–Huggins parameter has been introduced. In this expression, the interaction between droplets is assumed as the van der Waals type. From our experiment, the values of the Flory–Huggins parameters have been derived and the phase diagram was reproduced.
II. THEORY

A. Scattering functions

In SANS measurements for the three-component microemulsion system, neutrons are sensitive to the differences of scattering amplitudes among D$_2$O, hydrocarbon chains of decane molecules, and lipophilic tails of surfactants, and a layer of head-groups of surfactants. A total scattering intensity is calculated from the formula

$$I(Q) = \frac{\sum \phi_i \Delta \rho^2 \Omega \exp(-\frac{R_g^2 Q^2}{3})}{2\pi^2 \phi_w (1-\phi_w) \Delta \rho^2 dw},$$

(4)

where $I(Q)$ is an observed scattering intensity, $\phi_i$ is the volume fractions of heavy water, hydrocarbon chain of decane and tail of surfactant, $\phi_w$ that of head-group of surfactant, and $\Delta \rho_{AB}$'s are differences of scattering amplitudes between the component $A$ and $B$. Because the head-group layer is relatively thin as compared with the droplet radius, it gives very little differences if Eq. (1) is approximated by

$$I(Q) = \frac{\sum \phi_i \Delta \rho^2 \Omega \exp(-\frac{R_g^2 Q^2}{3})}{2\pi^2 \phi_w (1-\phi_w) \Delta \rho^2 dw}.$$  

Since the total scattering intensity depends only on volume fractions of components and is invariant over all temperature, the observed intensity $I^{obs}(Q)$ can be normalized by $I^{total}$ in order to avoid artifacts in experiments. It is known that the normalized intensity $I(Q)$ is a product of two parts, a form factor of a droplet $F(Q)$ ($\AA^3$) and a structure factor $S(Q)$ [no dimension] as

$$I(Q) = \frac{F^{obs}(Q)}{\int Q^2 F^{obs}(Q) dQ} = F(Q)S(Q)(\AA^3).$$

(3)

Kotlarchyk et al. have explained the scattering profiles of this system ($3 \times 10^{-3} < Q < 3.5 \times 10^{-2} \AA^{-1}$) by computing the form factor assuming a Schultz size distribution and by computing the structure factor adopting a mean spherical approximation model with a hard core plus attractive Yukawa tail as the potential between droplets. They concluded that the droplet size changes very little with varying temperature or composition and that the structure factor could be approximated by the Ornstein–Zernike form in very low-$Q$ region.

In the region where the critical scattering appears significantly ($Q < 1/R$, where $R$ is a droplet radius), the effect of the polydispersity on the form factor can be neglected because the form factors for various droplet sizes has a value of almost unity in this $Q$-region. On the other hand, Rička et al. revealed that the polydispersity of this system is very low and that the system can be thought rather monodisperse. Thus a simple Guinier approximation is applied as the form factor for all series of the data

$$F(Q) = \frac{I^G \exp(-\frac{R_g^2 Q^2}{3})}{\int Q^2 F^{obs}(Q) dQ}$$

$$= \frac{\phi_w \Delta \rho^2 \Omega \exp(-\frac{R_g^2 Q^2}{3})}{2\pi^2 \phi_w (1-\phi_w) \Delta \rho^2}$$

$$\Omega \exp(-\frac{R_g^2 Q^2}{3}) = \frac{\phi_w \Delta \rho^2 \Omega \exp(-\frac{R_g^2 Q^2}{3})}{2\pi^2 \phi_w (1-\phi_w) \Delta \rho^2},$$

(4)

where $I^G$ is the forward scattering defined by the Guinier approximation, $R_g$ the radius of gyration, and $\Omega$ the volume of each droplet.

