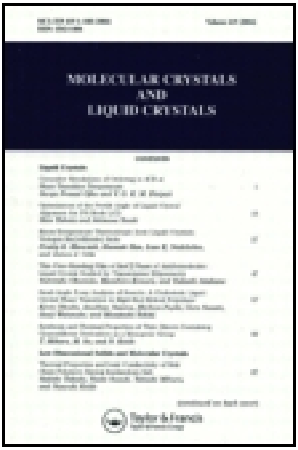

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Static and Dynamic Light Scattering Study of Aqueous Micellar Solutions Formed by Polydisperse Surfactant

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Version of record first published: 04 Oct 2006.

To cite this article: S. A. Konev , V. V. Nikitin , G. I. Olefirenko , I. K. Yudin & E. V. Zhuravleva (1991): Static and Dynamic Light Scattering Study of Aqueous Micellar Solutions Formed by Polydisperse Surfactant, Molecular Crystals and Liquid Crystals, 200:1, 19-27

To link to this article: http://dx.doi.org/10.1080/00268949108044227

Mol. Cryst. Liq. Cryst., 1991, Vol. 200, pp. 19–27
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Printed in the United States of America

Static and Dynamic Light Scattering Study of Aqueous Micellar Solutions Formed by Polydisperse Surfactant

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(Received August 10, 1990)

Static and dynamic light scattering was used for investigation of micellization and critical behaviour (in the vicinity of critical consolution point) in aqueous solution of nonionic surfactant polyethylenglycole monolaurate with a large distribution of molecular weight. In spite of the surfactant polydispersity the dynamic light scattering near the critical point was characterized by the single time exponential function, and critical exponents appeared to be close to the Ising exponent values. Kinetics of oil solubilization in the micellar solution was also studied.

INTRODUCTION

Formation of the micelles and microemulsions in surfactant solutions is the first stage in hierarchy of phase transitions which leads to various lyotropic liquid crystalline phases.[1–2]

Great interest is also aroused by the critical phenomena in micellar solutions and microemulsions where nonuniversal behaviour was found in a number of works.[3–8] The reasons of such nonuniversality are still obscure.

The recent results of accurate light scattering study of the nonionic surfactant *n*-dodecyloctaoxyethylene glycole monoether ($C_{12}E_8$) mixtures with H_2O and D_2O, obtained by Dietler and Cannell,[9] strongly support the Ising-like universal behavior and allow one to suppose that the reason of nonuniversality might lie in sample quality.

We studied static and dynamic light scattering (LS) near phase transitions (micellization and micellar phase separation) in aqueous solution of nonionic surfactant polyethylenglycole monolaurate ($C_{11}E_9$) with large distribution of molecular weight. It was interesting to compare results of the study of polydisperse amphiphile with other works[3–6,8,9] where specially synthetized surfactants were used, because the different degree of polydispersity might be one of the reasons of the nonuniversal behaviour.

TECHNIQUE

A commercial amphiphile produced by FERAK, Berlin, with relatively large polydispersity was used. In Figure 1 the $C_{11}E_9$ chromatogram is shown. The chromatogram permits to evaluate the polydispersity at least qualitatively. High purity water was obtained using Milli-Q system. Reagent-grade *n*-octane was used in the studies of the solubilization phenomena. Our cylindrical cells were made of optical water resistant PYREX glass (internal diameter is 10 mm). The cells were corked by closely fitting teflon plugs. All sample manipulations were performed in a dust-free box, filled with dry nitrogen. All solution components were filtrated through a microporous membrane filter with 0.22 μm pore size.

For LS measurements precision photon correlation spectrometer was used. The Ar^+ laser (0.4880 μm, 150 mW) was used for dynamic LS measurements in the vicinity of the critical micelle concentration (CMC). In other cases we used He–Ne laser (0.6328 μm, 15 mW). To avoid the possible effect of sample local heating in the vicinity of the consolution critical point, the incident light beam intensity was attenuated up to 1–0.2 mW. Scattered light was detected by photon counting system. To exclude the influence of instability of the laser and of the photomultiplier as well as the extinction, the ratio of the LS intensity to the intensity of the beam passed through the cylindrical cell was measured. For dynamic LS we worked out

