

Static Light Scattering Experiments with Aqueous Solutions of the Nonionic Tenside C₁₂E₅ with Critical and Non-critical Composition

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Concentration fluctuations with long range correlations as well as non-critical background contributions determine the light scattering properties of C₁₂E₅/H₂O mixtures of critical composition near the lower critical point (critical mass fraction $y_c = 0.0123$; critical temperature $T_c = 31.8^\circ\text{C}$). If the influence of the non-critical contributions is neglected, an evaluation of the light scattering data in terms of the power laws $\xi = \xi_0 \cdot \varepsilon^{-\nu}$ and $\chi_T = \chi_{T,0} \cdot \varepsilon^{-\gamma}$ (ξ being the correlation length of local concentration fluctuations and χ_T the generalized susceptibility; $\varepsilon = (T_c - T)/T_c$ is the reduced temperature) leads to values of the critical exponents ν and γ which are closer to the mean field values ($\nu = 0.5$; $\gamma = 1$) than to the values theoretically expected for binary liquid mixtures from the Landau-Ginzburg-Wilson model ($\nu = 0.63$, $\gamma = 1.24$). If the background contributions are taken into account empirically by adding temperature independent background terms ξ_b and $\chi_{T,b}$ respectively to the simple power laws, the analysis of the light scattering data leads to values of $\nu \approx 0.65$ and $\gamma \approx 1.2$, which are close to the values given by the Landau-Ginzburg-Wilson model. The background term ξ_b has a value of about $\xi_b \approx 6$ nm and the critical amplitude ξ_0 a value of about $\xi_0 \approx 1.2$ nm. This value for ξ_0 is one order of magnitude larger than that found for simple binary liquid mixtures ($O(\xi_0) \approx 0.1$ nm). — In mixtures of non-critical composition ($-0.79 < (y - y_c)/y_c < 0.63$) the scattered intensity shows an angular dependence which is also a function of temperature corresponding to correlation lengths $20 \text{ nm} < \xi < 60 \text{ nm}$ for $0.5 \text{ K} < (T_p - T) < 7.0 \text{ K}$. They are assumed to reflect contributions of micelles which also contribute to the scattering of the mixture of critical composition away from the critical temperature.

1. Introduction

Critical phenomena in binary mixtures of non-ionic surfactants of the type $\text{CH}_3 \cdot (\text{CH}_2)_{i-1} \cdot (\text{O} \cdot \text{CH}_2 \cdot \text{CH}_2)_j \cdot \text{OH}$ (abbreviated C_iE_j) and water in the vicinity of their lower critical point have been studied extensively in recent years [1]. In these systems, the value of critical composition is larger than the critical micelle concentration. Therefore, in a mixture of critical composition near the critical temperature concentration fluctuations with long range correlations occur in the presence of micelles formed by molecules of the surfactant. It has been the purpose of these studies to establish, whether the critical phenomena observed in aqueous solutions of non-ionic surfactants belong to the same universality class as binary mixtures of components which do not form micelles. The experimental data published so far are thought to be not conclusive in this respect.

In this contribution results of new static light scattering experiments are reported for the system $\text{C}_{12}\text{E}_5/\text{H}_2\text{O}$ (pentaethylene glycol dodecylether). The analysis of the data indicates that non-universal values of the critical exponent ν of the correlation length ξ of local concentration fluctuations and the critical exponent γ of the osmotic compressibility χ_T respectively found in aqueous solutions of non-ionic tensides might be caused by unresolved difficulties in the data analysis. It appears to be necessary to take into account non-critical background contributions. No unequivocal procedure has been worked out as yet to accomplish that.

2. Experimental Section

Materials

C_{12}E_5 was purchased from NIKKO Chemical Co. (Japan) in a sealed glass ampule (lot. no. 6003). It was stored in the dark at $T = -20^\circ\text{C}$ and used without further purification. A HPLC analysis of this lot showed no trace of an impurity. Water was bidistilled in a quartz still. Air was removed from the water by treating the hot water with a stream of argon during cooling.

Treatment of Glass Ware

All glassware with which C_{12}E_5 and its aqueous solutions came into contact was treated before use in the following manner: It was immersed into a solution prepared from equal volumes of a 1 molar aqueous solution of NaOH, ethanol and an aqueous solution of H_2O_2 (30%) and subjected to ultrasonic agitation. Thereafter, it was intensively rinsed with hot water. The round glass cells (external diameter 0.7 cm) used for the light scattering experiments were treated in the same way. Thereafter, the internal surface of each cell was treated for 24 h with an intermittent jet of boiling distilled water. This treatment was carried out in an apparatus which allowed the circulation of boiling distilled water. Finally, the cells were stored dustfree.