For large $Q$ region ($Q > 1/R$), the Porod theory is applied and the form factor is approximated as

$$F(Q) = P' Q^{-4}$$

with

$$P' = \frac{2\pi (\phi_w/\Omega) \Delta \rho^2}{\int Q^2 F^{obs}(Q) dQ} = \frac{3}{\pi (1-\phi_w) R^3}$$

(3)

where $P'$ is the normalized Porod constant, $S$ is the area of a droplet surface, and the shape of a droplet is assumed to be spherical. Because the droplet–droplet correlation, which is related to the density fluctuation, becomes so significant that one can neglect another kind of correlation at the near-critical region, a simple Ornstein–Zernike form is applied as a structure factor,

$$S(Q) = S(0)/(1+4\pi^2 Q^2).$$

(6)

B. The van der Waals theory

Because charged ions leave head-groups into water pool, a density fluctuation of ions is supposed to occur inside droplets for the ionic three-component microemulsion system. Therefore the assumption of the van der Waals interaction between droplets is relevant. Since the approximation used in the van der Waals model is known to be equal to the mean-field approximation, it can be applied to explain the mean-field critical behavior. The Gibbs’ free energy for the van der Waals gas is known as

$$F = N \psi(T) - N k_B T \ln \left[ \frac{e}{N} (V-Nb) \right] - \frac{N^2}{V} a$$

(7)

with $\psi(T)$, the free energy per particle of ideal gas, $N$, the number of particles, $b$, the effective volume of each particle, and $a$, an integrated potential energy of van der Waals force. By normalizing it in dimensionless form, one gets

$$f = \frac{F}{(V/N) k_B T}$$

$$= \frac{\phi}{\Omega} \left[ \frac{1}{\phi} b' + c(T) \right] - \phi^2 \chi(\phi,T),$$

(8)

using variables $\phi$, a volume fraction of surfactant and water which is the order parameter in this system, $\Omega \equiv \phi V/N$, a volume assigned to each particle, and $b' \equiv b/\Omega$, effective volume factor of each particle, where $c(T)$ includes the $\phi$-independent terms. The first term describes the entropy of mixing, and the third the excess enthalpy of mixing term.
with the Flory–Huggins parameter, $\chi(\phi,T) = a/\Omega k_B T$.
For a system with a lower critical solution temperature (LCST), this parameter should be written as

$$\chi(\phi,T) = \frac{\chi_h(\phi)}{T} - \chi_e(\phi),$$  \hspace{1cm} (9)$$

where $\chi_h(\phi)$ is an enthalpic part and $\chi_e(\phi)$ is an entropic part. From the general thermodynamic relationship between the forward scattering and the Gibbs' free energy, we have

$$S(0)^{-1} = 2\int_0^1 \left( \gamma_x - \gamma_y \right),$$  \hspace{1cm} (10)$$

with

$$\gamma_x(\phi) = \frac{1}{2\Omega(1 - \phi^{b^*})^2},$$  \hspace{1cm} (11)$$

$$\gamma_y(\phi) = \frac{\chi_h(\phi)}{T} - \chi_e(\phi),$$  \hspace{1cm} (12)$$

where $\gamma_x$ and $\gamma_y$ are called the generalized Flory–Huggins parameters. Note that we have put $d\Omega/d\phi = 0$ because the radius of a droplet is supposed to be independent of $\phi$. For a system with LCST, both the parameters $\gamma_x$ and $\gamma_y$ must be negative. From these equations, the temperature dependence of $S(0)$ yields

$$S(0)^{-1} = 2\gamma_x \left( \frac{1}{T_1} - \frac{1}{T_s} \right),$$  \hspace{1cm} (13)$$

where the spinodal temperature $T_s$ is given by

$$T_s = \gamma_x/(\gamma_e + \gamma_x).$$  \hspace{1cm} (14)$$

Therefore, spinodal points $T_s$ and the generalized Flory–Huggins parameters $\gamma_x$ and $\gamma_y$ can be determined experimentally if the system follows the mean-field behavior.

When a composition of a system is off-critical, a phase separation occurs at a binodal point before reaching a divergent spinodal point. At the binodal point, the forward scattering begins to decrease, because the coexisting compositions at the same temperature must be more apart from their divergent spinodal points than that before the decomposition. Thus one will see a “kink” at a binodal point in a plot $S(0)^{-1}$ vs $T^{-1}$.\(^\text{9}\) This is an unambiguous way to define a binodal point experimentally.