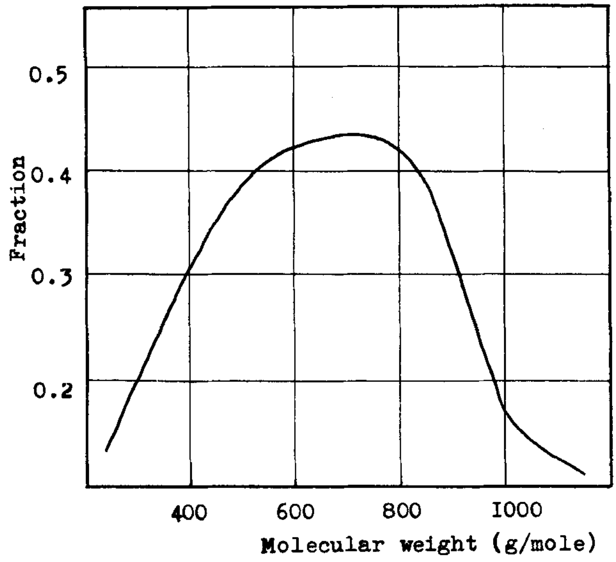

FIGURE 1 Distribution of molecular weight in the $C_{11}E_9$ surfactant.

a real-time 4-bits 128-channels correlator. All measurements as well as data processing were controlled by a microcomputer. Details of the experimental technique and methods of data analysis have been fully described elsewhere.[10]

RESULTS AND DISCUSSIONS

Phase diagram

LS method was used for the study of phase diagram of binary solution $C_{11}E_9$-water in the region of relatively small concentration (up to 15% $C_{11}E_9$) of for wide range of temperatures (Figure 2).

Specific features of nonionic amphiphiles water solutions is the appearance of phase separation with increasing temperature. Coexistence curve of such solutions has a lower critical point (LCP). Consolution temperature was identified with the jump in scattering intensity. The spinodal (dashed curve in Figure 2) was obtained by extrapolation of inverse scattering intensity temperature dependence to a zero value. In our case the coexistence curve is highly asymmetric, and LCP is located not in the minimum of coexistence curve (0.7 ± 0.1 g/cm $C_{11}E_9$), but is shifted to the region of higher amphiphile concentration (7.5 ± 0.5 g/m $C_{11}E_9$). It may be explained by the high polydispersity of surfactant which reveals itself as an effective impurity shifting the transition point.

Micellization

Micellar phase is the simplest of lyotropic phases. Formation of micellar phase is characterized by critical micelle concentration. In case of static LS, CMC corre-

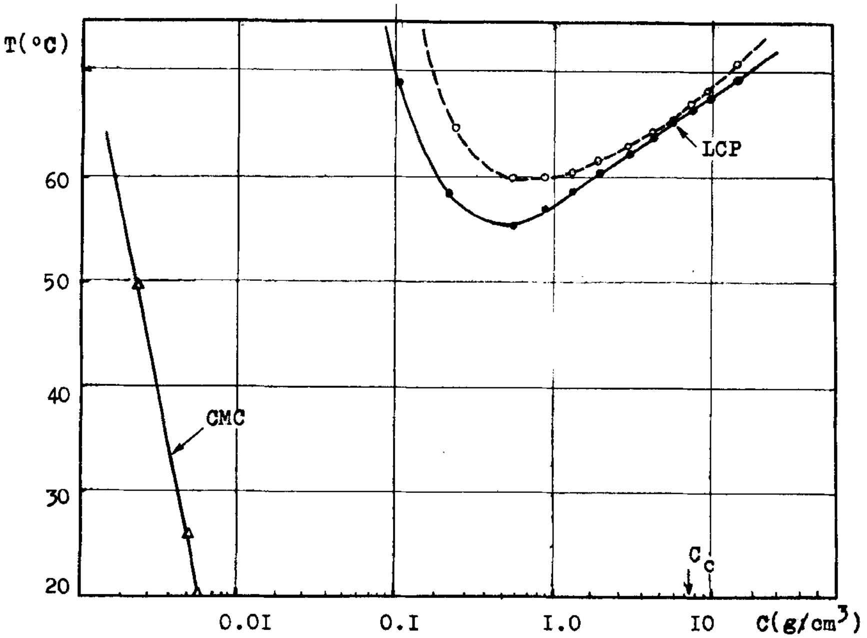

FIGURE 2 Phase diagram of the water $C_{11}E_9$ solution.

sponds to inflection point on the curve of concentration dependence of scattered light intensity. In dynamic light scattering CMC was identified by the appearance of the particles having the radius of 20–30 Å.