Sample Preparation

The ampule containing C_{12}E_5 was transferred into a glove box with a nitrogen atmosphere free of oxygen (<60 ppm). The ampule was heated to about 22°C to let its content melt and broken, thereafter. Using a glass funnel with a thin stem the melt was transferred into smaller ampules. These ampules were flame sealed and stored again in the dark at -20°C until use. The portioned material was used one after the other to prepare stock solutions of $\text{C}_{12}\text{E}_5/\text{H}_2\text{O}$ of a composition of roughly $y = 2y_c$ (y being the mass fraction of

C_{12}E_5). The mixtures used for the light scattering experiments were prepared from these stock solutions by dilution within the glass cells used for the light scattering experiment. These manipulations were also carried out within the glove box mentioned above. The glass cells were flame-sealed under vacuum. The samples were not filtered before the experiments. Only those samples were used for

Table 1
Characterization of the samples used in the light scattering experiments
 y : mass fraction of C_{12}E_5 ; T_P : temperature of phase separation

No.	y	$T_P/^\circ\text{C}$
1	0.0025	32.74
2	0.0620	32.21
3	0.0106	31.80
4	0.0122 (y_c)	31.79 (T_c)
5	0.0124 (y_c)	31.83 (T_c)
6	0.0201	31.96

the scattering experiments in which no dust could be detected in the mixtures by visual observation of the scattered intensity. Nevertheless, the samples were spun with care under low centrifugal force before putting them into the light scattering photometer.

The mixtures used came into contact only with glassware treated in the manner described above. Contact with metal and plastic was avoided completely. These precautions were necessary to have samples exhibiting only a small rate of decrease of the temperature of phase separation with time ($dT_P/dt \approx 33 \text{ mK} \cdot \text{week}^{-1}$ corresponding to a value of $\Delta T_P \approx 100 \text{ mK}$ during a run of a light scattering experiment. Despite these precautions, critical mixtures of the same composition prepared from different stock solutions of the same lot had slightly different critical temperatures and different values of dT_P/dt .

Critical Data

The critical composition of the system $\text{C}_{12}\text{E}_5/\text{H}_2\text{O}$ was determined by two independent methods:

(a) The composition of the mixture with the lowest temperature of phase separation was determined. For that mixture the ratio of the volumes V'/V'' of the two fluid phases coexisting at a temperature near by T_c was $V'/V'' \approx 1$. The critical composition determined in this way had a value of $y_c = 0.0123 \pm 0.0003$. This value is close to that reported in the literature by Kuwahara et al. ($y_c = 0.0120 \pm 0.0004$ [2]). Wilcoxon reports a larger value ($y_c = 0.015$ [3]). The temperature of phase separation of a mixture of that composition had a value of $T_c = 31.8^\circ\text{C}$. T_c was taken as the temperature at which the characteristic scattering pattern of spinodal decomposition was observed upon raising the temperature of a homogeneous mixture slowly. Noncritical mixtures did not show this characteristic pattern. The value $T_c = 31.8^\circ\text{C}$ indicates a satisfactory purity of the critical mixture. Schubert et al. [4] have worked out a purification technique for nonionic surfactants of the type C_iE_j and have taken the lower critical temperature of $\text{C}_i\text{E}_j/\text{H}_2\text{O}$ mixtures as a measure of the purity of the sample. For $\text{C}_{12}\text{E}_5/\text{H}_2\text{O}$, these authors give a value of $T_c = 32.0^\circ\text{C}$ (Kuwahara et al. [2] $T_c = 31.91^\circ\text{C}$; Wilcoxon [3] $T_c = 32.13^\circ\text{C}$).

(b) The ratio of light intensity $I(\theta_1)/I(\theta_2)$ scattered by a sample under a scattering angle of $\theta_1 = 45^\circ$ and $\theta_2 = 135^\circ$ respectively as a function of concentration at different values of the temperature difference ($T_P - T$) was measured. A plot of $I(\theta_1)/I(\theta_2)$ versus composition at fixed small temperature differences $T_P - T$ shows a maximum at the critical composition. This behavior is expected. The scattered intensity caused by concentration fluctuations with long range correlations should peak at the critical composition. The value of the critical composition determined this way was in agreement with the value obtained by method (a).

The results of measurements with six samples of critical and non-critical composition are reported in this communication. They are characterized by the data given in Table 1. Fig. 1 shows the phase diagram obtained by Hamano et al. [2]. The composition of the samples used are indicated by arrows.

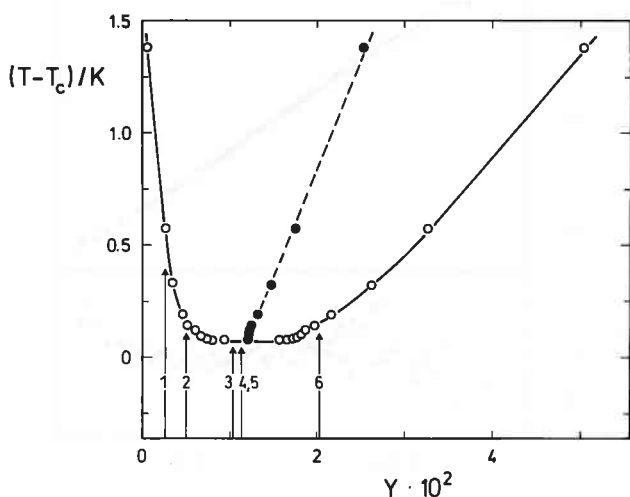


Fig. 1
Characterization of the samples used in this study in relation to the phase diagram of system. The phase diagram is constructed from data taken from Ref. [2]. The dashed line represents the rectilinear diameter. The six samples studied are indicated by arrows

