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The Effect of Traces of Hexyloxyethoxyethanol on the 2-Butoxyethanol + Water Liquid–Liquid Coexistence Curve[1]

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A cloudy region found in the liquid system 2-butoxyethanol + water with traces of 2-(2-hexyloxyethoxy) ethanol, at the water-rich part of the phase diagram, is studied with light scattering. Our results indicate that the cloudy region corresponds to a phase separation. We present the cloud points for two series of mixtures at constant 2-(2-hexyloxyethoxy) ethanol concentration (1 and 1.5 wt%). Some comments are made to explain the apparent stability of that cloudy region.

KEY WORDS: cloud point; phase equilibria; polyoxyetheylene alkyl ethers.

1. INTRODUCTION

Systematic studies of aqueous solutions of amphiphilic molecules with small aliphatic tails, hence with no clearly defined amphipaty to be considered as conventional surfactants, are quite interesting. In particular, polyoxyetheylene alkyl ethers (C_nE_m) provide a sequence of amphiphiles, ranging from those that form simply associated nonideal solutions to those that form structured liquids, such as micelles and liquid crystals. Investigations of these systems appear to be very useful to clarify the effect of amphiphillic molecule length on the formation of structured liquids and, in particular, the minimal length to obtain surfactant-like behavior.

A remarkable example is the 2-butoxyethanol (2BE; ethylene glycol monobutyl ether; C_4E_1) + water (W) mixture. Here, the concentration dependence of its surface, bulk, and transport properties is very similar to

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that associated with micellization of normal surfactants. As examples, we mention the behavior of the apparent molar heat capacity [1–4], the concentration behavior of thermal expansion coefficients [5], the partial molar enthalphy [6], the surface tension [7], the transient foam stability [7], and the mutual diffusion [9]. Therefore, aggregates or micellar-like structures in this system in the water-rich region (2BE mole fractions of about 0.018) have been conjectured. This had led 2BE to be classified as a borderline surfactant. The characteristic concentration above which aggregation is present also has been found by ultrasonic experiments [9]. The formation of micellar structures is also suggested by the phase diagram [7], which is similar to those observed in nonionic surfactants. In particular, the phase diagram presents a lower critical solution temperature. Direct confirmation of the presence of micellar aggregates in this mixture has been obtained by light scattering [10–12] and, recently, by small-angle neutron scattering [13, 14].

2-(2-Hexyloxyethoxy) ethanol (HEE; C_6E_2) + W is another system with a behavior very similar to that of the 2BE + W system [15]. The phase diagram presents a lower critical solution temperature [15]. Surface as a function of the concentration [15] shows a drastic decrease until a constant value is observed. Transient foam stability measurements as a function of the concentration [5] also show a peak at about the same concentration where surface tension reaches its constant value (HEE mole fraction = 0.0016 at 282.15 K and 0.0023 at 258.15 K). Surface tension drop and foam stability peak decrease as the temperature increases. All this information, in conjunction with the measurements of apparent molar volume and sound velocity at 278.15 K presented quite recently [16] induced Sanchez et al. [15] to postulate that the properties of HEE + W can also be interpreted in terms of the formation of aggregate or micelle-like structures.

When a mixture is made up with water and two borderline surfactants as those mentioned above, some interesting questions arise. For instance, Does this mixture behave like a normal ternary mixture? or Is there a specific zone in the water rich-region where pseudoaggregates are more stable than in their corresponding binary water solutions? In particular, the mixture HEE + 2BE + W is a good candidate for this kind of studies, since there is a great deal of experimental evidence available for the binary aqueous solutions as mentioned above. This mixture presents a phase separation in the water-rich region, but below 12 wt% in 2BE (1 wt% HEE) it has been very difficult to obtain a clear definition of this phase separation. In addition, a quite stable cloudy region has been found in this mixture also in the water-rich region (2BE, 3–4 wt%; HEE, 1–1.5 wt%). Therefore, it is important, as a first step, to determine the nature of this cloudy region, since it could indicate the presence of some kind of aggregation or a metastable state of the ternary system starting a phase separation. Light scattering could be a good technique to characterize this region. Rayleigh ratios, R ($R = I_s r^2/Iv$, where I_s/I is the ratio of scattered to incident light, r is the distance from the scattering center to the detector, and v is the scattering volume), obtained by light scattering can give a sharp boundary of cloudy regions (cloud point), and dynamic light scattering can give a rough idea of the size of the aggregates or about the size of the little droplets at the onset of the phase separation.

The purpose of this paper is to present our measurements with light scattering devoted to understanding the nature of the cloudy region presented by the 2BE + W system with traces of HEE. Our results are consistent with the fact that this cloudy region corresponds to a phase separation.