### III. EXPERIMENT

All the samples were prepared at the same water-to-AOT ratio as the 3/5/95 composition microemulsion, which means 3 g of AOT is dissolved in 5 ml of water and 95 ml of n-decane.\(^\text{2}\) The surfactant and water mixture volume fraction against the n-decane, $\phi$, is the order parameter, because it is directly proportional to the droplet density in the whole system (see Fig. 1). The 99% AOT purchased from Aldrich Chemical Company was used for our examination without further purification, because impurities only influence the absolute value of the transition temperature.\(^\text{6}\) The samples were prepared within 5 days after opening a seal of the bottle to avoid a chemical change of surfactant molecules. The 99.8% heavy water supplied by Molec and the 99% n-decane by Aldrich Chemical Company were used without any treatments. All the experiments were performed within one day, after the sample preparation to avoid the hydrolysis of AOT. They were contained in a niobium cell with 1 mm thick quartz window, and placed in an electric furnace controlled within 0.1 K by a computer.

SANS measurements were carried out with the SANS spectrometer in RISØ National Laboratory. The 15 and 4 Å incident neutron beams, taken from the cold neutron source and monochromized by the mechanical velocity selector, were used for the low-$Q$ region ($2.3 \times 10^{-3} < Q < 1.7 \times 10^{-2}$ Å$^{-1}$) and the high-$Q$ region ($1.7 \times 10^{-2} < Q < 6.6 \times 10^{-2}$ Å$^{-1}$), respectively. The wavelength resolution was 18%. The multiwire two-dimensional position sensitive proportional counter placed at 6 m from the sample position was used. The raw data were radially integrated and calibrated into differential cross sections vs wave number.

![Figure 1](https://example.com/fig1.png)

**FIG. 1.** Ternary phase diagram at room temperature. Compositions are indicated by volume percent. The dashed arrow denotes the constant AOT and water molar ratio, which is thought to be the order parameter $\phi$ in this study. Open squares are the compositions used in our experiment.

![Figure 2](https://example.com/fig2.png)

**FIG. 2.** The scattering profile for $\phi=0.1031$ at $T=295.72$ K in the Guinier plot is presented. The straight line indicates the fitted Guinier approximation.

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IV. EXPERIMENTAL RESULTS AND ANALYSIS

Following the results discussed in the Sec. I, the droplet shape is assumed to be spherical. The droplet size was derived from the observed scattering curve assuming the Guinier approximation of Eq. (4). Figure 2 shows the Guinier plot for $\phi=0.1031$ at the temperature far from the phase separation point. In this plot we find a wide straight line region corresponding to the Guinier formula. From the slope of the fitted straight line, a radius of gyration $R_G$ was derived to be 53.4 Å. Assuming a spherical shape, the radius is calculated to be 68.9 Å. The radius was also calculated from an intercept on the ordinate of the straight line, $F(0)$, with Eq. (4), resulting that the droplet radius is 75.3 Å, which coincides with the value from $R_G$ with the accuracy of $\sim 10\%$. From these evidences, droplets can be supposed to be rather monodisperse. As concerns the temperature dependence of a droplet radius, we found that the droplet radius tends to decrease with increasing temperature. In Fig. 3, the Guinier radius for $\phi=0.1031$ is denoted and one can see the Guinier radius depends linearly upon temperature with a rate of $-0.33 \mu \text{K}^{-1}$. We assumed the same rate for all the composition for the form factor calculation.

Figure 4 shows the temperature variations of the profiles for $\phi=0.1031$. At the high-$Q$ region ($Q > 4 \times 10^{-2} \text{ Å}^{-1} \sim 1/R$), all the scattering curves followed the $Q^{-4}$ law, and the Porod constants were almost the same for all the temperatures.

In Fig. 5, typical temperature variations of the structure factor for $\phi=0.1031$ are given in the Zimm plot. If $S(Q)$ follows Eq. (6), the scattering profile must be a straight line with a slope $S_0^{-1}$ and an intercept on the ordinate at $S_0^{-1}$. In other compositions, $\phi=0.0744, 0.0950$, and 0.1278, similar behaviors have been observed. These experimental evidences have shown that the structure factor near the critical point follows the Ornstein–Zernike formula in the $Q$-region below $8 \times 10^{-3} \text{ Å}^{-1}$. From the fitted straight line for each $S(Q)$ against $Q^2$ the temperature dependence of the forward scattering $S_0$ and the correlation length $\xi$ were obtained as are presented in Fig. 6. The inverse forward scattering is experimentally found to be proportional to the inverse absolute temperature below $T^{-1}=3.3 \times 10^{-3} \text{ K}^{-1}$ within 10 K from the transition point. This means that the spinodal point can be obtained from the intercept of these fitted straight lines on the abscissa, and that the critical exponent $\gamma$ for the susceptibility $\chi$ is $\sim 1.0$, which is the mean-field value.
FIG. 6. The temperature dependence of the forward scattering and the correlation length for all the observed samples are presented. (a) $\phi = 0.0744$; (b) $\phi = 0.0950$; (c) $\phi = 0.1031$; and (d) $\phi = 0.1278$. The horizontal axis indicates the inverse temperature and the vertical axis the inverse forward scattering (left-side figure) and the inverse square of correlation length (right-side figure). The solid lines for the left-side figures show the fitted lines to the data points below decomposition, and the dashed lines are the fitted lines above decomposition. From the intercept of abscissa of the solid lines, spinodal points $T_\nu$ were determined. The binodal points were determined from the "kink," i.e., the cross points of the two fitted lines.