Light Scattering Photometer

The light scattering photometer and the corrections applied to the primary data (correction for fluctuating primary intensity, dead time and dark counts of the photo multiplier tube, transmission and scattering volume) have been described in Ref. [5]. The incident Ar⁺-laser light had a wave length of $\lambda_0 = 488.0$ nm. The proper alignment of the instrument was checked by measuring the angular dependence of light scattered by a sample of benzene in the range $30^\circ < \theta < 135^\circ$ in steps of 5° . The photometer was considered to be properly aligned when the angular variation of the scattered intensity was $< 2\%$ after correction for the change of scattering volume with scattering angle. Measurements of the depolarized component of the scattered light showed no contribution of double and multiple scattering to the measured intensity in the temperature range $T_p - T > 0.2$ K used in this study.

Data Analysis

The light scattering experiments with the samples of critical and non-critical composition are analyzed on the basis of the Ornstein-Zernike-Debye method:

$$I_s(q, T_c - T)/I_0 = A \cdot T \cdot \chi_T / [1 + (q\xi)^2] \quad (1)$$

with the scattered light intensity I_s and the incident light intensity I_0 respectively; $q = 4\pi \cdot n/\lambda_0 \cdot \sin(\theta/2)$ is the absolute value of the scattering vector, λ_0 the wave length of the monochromatic incident light in vacuum, n the index of refraction of the mixture and θ the scattering angle. T is the absolute temperature, χ_T a generalized susceptibility and ξ the correlation length of the local concentration fluctuations. The constant A takes into account the optical properties of the mixture.

Eq (1) is applicable to a good approximation for values of the scaling variable $q \cdot \xi < 5$. This requirement is met in this study.

The temperature dependence of the correlation length ξ of local concentration fluctuations in a mixture of critical composition and that of the generalized susceptibility χ_T is expected to be given by:

$$\lim_{T \rightarrow T_c} \xi = \xi_0 \cdot \varepsilon^{-\nu} \quad (2)$$

and

$$\lim_{T \rightarrow T_c} \chi_T = \chi_{T,0} \cdot \varepsilon^{-\gamma} \quad (3)$$

with the system specific critical amplitudes ξ_0 and $\chi_{T,0}$ and the universal critical exponents ν and γ . The Landau-Ginsburg-Wilson model predicts theoretical values of $\nu = 0.63$ and $\gamma = 1.24$; ε is the reduced temperature difference from the critical temperature ($\varepsilon = (T_c - T)/T_c$).

3. Results and Discussion

Mixtures of Critical Composition

The temperature dependence of the correlation length ξ is obtained from a set of measurements of I_s versus q at different fixed values of $T_c(\text{visual}) - T$ on the basis of Eq. (1): The reciprocal of the ratio of the corrected scattered intensity I_s divided by the thermodynamic temperature T is plotted as function of q^2 . A linear relation is expected. The ratio of slope/intercept of the straight line (T/I_s versus q^2) gives the value of ξ^2 for each temperature difference $T_c(\text{visual}) - T$. In this way a data set of $\xi(T_c - T)$ is obtained.

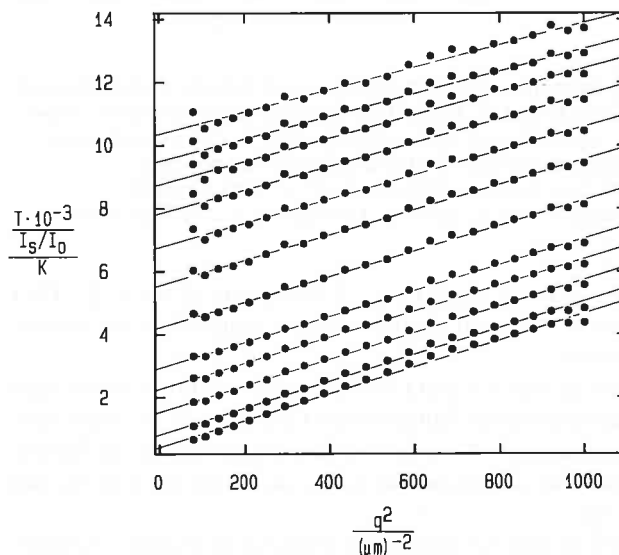


Fig. 2
Ornstein-Zernike-Debye plot of scattered intensity as function of the square of the scattering vector (see Eq. (1)) of a C₁₂E₅/H₂O mixture of critical composition (sample 5, see Table 1). Parameter: Temperature difference $\Delta T (= T_c - T)$. From above down: $\Delta T = 8.868$ K, 7.869 K, 6.868 K, 5.869 K, 4.869 K, 3.869 K, 2.869 K, 1.969 K, 1.519 K, 0.509 K, 0.209 K; $T_c(\text{fit}) = 31.699^\circ\text{C}$

The value of the intercept of the straight line (intercept: $\lim_{q^2 \rightarrow 0}$) for each temperature difference $T_c(\text{visual})-T$ is proportional to the generalized susceptibility χ_T . In this way a data set of $\Gamma(T_c-T)$ is obtained (Γ : generalized susceptibility in arbitrary units).