The results of our measurements are presented in Figure 3. In this figure the concentration dependences of LS intensity for two values of temperature and also micelle radius as a function of concentration are drawn. CMC defined by both methods coincides with each other. Concentration dependence of scattered light intensity makes it possible to calculate micellar molecular weight. For Rayleigh scattering the following equation can be written[11]:

$$\frac{cK}{R} = \frac{1}{M} + 2B_2c \tag{1}$$

In Equation (1) M is the micellar molecular weight, B_2 is the second virial coefficient characterizing micelles interaction, c is the concentration of amphiphile aggregated in micelles. The Rayleigh ratio is defined by equation:

$$R = A\frac{I_S}{I_o} \tag{2}$$

where I_S and I_o are the intensities of scattered and incident light respectively, A is a constant, which is proportional to photon counting system aperture. The value

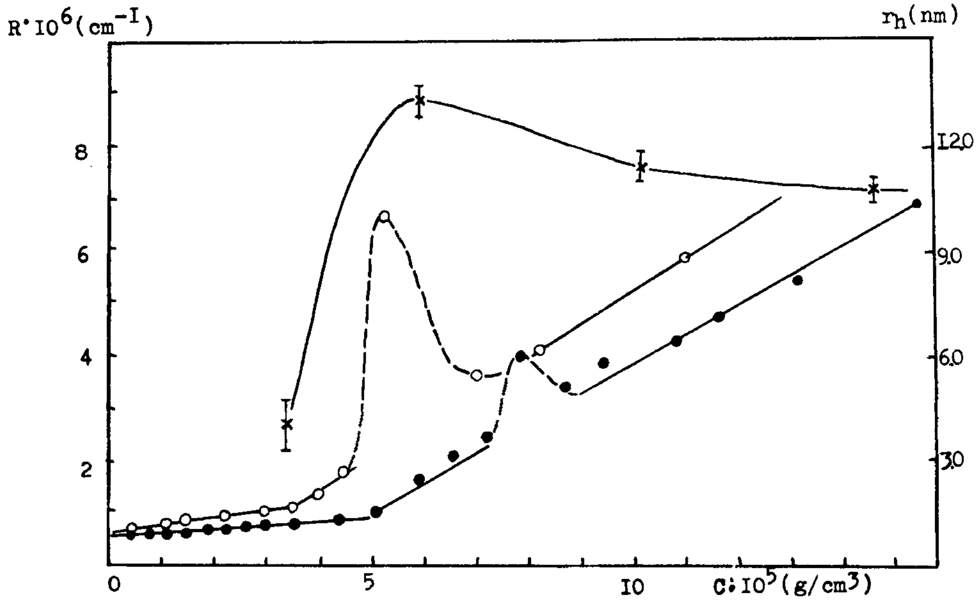

FIGURE 3 Rayleigh ratio (circles) and hydrodynamic radius of micelles (crosses) in the water–$C_{11}E_9$ dilute solution.

of A is defined with the help of the set-up calibration by the LS in pure water. Coefficient K can be given as

$$K = \frac{2\pi^2 n^2}{\lambda^4 N}\left(\frac{dn}{dc}\right)^2 \tag{3}$$

where N is the Avogadro number, λ is the wavelength of incident light, n is the refractive index. Fitting experimental data by Equation (1) we obtained for $T = 26°\mathrm{C}$ $M = 0.8 \cdot 10^5$ and aggregation number is 130; for $T = 50.1°\mathrm{C}$ $M = 0.9 \cdot 10^5$, and aggregation number is 150. These results are in a good agreement with our data of micelle size measurements by dynamic LS.

It is interesting to note that in concentration dependence of scattered light intensity (Figure 3) a peak was observed for concentrations slightly higher than CMC. Similar effects are also obtained in References 12, 13. Such an increase in scattering intensity may be explained by solubilization of water insoluble impurities. This conclusion is supported by the micelle size measurements with dynamic LS.

If micelles are considered to be noninteracted Brownian particles then their diffusion coefficient D and hydrodynamical radius r_h are correlated by the Einstein-Stokes formula[11]:

$$D = \frac{k_B T}{6\pi r_h \eta} \tag{4}$$

where k_B is the Boltzmann constant, T is the temperature, η is the dynamic viscosity of the solvent. The diffusion coefficient can be determined from the time dependent LS intensity correlation function $G(\tau)$

$$G(\tau) = G(O)\exp(-2Dk^2\tau) \tag{5}$$

where $k = (4\pi n/\lambda)\sin(\theta/2)$. The uncertancy of the measured $G(\tau)$ in the vicinity of CMC is large, because the LS intensity is weak. Therefore, the fit of the data enables one to obtain only the single (average) particle size. One can see in Figure 3 that the micelle radius increases more than twice at the concentrations corresponding to the intensity peak.