2. EXPERIMENTS

2.1. Materials

HEE and 2BE of 99.7 wt% purity were supplied by Aldrich Chemical Company. Water was doubly distilled. The ternary mixtures were prepared by weight, with the estimated uncertainty in the quoted concentration (wt%) to be less than 0.02.

2.2. Instrumental Design and Operation

Light-scattering experiments were performed with the setup presented in Fig. 1. Laser light was produced by an argon-ion laser (Spectra Physics 2060-4S), operating at a wavelength of 514.5 nm with a power of 400 mW. Using a 25-cm focusing lens, the laser beam was focused to a beam waist of 0.7 mm in the center of a cuvette, at 90° from the detection direction. The solid angle subtended by the scattering volume and the photomultiplier was optimized for dynamic light scattering by mounting two 0.6-mm pinholes in the optical detection system. Dispersed light was detected with a photomultiplier (THORN EMI 9863B/100) and electrical signals were preamplified and shaped with a preamplifier/discriminator (ALV/PM-PD). Counts per second and correlation functions were obtained by a multiple-tau digital correlator (ALV 5000). The measured homodyne correlation function $g_2(q, t)$ was related to the normalized dynamic structure factor $g_1(q, t)$ by applying the well-known Gaussian approximation:

$$g_2(q, t) = 1 + B[g_1(q, t)]^2 \qquad (1)$$

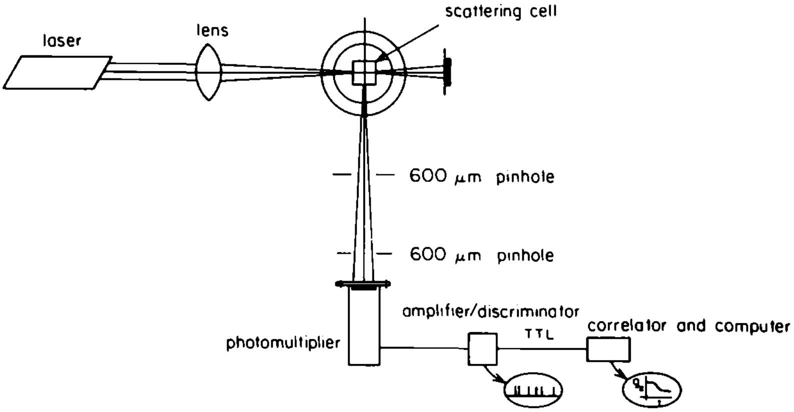

Fig. 1. Schematics of the experimental setup.

where q is the wave vector change in the scattering event, and B is a characteristic of the optical detection system.

Cuvettes (4 ml), scrupulously cleaned, and containing the samples, were place in a water thermal bath in the scattering area, as shown in Fig. 1. The temperature of the water thermal bath was kept constant within +0.01 K, with the aid of a controller (Tronac PTC-41). Temperature measurements were done with a platinum resistance thermometer (Guildline 9540). Light-scattering measurements were obtained after, at least, 30 min of thermal stabilization of the samples.

3. RESULTS AND DISCUSSION

The boundary of the cloudy region was determined through measurements of Rayleigh ratios at 90°, R_{90}, i.e., the incident and the scattered light form a 90° angle. We obtained the scattered light for two series of HEE + 2BE + W mixtures. In each series, the HEE concentration was fixed and the 2BE concentration was varied. The fixed values for HEE were 1 and 1.5 wt%. Figure 2 shows an example of Reyleigh ratios obtained for several mixtures at different 2BE concentrations (HEE = 1.5 wt%), as a function of the temperature. The Rayleigh ratio is a scattering cross section related to the intensity of fluctuations in the dielectric constant of the medium, which are, in our case, due to the number and size of the scatterers, i.e., aggregates or small droplets at the onset of the phase transformation. Therefore, when the temperature is increased from below in the phase diagram to reach the cloudy region, the R_{90} is almost a constant, until the aggregate or small droplet concentration is sufficiently high and

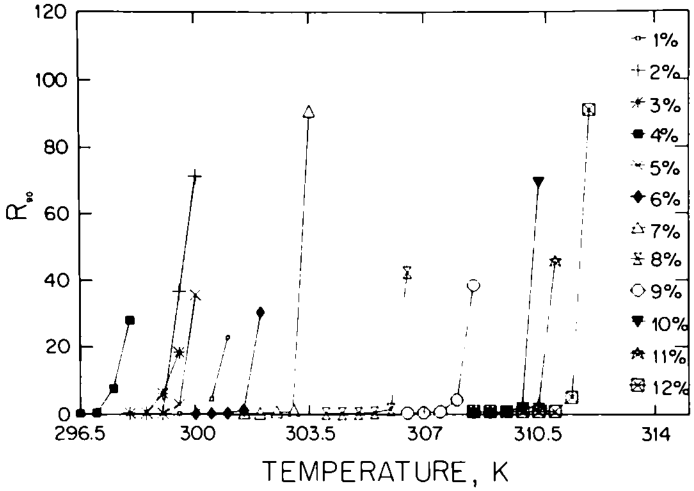

Fig. 2. R_{90}, in arbitrary units, as a function of the temperature for several concentrations of 2BE in the ternary mixture. The concentration in HEE was fixed to 1.5 wt%.