Fig. 2 shows a plot of T/I_s versus q^2 obtained with a $C_{12}E_5/H_2O$ mixture of critical composition at different values of $T_c(\text{visual})-T$. The curves have a positive slope. It is noteworthy that the slope of the lines remains approximately constant up to the largest difference (T_c-T) ≈ 9 K used in the experiments. In corresponding experiments with a critical mixture of $2-C_4E_1/H_2O$ ($2-C_4E_1$ is the abbreviation for 2-butoxy-ethanol) at its lower critical point, the T/I_s versus q^2 curves have zero slope at temperatures away from the critical (see Fig. 3). ($2-C_4E_1$ is not a typical non-ionic tenside). This is interpreted as an indication of the existence of non-critical background contributions to the scattered light intensity in the case of the micelle-forming mixtures. This interpretation is supported by the results of light scattering experiments with $C_{12}E_5/H_2O$ mixtures of non-critical composition (see Fig. 7 and Fig. 8).

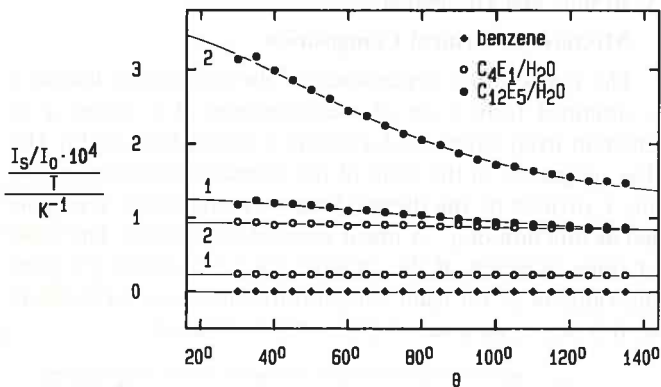


Fig. 3
Light intensity scattered from samples of benzene and mixtures of $2-C_4E_1/H_2O$ and $C_{12}E_5/H_2O$ (both of critical composition) respectively as function of the scattering angle θ . I_s : scattered intensity; I_0 : incident intensity; T : thermodynamic temperature. Parameters: benzene, temperature $T = 31.83^\circ\text{C}$; curve 1: $T_c(\text{visual})-T \approx 6$ K, curve 2: $T_c(\text{visual})-T \approx 2$ K respectively.

The $\xi(T_c-T)$ and $\Gamma(T_c-T)$ data sets of the $C_{12}E_5/H_2O$ mixtures of critical composition are analysed in the following ways:

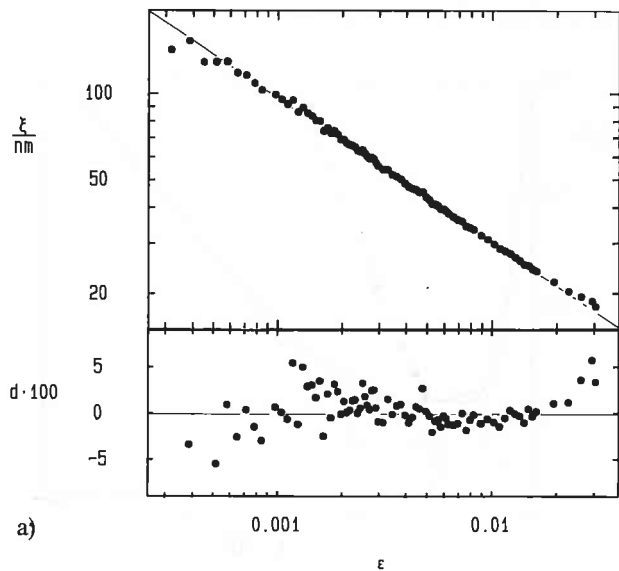
(a) The Eqs. (2) and (3) respectively are fitted to the data using the program Minuit of the Cern Library [7] with three free parameters (T_c, ν, ξ_0) and ($T_c, \gamma, \Gamma_0 (= A \cdot \chi_{T,o})$). Results of such fits are shown in Table 2a, Table 2b, Fig. 5a and Fig. 6a.

(b) The Eqs. (2) and (3) are modified to include a temperature independent, empirical background term to take into account "non-critical background" contributions ξ_b and Γ_b :

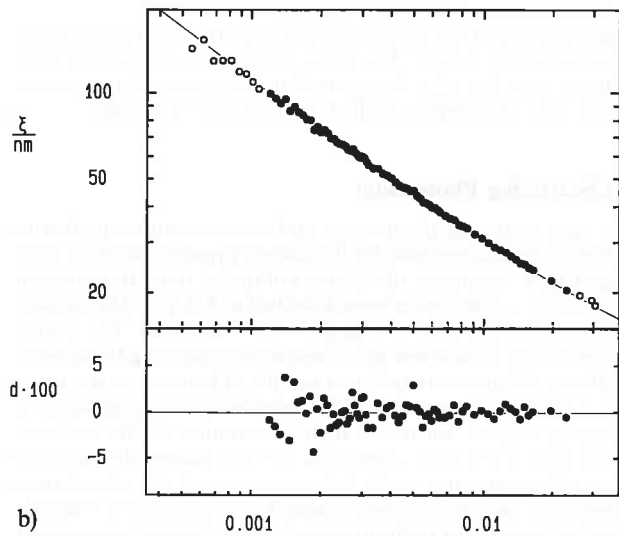
$$\xi = \xi_0 \cdot \varepsilon^{-\nu} + \xi_b, \quad (4)$$