Since the reduced temperature can be defined as $\epsilon = |T - T_c|/T$ with the spinodal point $T_c$ also in near-critical region, the double logarithmic plot of the susceptibility $\chi$ and the correlation length $\xi$ vs the normalized temperature $\epsilon$ is possible. In Fig. 7, such the plot for $\phi = 0.1031$ is given. For the critical exponent of susceptibility, mean-field value ($\gamma = 1.0$) was verified (see Table I). But the critical exponent $\nu$ does not follow a straight line if the whole temper-
FIG. 7. The double logarithmic plots for (a) the forward scattering and (b) the correlation length vs the reduced temperature for $\phi=0.1031$. The solid line in (a) indicates the line of slope $-1$, which is consistent with the mean-field. The solid line in (b) is the line of slope $-0.5$, the mean-field value, is a guide for the eyes. The dashed line of (b) may be the limitation of the "critical" region, i.e., $D$ means the twice the radius of a droplet.

ature range is concerned. Therefore, we suggest that the "critical" region should be restricted within $\sim 4$ K from $T_s$, for which $\nu=0.5$ holds, because the Fisher's relation $\gamma=(2/\eta)$ holds. The Fisher's relation $\gamma=(2/\eta)$ is assumed to obey the system ceases to show a "critical" behavior when its correlation length $\xi<D$ due to the excluded volume effect of the droplets. Such a behavior might coincide with the Rouch et al. conjecture "a crossover from critical to single particle behavior."$^{16}$

Based on the resulting mean-field behavior, we have compared the temperature variation of the susceptibility (see the solid lines in Fig. 6) with Eqs. (13) and (14). From the slope of the fitted straight line and the extrapolation onto the abscissa, $\Gamma_H$ and $T_s$ were obtained (see Table I). The composition dependence of $\Gamma_H$, as is shown in Fig. 8(a), seemed to be expressed by a second order polynomial of the order parameter $\phi$. By a least-square fitting, the coefficients were obtained as

$$\Gamma_H = 1322 - 72920 \phi + 349900 \phi^2 \text{(K)}. \quad (15)$$

Here, we assumed that $b'=4$, which is a typical value of this parameter from the textbook.$^{18}$ (Note that this value was not sensitive to the final results.) $\Gamma_H$ is calculated from Eq. (11), and $\Gamma_H$ is calculated using the experimental value of $T_s$ from Eq. (14) (see Table I). The entropic part of the generalized Flory-Huggins parameter $\Gamma_\sigma$, as is shown in Fig. 8(b), also seems to be fitted to the second order polynomial as