Critical Consolution Point

Consolution in micellar and microemulsion solutions is accompanied by opalescence. Since consolution occurs in a system having incidentally aggregated particles (micelles), a number of non-trivial questions arises: 1) can this transition be described by universal scaling laws? 2) is the dynamic scattering in the critical region of micellar solution determined by only one characteristic size, i.e., correlation length of concentration fluctuations? 3) what is the structure of two coexisting phases in micellar solution?

In the vicinity of the critical point the LS intensity is proportional to the space correlation function of critical fluctuations

$$I \sim G(k, \xi) = \chi(O, \xi) \cdot \phi(k, \xi) \tag{6}$$

where $\chi(O, \xi)$ is the critical susceptibility dependent upon the correlation length of critical fluctuation, $\phi(k, \xi)$ is the scaled function. In micellar phase critical fluctuations are probably related to the concentration of micelles. In the Ornstein-Zernike approximation

$$G(k, \xi) = \xi^2/[1 + (k\xi)^2] \tag{7}$$

and

$$\chi(O) \sim \xi^2 \sim t^{-\gamma} \tag{8}$$

where $\xi = \xi_o t^{-\nu}$, $t = |T - T_c|/T_c$, $\gamma = 2\nu$ (the meanfield value of ν is 0.5, the Ising-like scaling value of ν, which is universal for simple fluids and mixtures, is 0.63), is the bare correlation length. On the other hand, the correlation length can be determined by the dynamic LS. In hydrodynamic regime ($k\xi << 1$) one can find the correlation length with the help of the formula (4) if to substitute ξ instead of r_h.

The temperature dependences of the critical susceptibility and correlation length are represented in Figures 4 and 5. We limited the range of fitting by values of $t > 2 \cdot 10^{-3}$ where the condition $k\xi << 1$ is correct. Measurements of the time-dependent correlation function of depolarized light show that the multiple scattering effects are not negligible even at 1°C outside of the critical point. Therefore we did not try to analyze its immediate vicinity. The values of γ, ν and ξ_o are 1.3 ± 0.1, 0.65 ± 0.05 and 0.6 ± 0.1 nm correspondingly.

A number of authors studied critical behaviour of aqueous micellar solution of polyethylenglycol monoether (C_nE_m).[3-6,8,9] Nonuniversality of the critical exponents γ and ν was found. It should be noticed, however, that the measurement accuracy is restricted in many cases by amphiphile instability in the solution as well as by the appearance of multiple scattering near a transition (see Reference 9). Therefore the critical exponents data in micellar solutions must be handled with care. Another factor which is difficult to take into account is polydispersity of amphiphile molecules. Probably its effect on the critical properties is similar to impurity influence (see phase diagram in Figure 2). So the renormalization of the critical exponent may occur.[14] Thus the problem might lie in samples which were used. However, as one can see in Table I, there is also a definite correlation between the bare correlation length and the values of critical exponents: "small" ξ_o corresponds to the scaling values of γ and ν, though the values of r_h do not differ drastically.

We processed measured time-dependent correlation functions with polydisperse analysis programs. These correlation functions appeared to be discribed by only one characteristic time. Hence, in spite of polydispersity of our surfactant, the