$$\Gamma = \Gamma_0 \cdot \varepsilon^{-\gamma} + \Gamma_b. \quad (5)$$

Results of such four parameter fits (T_c, ν, ξ_0, ξ_b) and ($T_c, \gamma, \Gamma_0, \Gamma_b$) are shown in Table 2a, Table 2b, Fig. 4b and Fig. 5b.



a)



b)

Fig. 4
Correlation length ξ as function of the reduced temperature difference $\varepsilon (= T_c-T)/T_c$, double logarithmic plot). The data refer to sample 5 with critical composition (see Table 1)

a) Three parameter fit (T_c, ξ_0, ν) using Eq. (2); d : deviation. The drawn outline represents the function $\xi = \xi_0 \cdot \varepsilon^{-\nu}$ with $T_c = 304.877$ K, $\xi_0 = 2.97$ nm, $\nu = 0.50$

b) Four parameter fit (T_c, ξ_0, ν, ξ_b) using Eq. (4); d : deviation. The drawn outline represents the function $\xi = \xi_0 \cdot \varepsilon^{-\nu} + \xi_b$ with $T_c = 304.947$ K, $\xi_0 = 1.33$ nm, $\nu = 0.63$, $\xi_b = 5.9$ nm

Attempts to use the Wegner expansion of Eqs. (2) and (3) (e.g. $\xi = \xi_0 \cdot \varepsilon^{-\nu} \cdot (1 + A_\xi \cdot \varepsilon^{0.5})$) for the representation of the data lead to larger values of the variance of the fits.

The following conclusions can be drawn from data compiled in Tables 2a and 2b:

Table 2

a) Results of the data analysis of static light scattering experiments with $C_{12}E_5/H_2O$ mixtures of critical composition (sample 4 and sample 5; see Table 1): critical amplitude and critical exponent of the correlation length of local concentration fluctuations. σ_{fit}^2 : variance of the fit, n : number of data points

Fit to Eq. (2); free parameters: T_c, ν, ξ_0 ; $n = 75$
 temperature range $9 \text{ K} < (T_c(\text{visual})-T) < 0.05 \text{ K}$

sample	T_c/K	ν	ξ_0/nm	$\sigma_{fit}^2 \cdot 10$
4	304.849 ± 0.012	0.49 ± 0.01	3.19 ± 0.08	5.02
5	304.877 ± 0.034	0.50 ± 0.02	2.97 ± 0.22	2.65

Fit to Eq. (2); free parameters: T_c, ν, ξ_0 ; reduced data set; $n_4 = 65, n_5 = 71$
 temperature range $7 \text{ K} < (T_c(\text{visual})-T) < 0.2 \text{ K}$

sample	T_c/K	ν	ξ_0/nm	$\sigma_{fit}^2 \cdot 10$
4	304.815 ± 0.016	0.49 ± 0.01	3.22 ± 0.09	3.62
5	304.838 ± 0.011	0.50 ± 0.01	3.04 ± 0.06	1.32

Fit to Eq. (4); free parameters: T_c, ν, ξ_0, ξ_b ; $n = 75$
 temperature range $9 \text{ K} < (T_c(\text{visual})-T) < 0.05 \text{ K}$

sample	T_c/K	ν	ξ_0/nm	ξ_b/nm	$\sigma_{fit}^2 \cdot 10$
4	304.971 ± 0.033	0.67 ± 0.04	1.11 ± 0.23	7.1 ± 1.0	3.42
5	304.983 ± 0.017	0.68 ± 0.02	1.05 ± 0.12	7.2 ± 0.6	1.13

Fit to Eq. (4); free parameters: T_c, ν, ξ_0, ξ_b ; reduced data set;
 $n_4 = 65, n_5 = 71$
 temperature range $7 \text{ K} < (T_c(\text{visual})-T) < 0.2 \text{ K}$

sample	T_c/K	ν	ξ_0/nm	ξ_b/nm	$\sigma_{fit}^2 \cdot 10$
4	304.930 ± 0.051	0.63 ± 0.06	1.33 ± 0.43	6.3 ± 1.8	3.22
5	304.947 ± 0.034	0.63 ± 0.04	1.33 ± 0.29	5.9 ± 1.2	1.08

b) Results of the data analysis of static light scattering experiments with $C_{12}E_5/H_2O$ mixtures of critical composition (sample 4 and sample 5; see Table 1): critical amplitude and critical exponent of the generalized susceptibility. σ_{fit}^2 : variance of the fit, n : number of data points