$$\Gamma_\sigma(\phi) = -18.63 - 7.840 \phi - 242.4 \phi^2. \quad (16)$$

<table>
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<th>$\phi$</th>
<th>$T_s$ (K)</th>
<th>$T_H$ (K)</th>
<th>$\Gamma_H \times 10^5$ (K)</th>
<th>$\Gamma_\sigma \times 10$</th>
<th>$\gamma$</th>
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<tr>
<td>0.0744</td>
<td>312.5</td>
<td>312.1</td>
<td>$-2.168 \pm 0.053$</td>
<td>$-2.056 \pm 0.035$</td>
<td>1.029 ± 0.009</td>
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<tr>
<td>0.0959</td>
<td>310.1</td>
<td>309.6</td>
<td>$-2.433 \pm 0.147$</td>
<td>$-2.154 \pm 0.096$</td>
<td>0.924 ± 0.030</td>
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<tr>
<td>0.1031</td>
<td>311.3</td>
<td>310.6</td>
<td>$-2.489 \pm 0.029$</td>
<td>$-2.204 \pm 0.019$</td>
<td>0.997 ± 0.010</td>
</tr>
<tr>
<td>0.1278</td>
<td>316.0</td>
<td>312.2</td>
<td>$-2.280 \pm 0.006$</td>
<td>$-2.359 \pm 0.004$</td>
<td>1.001 ± 0.002</td>
</tr>
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TABLE I. Observed spinodal points ($T_s$), binodal points ($T_H$), Flory-Huggins parameters ($\Gamma_H$ and $\Gamma_\sigma$), and critical parameter $\gamma$ for all the samples.
FIG. 9. The resulting phase diagram is demonstrated. The open circles indicate the observed spinodal points and full triangles the observed binodal points. Calculated spinodal and binodal lines are shown by the dotted and solid lines, respectively.

Substitution of the expressions of the Flory–Huggins parameters to Eq. (11) leads to the $\phi$-dependence of the spinodal temperature expressed in units of K,

$$T_s = \frac{-1322 - 72,920\phi + 349,900\phi^2}{1/[2\phi(1-\phi')]^2 - 18.63 - 7.840\phi - 242.442\phi^2},$$

which is indicated by the dashed line in Fig. 9 and explains well the observed spinodal points.

The observed binodal temperature $T_B$'s are also given in Table I. From the definition of $T_B$ [Eq. (10)], the free energy can be expressed as a function of the order parameter $\phi$. As is commonly treated for the spinodal decomposition, the binodal points are calculated from points of contact of a common tangent line to the free energy curve with double minimum for each temperature. The solid line appearing in Fig. 9, represents the calculated binodal line in this way.

V. DISCUSSION

The most important point of this experiment is the finding of mean-field behavior of the system at the near-critical region. In this region, the correlation length is not very large. It was about the same order of magnitude as the droplet radius. Therefore, the correlation length may be comparable with the range of interaction among droplets which is thought to be resulting from an electronic origin. If one approaches closer to the critical point, the correlation length grows more. Then the mean-field approximation must break down and another behavior, e.g., 3D-Ising, will appear. We suppose that the previous results in literature which indicated somewhat different values from the exact Ising values, might be due to such a crossover. Further careful experiments are necessary to determine the "real" critical region and its behavior.

The other point that should be discussed is the curious behavior of the correlation length. Although the susceptibility especially at the temperature far from the transition point. From the fitted straight line in a double logarithmic plot of the correlation length at the mean-field region, the bare correlation length $\xi_0$ was ~10 Å. This value is about one order of magnitude less than the droplet diameter, and such a droplet density fluctuation is impossible. Now, we admit that this point is not solved and remains as a future problem, but this must be discussed with respect to the relation between the correlation length and the droplet shape because these are comparable in this region.

The third point is some discrepancy of the observed spinodal and binodal points from the calculated curves. One possibility is the composition fluctuation which comes from the sample preparation because the phase behavior is quite sensitive to the composition in such a multicomponent system. But we believe that the composition error was <0.4% and such an artificial effect can be neglected. In the proposed model, the droplet is assumed to keep the rigid shape through the phase separation and the mixture acts as one component system. But from our result, the droplet radius changes a little with increasing temperature (see Fig. 3). When the temperature approaches the binodal line where the phase separation starts, the droplet density fluctuation increases drastically and might influence the droplet shape, although Kotlarchyk et al. emphasized the rigidity of the droplet surface through the transition. Figure 10 displays the difference of scattering profiles before and after the decomposition. Above the binodal point, the Porod constant is obviously changed. Thus it is likely that such an effect influences the phase transition point.

VI. CONCLUSION

As in the case of the phase decomposition in polymer–polymer mixtures and some micellar systems, the mean-field behavior at near-critical region in the three-component microemulsion system was observed. In order...
to explain the critical behavior, the van der Waals model with the Flory–Huggins interaction parameter is introduced. Comparing the experimental results with the free energy expression, the phase diagram in terms of temperature vs droplet density is calculated. A reasonable result is obtained in the region of dilute water composition range where the structure is thought to be the dispersion of the water-in-oil droplets with the same radius.

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