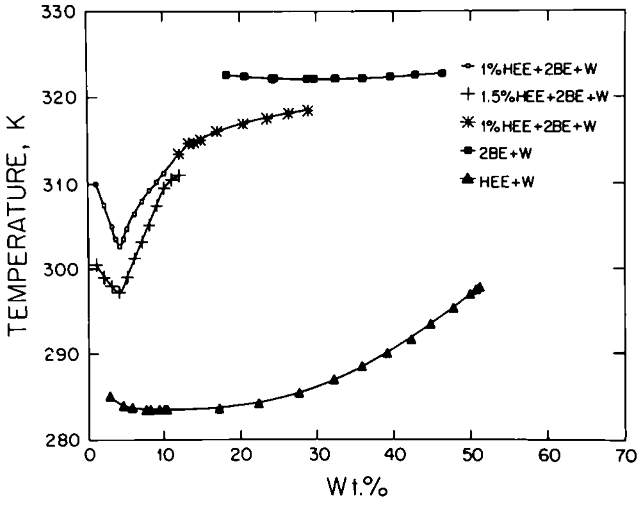

Fig. 3. Cloud point for the phase separation of the ternary mixtures in the water-rich region (HEE, 1.0 and 1.5 wt%), as a function of the 2BE wt%. For the case of 1.0 wt% in HEE, the data for concentrations above 12 wt% in 2BE are from Ref. 15. The data for the phase separation of the binary mixtures 2BE + W and HEE + W as a function of alcohol wt% [8, 15] were included for comparison.

the average size is sufficiently large to scatter an appreciable amount of light to a quite sensitive detector. Here R_{90} will increase dramatically. Hence, we can find the border of the cloudy region when the photon counts are significantly different from the background counts in the sample far beyond the cloudy region. With this technique, we are able to see when the system undergoes a sharp change in its turbidity not yet visible to the eye. The boundary of the cloudy region for the mixtures studied here was determined with a precision of ± 0.25 K. These results are shown in Fig. 3. The shape of these curves reflects the overlapping at some concentrations in Fig. 2. Here, we included some of the data obtained by Sanchez et al. [15] above 12 wt% in 2BE, by visually observing the phase separation. As we can see in Fig. 3, our curve for the case of 1 wt% in HEE is a continuation of the phase separation line observed visually by the authors just mentioned. Therefore, that curve must correspond to a boundary at which the system nucleates from the ternary liquid phase, generating cloud-point curves for the ternary system under discussion, in the water-rich range.

A confirmation in favor of the cloud-point curves can be found in the exponential decay rates of the correlation functions, where translational diffusion coefficients could be calculated by applying a standard cumulant expansion. We separated the effect of shear viscosity from the diffusive motion by applying the Stokes–Einstein relation. The resulting characteristic lengths were of the order of 0.2–2 μm. These numbers are consistent with macroscopic structures like small droplets formed at the onset of a phase separation, rather than with micellar aggregates. In a further experiment several samples were stabilized well above the cloud point, at 315 K, and after 24 h they showed phase separation. In the range of 2–5 wt%, however, these observations are difficult because the volume of the new phase is very small.

The cloud point is taken as that temperature at which the system undergoes a sharp change in its turbidity. This is the point at which the concentration of droplets is sufficiently high and the average droplet size is sufficiently large that an appreciable amount of scattered light becomes visible to the eye. This occurs at a time interval after a quench, when supersaturation falls dramatically, and this time increases markedly with decreasing supersaturation. Thus, although the nucleation rate may be high, its effects will not be observed unless the observer waits sufficiently long for the droplets to grow to a relatively large size. This is in agreement with Langer–Schwartz theory [17, 18] on the coupling between nucleation and growth during a phase separation. Hence, in the system under discussion, if samples are not heated slowly enough, the temperature will be above the point at which nucleation is rapid before clouding is observed. The apparent cloud point could appear at a higher temperature than the true cloud point, thus, the system appeared to be anomalously stable, making difficult the visual determination of the cloud point, as in Ref. 15. In our case, photon-correlation light scattering enabled us to see at the very beginning the first events of the nucleation processes of the phase transformation. In addition, in a ternary system other factor can limit the rate at which a transformation can occur. In particular, in these systems there are three mutual diffusion coefficients to be coupled to reach the equilibrium values, and therefore the time of growth of the new phase becomes longer.

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