Fit to Eq. (3); free parameters: T_c, γ, Γ_0 ; $n = 75$
 temperature range $9 \text{ K} < (T_c(\text{visual})-T) < 0.5 \text{ K}$

sample	T_c/K	γ	$\Gamma_0 \cdot 10^3 / \text{a.u.}$	$\sigma_{fit}^2 \cdot 10^5$
4	304.786 ± 0.010	0.87 ± 0.01	4.37 ± 0.21	4.06
5	304.821 ± 0.008	0.88 ± 0.01	4.02 ± 0.20	4.52

Fit to Eq. (3); free parameters: T_c, γ, Γ_0 ; reduced data set; $n_4 = 65, n_5 = 71$
 temperature range $7 \text{ K} < (T_c(\text{visual})-T) < 0.2 \text{ K}$

sample	T_c/K	γ	$\Gamma_0 \cdot 10^3 / \text{a.u.}$	$\sigma_{fit}^2 \cdot 10^5$
4	304.737 ± 0.013	0.88 ± 0.01	4.12 ± 0.21	2.99
5	304.762 ± 0.011	0.88 ± 0.01	3.77 ± 0.16	1.37

Fit to Eq. (5); free parameters: $T_c, \gamma, \Gamma_0, \Gamma_b$; $n = 75$
 temperature range $9 \text{ K} < (T_c(\text{visual})-T) < 0.5 \text{ K}$

sample	T_c/K	γ	$\Gamma_0 \cdot 10^3 / \text{a.u.}$	$\Gamma_b \cdot 10^3 / \text{a.u.}$	$\sigma_{fit}^2 \cdot 10^5$
4	304.933 ± 0.094	1.17 ± 0.11	0.89 ± 0.58	44 ± 10	0.65
5	304.955 ± 0.088	1.18 ± 0.10	0.82 ± 0.09	44.4 ± 8.8	0.26

Fit to Eq. (5); free parameters: $T_c, \gamma, \Gamma_0, \Gamma_b$; reduced data set;
 $n_4 = 65, n_5 = 71$

temperature range $7 \text{ K} < (T_c(\text{visual})-T) < 0.2 \text{ K}$

sample	T_c/K	γ	$\Gamma_0 \cdot 10^3 / \text{a.u.}$	$\Gamma_b \cdot 10^3 / \text{a.u.}$	$\sigma_{fit}^2 \cdot 10^5$
4	304.921 ± 0.031	1.17 ± 0.04	0.89 ± 0.20	45.3 ± 3.9	1.12
5	304.930 ± 0.018	1.14 ± 0.02	0.98 ± 0.13	40.1 ± 2.5	0.33

(1) Concentration fluctuations with long range correlations as well as non-critical contributions determine the light scattering properties of $C_{12}E_5/H_2O$ mixtures of critical composition near the lower critical point. The non-critical background contributions are assumed to be caused by micelles formed by the non-ionic tenside molecules.

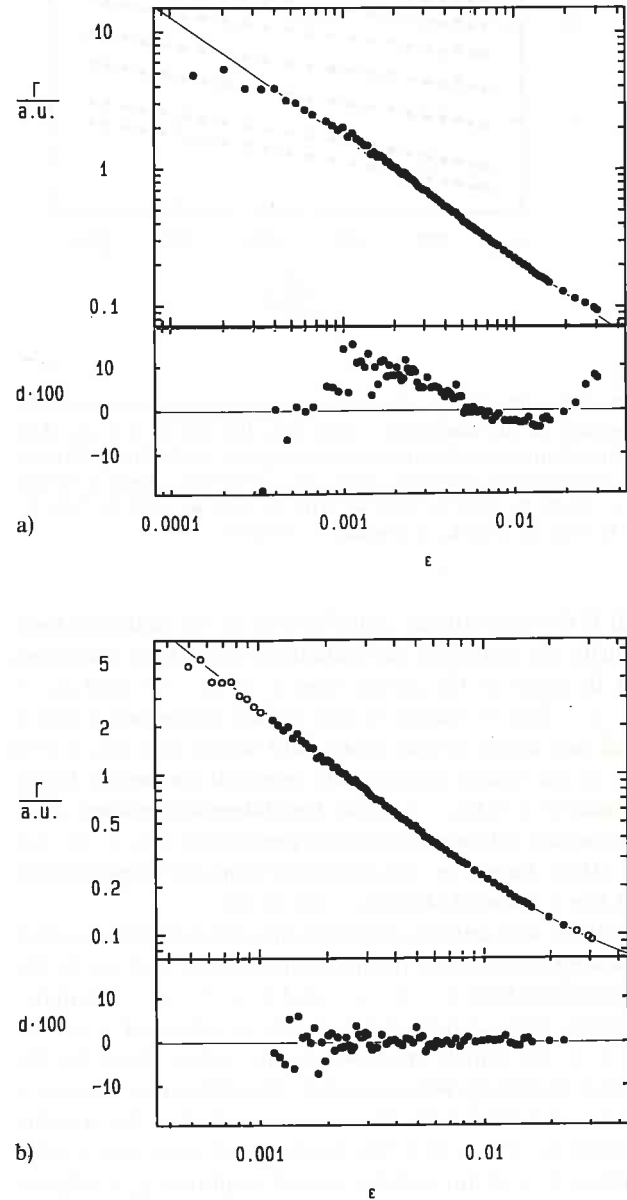


Fig. 5 Generalized susceptibility Γ expressed in relative units as function of the reduced temperature difference $\epsilon (= T_c - T)/T_c$, double logarithmic plot). The data refer to sample 5 with critical composition (see Table 1)