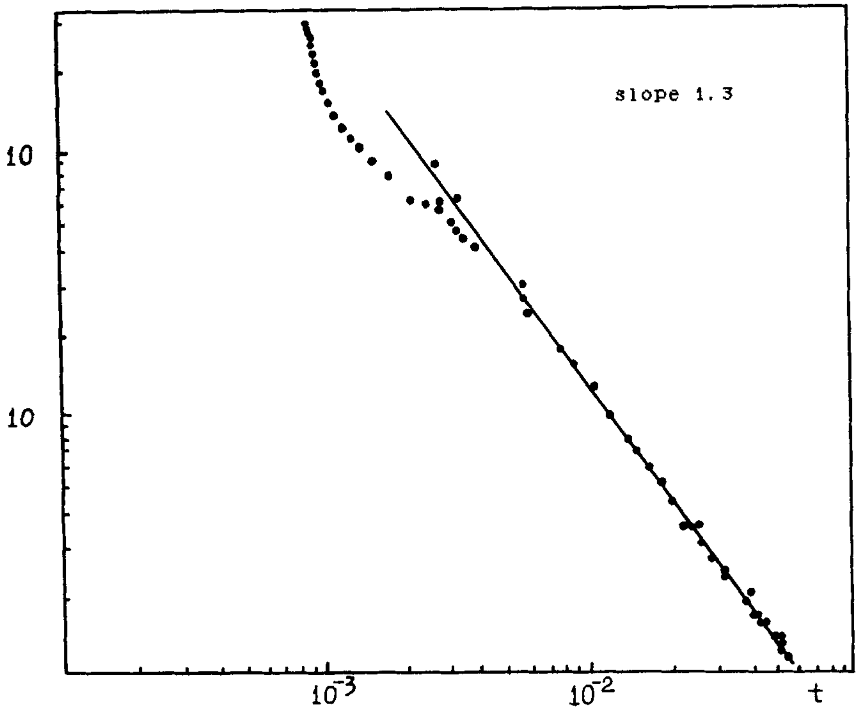

FIGURE 4 Light scattering intensity versus reduced temperature in the vicinity of the critical consolution point in the water–$C_{11}E_9$ solution.

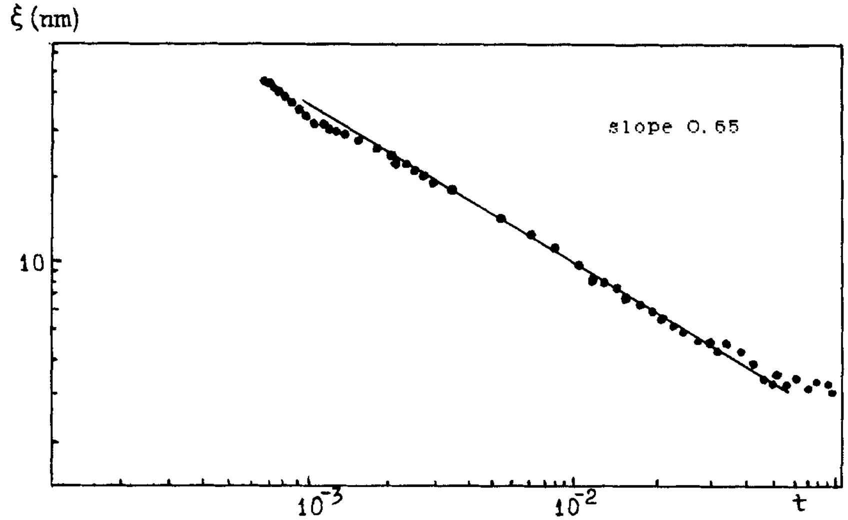

FIGURE 5 Effective hydrodynamic radius (correlation length) in the vicinity of the critical consolution point in the water–$C_{11}E_9$ solution.

TABLE I

Critical properties of some aqueous micellar solutions of polyethylenglycole monoethers

	C_6E_3	C_8E_4	$C_{11}E_9$	$C_{12}E_8$	$C_{12}E_5$
T, C	44.7 + 0.1	40.3 + 0.1	65.0 + 0.1	78.370 + 0.002	31.9
C, wt. %	13.0	7.0	7.5	3.9	1.2
r, nm	0.34 + 0.03	0.54 + 0.05	0.6 + 0.1	0.75 + 0.02	3.3 + 0.2
r, nm	1.4	2.5	3.0		3.0
	1.25 + 0.003	1.15 + 0.03	1.3 + 0.1	1.20 + 0.04	1.03 + 0.03
	0.63 + 0.03	0.57 + 0.03	0.65 + 0.05	0.63 + 0.01	0.51 + 0.02
Reference	3	3	our data	9	6

system is characterized by the single correlation length. After phase separation of the system far from the critical point, particles with micellar size in both phases were observed. Consequently one can speak about separation of the system into the "micellar gas" and "micellar liquid."

The results presented in Table I show that the value of the bare correlation length and the average molecular weight rather than polydispersity are responsible to the character of the critical behaviour.

Solubilization

We have carried out preliminary investigations of the process of *n*-octane solubilization in the aqueous solution of $C_{11}E_9$ depending on the *n*-octane concentration at constant surfactant content for a number of temperatures. Kinetics of the solubilization process is shown in Figure 6.