a) Three parameter fit (T_c, Γ_0, γ) using Eq. (3); d : deviation. The drawn outline represents the function $\Gamma = \Gamma_0 \cdot \epsilon^{-\gamma}$ with $T_c = 304.821 \text{ K}, \Gamma_0 = 4.02 \cdot 10^{-3} \text{ a.u.}, \gamma = 0.88$

b) Four parameter fit ($T_c, \Gamma_0, \gamma, \Gamma_b$) using Eq. (6); d : deviation. The drawn outline represents the function $\Gamma = \Gamma_0 \cdot \epsilon^{-\gamma} + \Gamma_b$ with $T_c = 304.930 \text{ K}, \Gamma_0 = 0.98 \cdot 10^{-3} \text{ a.u.}, \gamma = 1.14, \Gamma_b = 40.1 \cdot 10^{-3} \text{ a.u.}$

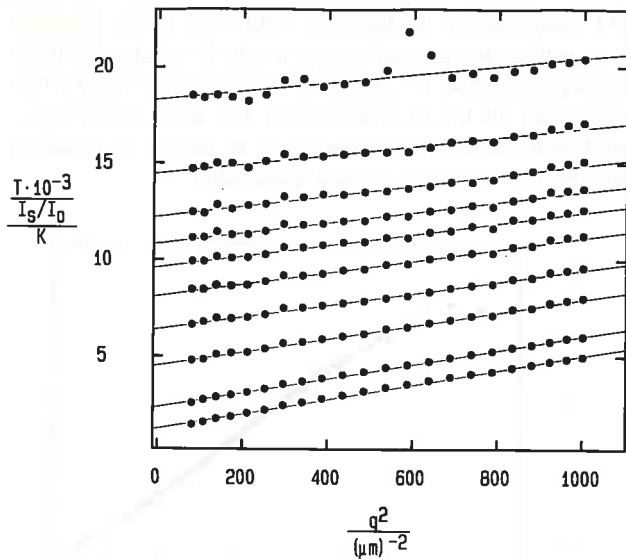


Fig. 6
Ornstein-Zernike-Debye plot of scattered intensity as function of the square of the scattering vector (see Eq. (1)) of a $C_{12}E_5/H_2O$ mixture of non-critical composition (sample 6, see Table 1). Parameter: Temperature difference $\Delta T (= T_p - T)$. From above to below $\Delta T = 13.89$ K, 9.52 K, 6.96 K, 6.05 K, 4.96 K, 3.96 K, 2.96 K, 1.96 K, 0.96 K, 0.46 K; $T_c(\text{visual}) = 31.96^\circ\text{C}$

(2) If the non-critical contributions to the scattered light intensity are neglected, an evaluation of the light scattering data in terms of the power laws $\xi = \xi_o \cdot \varepsilon^{-\nu}$ and $\chi_T = \chi_{T,o} \cdot \varepsilon^{-\gamma}$ lead to values of the critical exponents ν and γ which are closer to the mean field values ($\nu = 0.5$, $\gamma = 1$) than to the values theoretically expected for binary liquid mixtures ($\nu = 0.63$, $\gamma = 1.24$). The difference between γ and 2ν (exponent relation, theoretical prediction: $\gamma = \nu \cdot (2 - \eta)$; $\eta = 0.031$; here $\gamma \approx 2\nu$) calculated from the experimental data has a value of about $(\gamma - 2\nu) \approx 0.1$.

(3) If the non-critical contributions are taken into account by adding temperature independent terms ξ_b and $\chi_{T,b}$ to the simple power laws $\xi = \xi_o \cdot \varepsilon^{-\nu}$ and $\Gamma = \Gamma_o \cdot \varepsilon^{-\gamma}$, the analysis of the light scattering data leads to values of $\nu \approx 0.65$ and $\gamma \approx 1.2$, which are close to the values given by the Landau-Ginzburg-Wilson model. The difference between γ and 2ν calculated from the experimental data has a value of about $(\gamma - 2\nu) \approx 0.1$. The background term has a value of about $\xi_b \approx 6$ nm and the critical amplitude ξ_o a value of about $\xi_o \approx 1.2$ nm. This value of ξ_o is larger by an order of magnitude than the corresponding value of simple binary liquid mixtures ($O(\xi_o) = 0.1$ nm). The approach to add a temperature independent term ξ_b and Γ_b respectively to the simple power law for ξ and Γ is entirely empirical and lacks a theoretical foundation. Therefore the value of ξ_b should not be related to the size of micelles present in the mixture.

Wilcoxon [3] concluded from small angle neutron scattering experiments with $C_{12}E_5/D_2O$ mixtures (concentration range: $0.005 < y < 0.03$) that the mixtures contained micelles with a radius of gyration of 2 nm to 3 nm. Brown et al. [8] conclude from NMR self-diffusion measurements and

static and dynamic light scattering experiments with $C_{12}E_5/H_2O$ mixtures in a wide concentration range ($y < 0.15$, $4^\circ\text{C} < T < 30^\circ\text{C}$) that the micelles have a hydrodynamical radius of ≥ 6 nm.

(4) The variance of the fit of the different data sets to Eqs. (2)/(4) and Eqs. (3)/(5) respectively has approximately the same value. The well known strong correlation in the data analysis between the values of the critical amplitudes (ξ_o , Γ_o) and the critical exponents (ν , γ) is also observed.

All together 4 samples of critical composition were studied in this investigation. The results of two of them are reported in detail here. The values of the relevant parameters averaged over these two samples are:

– Three parameter fit (T_c , ν , ξ_o ; T_c , γ , Γ_o): $\nu = 0.50 \pm 0.01$; $\gamma = 0.88 \pm 0.01$; $\xi_o = (3.1 \pm 0.2)$ nm.

The values of ν , γ and ξ_o given in the literature for $C_{12}E_5/H_2O$ mixtures of critical composition are: Kuwahara et al. [2]: $\nu = 0.514 \pm 0.012$; $\gamma = 1.035 \pm 0.028$; $\xi_o = (3.27 \pm 0.23)$ nm; Wilcoxon [3]: $\nu = 0.55$; $\gamma = 1.13$; $\xi_o = 2.0$ nm.

– Four parameter fit (T_c , ν , ξ_o , ξ_b ; T_c , γ , Γ_o , Γ_b): $\nu = 0.65 \pm 0.04$; $\gamma = 1.17 \pm 0.11$; $\xi_o = (1.2 \pm 0.1)$ nm; $\xi_b = (6.6 \pm 1.5)$ nm.

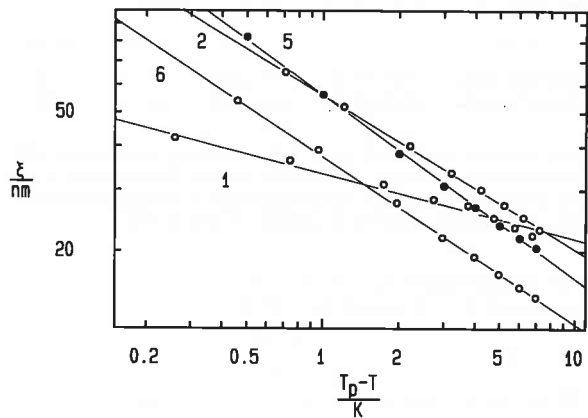


Fig. 7
Correlation length ξ as function of the reduced temperature difference $\varepsilon (= T_c - T)/T_c$, double logarithmic plot) of $C_{12}E_5/H_2O$ mixtures of non-critical composition. The data refer to samples 1, 2 and 6 (see Table 1). The data of sample 5 (critical composition) are shown also to allow a comparison.

Mixtures of Non-Critical Composition

The light scattering data of the three $C_{12}E_5/H_2O$ -mixtures of non-critical composition ($-0.79 < (y - y_c)/y_c < 0.63$) are also analyzed on the basis of Eq. (1). Ornstein-Zernike-Debye plots of sample 6 (see Table 1) shown in Fig. 6 demonstrate the angular dependence of scattered light intensity. This angular dependence is not caused by local concentration fluctuations with long range correlations. It is attributed to the scattering of light caused by the presence of micelles. The correlation lengths ξ obtained from these data range from $20 \text{ nm} < \xi < 60 \text{ nm}$ at temperatures $0.5 \text{ K} < (T_p(\text{visual}) - T) < 7.0 \text{ K}$ (see Fig. 7). Similar results are reported by Wilcoxon [3] on the basis of light scattering meas-

urements with C₁₂E₅/H₂O mixtures in the composition range $-0.067 < (y - y_c)/y_c < 0.1$.

In Fig. 8 plots of the correlation length ξ as function of composition at different temperature differences $T_p - T$ are shown. The curves demonstrate that concentration fluctuations with long range correlation dominate the scattering properties of the C₁₂E₅/H₂O mixture of critical composition. They also demonstrate the existence of background contributions.

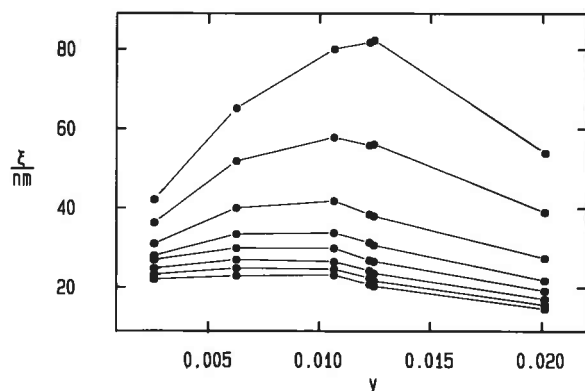


Fig. 8
Correlation length ξ as function of composition y (mass fraction) of C₁₂E₅/H₂O mixtures at different temperature differences ($T_p - T$). From above to below: $(T_p - T)/K = 0.5, 1, 2, 3, 5, 6, 7$. The drawn lines are guides to the eye

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