After addition of *n*-octane to the micellar solution and its smearing the micelle size grows rapidly and reaches maximum in an hour. Then the size decreases and reaches the equilibrium value in 5–10 hours. Furthermore the magnitude of the maximum size (which is of the order of magnitude of the equilibrium value) increases with *n*-octane concentration. This phenomenon can be explained apparently by the fact that at the initial stage oil is mainly solubilized by few micelles only. Incidentally their sizes grow up to the equilibrium magnitudes reached after oil is uniformly redistributed by slow diffusion process.

The main question arising when investigating the solubilization process is what solubilized micelles look like. At low oil concentration we deal with usual swollen micelles. At a relatively large oil concentration noninteracted micelles approximation becomes incorrect. In fact one can speak of the "effective size" r_{eff} which is obtained by dynamic scattering (Equation 4–5). Moreover when the effective size becomes comparable with the wavelength ($kr_{\text{eff}} \approx 1$) the new questions arise. What k-dependent time correlation function corresponds to this effective size? Practically it is very difficult to distinguish the interacted microemulsion particles from critical fluctuations.

As the *n*-octane concentration increases the effective size grows. At the *n*-octane concentration $0.4 \cdot 10^{-3}$ g/cm the effective size reaches 100 nm and does not change with further increase of the *n*-octane concentration. At the *n*-octane concentration for about $0.6 \cdot 10^{-3}$ g/cm the solubilization reaches its maximum and the phase separation is observed. Since the maximum observed size corresponds to the regime

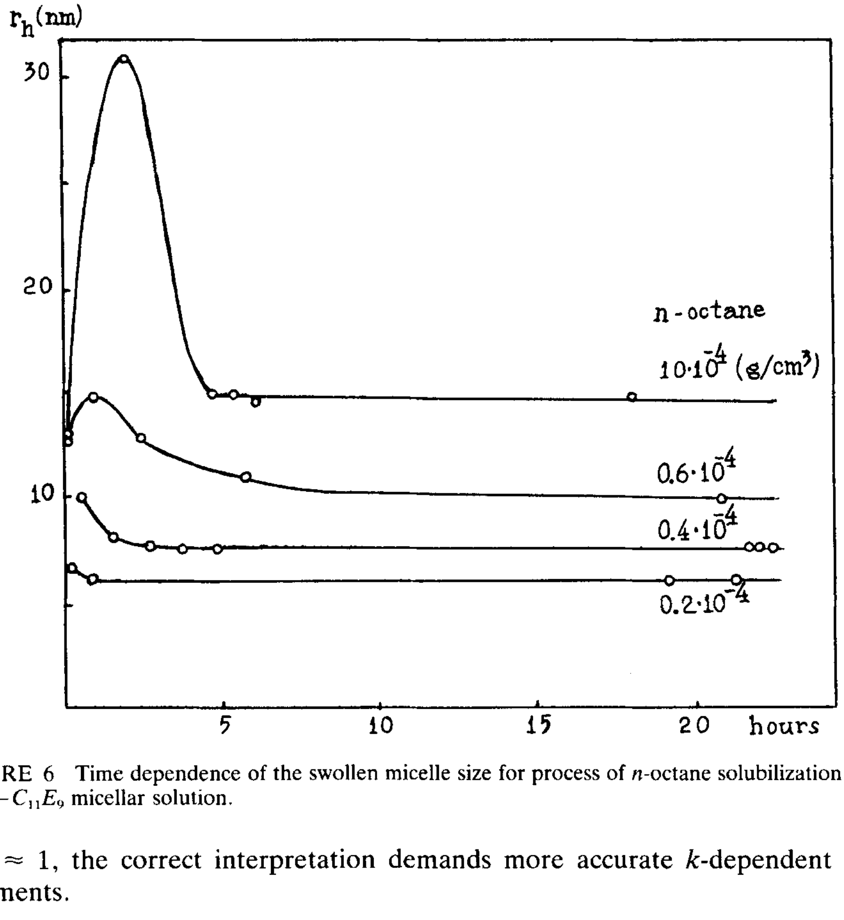

FIGURE 6 Time dependence of the swollen micelle size for process of *n*-octane solubilization in the water–$C_{11}E_9$ micellar solution.

$kr_{\text{eff}} \approx 1$, the correct interpretation demands more accurate k-dependent measurements.

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