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Anisotropic light scattering in water-alcohol mixtures

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Abstract

We have studied the depolarized Rayleigh-Wing light scattering of aqueous solutions of 2-butoxyethanol (C_4E_1) as a function of the temperature and concentration. The measured spectra give information on the rotational dynamics of water molecules. Their analysis confirm the amphiphilic character of the ethoxylated alcohol molecules that originates micellar structures. In addition, the water dynamics shows, in agreement with recent small angle neutron scattering measurements, the simultaneous presence of micelles and concentration fluctuations. This latter is dominant at high temperatures when one approaches the demixtion curve.

INTRODUCTION

It is well known the interest for the physical properties of water solutions of nonionic amphiphile molecules. In particular the most studied amphiphiles are the long-chain polyoxyethylene monoalkyl esters which in aqueous solution at room temperature form well defined supramolecular aggregates as micelles, or adding an oil, microemulsions. Their chemical formula is $C_mH_{2m+1}(OCH_2CH_2)_nOH$ or C_mE_n for short. Apart of these aggregation properties, C_mE_n water solutions exhibit a tendency to demix with increasing temperature, and separate at a lower critical solution temperature (LCST) for critical concentrations lying in the very rich water region of composition [1]. The LCST is usually located above the room temperature [1].

Short chain normal alcohols (C_mE_0), and alkoxyethanols (C_mE_1) can be considered as low n and m members of the C_mE_n series. Depending on the length (hydrophobicity) of the alkyl chain, they exhibit different phase behaviors: in fact, normal alcohols with $m \leq 3$ are completely miscible with water, for $m > 3$ they become immiscible displaying a closed loop of solubility. Shorter alkoxyethanols also display similar trends: up to C_3E_1 they are miscible with water in all proportions and temperatures, while C_4E_1 (2-butoxyethanol or BE) aqueous solutions demix at a LCST $T_c = 42.9^\circ C$ and $X_c = 0.052$ (X represents the BE mole fraction) [2]. The phase diagram of this latter mixture is shown in figure 1, and it can be observed that is quite similar to that observed in long-chain C_mE_n amphiphile solutions [1]. These latter feature and many anomalous physical properties exhibited by BE-water solutions are attributed to the formation of molecular aggregates. Although the previously described behavior in the phase diagram and the presence of definite maxima in the partial molar heat capacity [3] at a characteristic concentration, make the BE solution quite similar to C_mE_n , suggesting that among the C_mE_1 , BE has the minimal length to form micellar aggregates, the conclusive confirmation on

the presence of such structures is far from being completely established. However, the investigation of these systems is very useful in order to clarify the effect of amphiphilic molecules length (and in particular the requirement of a minimal length) on the formation of surfactant structures. In addition to the partial molar heat capacity [3] measurements a surfactant-like behavior of the simplest ethoxylated alcohols as C_4E_1 and C_6E_2 is shown by [4] measurements of density, refractive index and NMR performed on water solutions (and on water solutions with the addition of NaCl salt (brine)) with the indication that some kind of micellar structure is present in the mixture above an amphiphile mole fraction X of about 0.018. This behavior is similar to those observed in water solutions of known surfactants (e.g. sodium octanoate and sodium dodecyl sulfonate) at their critical micellar concentration (C.M.C.) [5,6]. The existence of such a characteristic concentration above which aggregation processes are present, has been also found by ultrasonic and hypersonic experiments [7,8,9] and is reported in figure 1. For the $X = 0.018$ sound velocity data show well defined peaks [9].

Figure 1. The phase diagram of the BE-water solution (Ref. [2]). Dashed line is the C.M.C. curve corresponding to partial molar specific heat (triangles) and sound velocity (dots) maxima. Squares refers to surface tension data.

In addition the ultrasonic absorption presents two well defined relaxation processes, one connected with the amphiphilic association (the lower relaxation frequency $f < 5$ MHz), and the other one to the amphiphile water hydrogen bonding (the higher relaxation frequency $f \sim 40$ MHz). Such a low relaxation frequency (5 MHz) was observed only in alkoxy ethanols of hydrophobic tail length C_4 or longer. The above experimental findings suggest that these amphiphilic alcohols remain monomolecularly dispersed in water for very low concentrations (lower than 0.018), while for higher concentrations the amphiphilic molecules form micellar-like structures that become more effective when temperature decreases. Viscosity data confirm this structural

picture. Furthermore, the comparison of recent Small-angle neutron scattering (S.A.N.S.) [10] and light scattering data (elastic and quasi-elastic) [11] carried out on water-butoxyethanol (C_4E_1) mixtures as a function of temperature, $-10 \leq T \leq 45^\circ\text{C}$ in the concentration range $0.015 \leq X \leq 0.09$ where ultrasonic attenuation exhibits peak values, seems to support this point of view, indicating the presence in the solution of dispersed micellar-like structures whose dimension increases slowly with temperature.

Besides to the many different experimental studies performed on water-BE solutions, at this time no definitive structural model exists for the nature of such aggregates: for example if they are either composed of molecules of the same species, or mixed. For example, in order to analyze Rayleigh and Raman scattering data, it was suggested a model for the internal molecular structure of the mixture which also seems to explain the critical phase separation [12,13,14]. In such a model it is proposed the simultaneous presence of two local structures of type $g[(H_2O)_{50}BuEtOH]$ and $h[(H_2O)_4BuEtOH]$ with g and h increasing with temperature from 10 to several hundreds. In these works the phase separation is explained in terms of these two structures with the increase in h and g up to the critical temperature; in particular it is suggested that the demixing occurs at the end of the growth of the local structures, already existing at low temperatures.

A definitive confirmation that micelles are originated in the water-BE system comes from two very recent studies: a measure of the surface tension [15] and a S.A.N.S. experiment [16], both performed at different concentrations and temperatures. In Fig. 2 is reported, for the temperatures 4 and 40°C , the surface tension γ of the BE-water mixture versus the BE concentration C ($\text{mol}\cdot\text{l}^{-1}$).

Figure 2. Surface tension γ as function of C ($\text{mol}\cdot\text{l}^{-1}$), of BE-water, at $T=4$ and 40°C .

As can be observed, the γ behavior vs. C is typical of aqueous surfactant solutions forming micelles [17]. In particular, increasing the BE

concentration (the surfactant in the present case) γ decreases; when the "critical micellar concentration" (C.M.C.) is reached, γ remains constant and does not change for further C-increases. This is the point where micelles start to form in the bulk. In Fig. 1 we report the corresponding C.M.C. data as determined from the γ measurements; for comparison are also plotted the values corresponding to partial molar specific heat and sound velocity maxima [4,9]. As it can be observed we have a good agreement in these different data, this confirms that the suggestions of different experiments (hipersound, density, viscosity, NMR and specific heat) are right: BE molecules in water are associated in micelles. In addition, such finding is confirmed by the data of an accurate and recent S.A.N.S. experiment [16], performed on water solutions of BE ($C_{12}E_1$) and $C_{12}E_3$ (a nonionic surfactant) at different temperatures; the corresponding spectra show clearly the existence of micellar aggregates in BE solutions above the C.M.C.. The size of micelles is constant; its shape is spherical and the radius corresponds to the length of the surfactant. In addition, it is observed at all the temperatures the presence of concentration fluctuations that contribute strongly to the scattered intensity. Such fluctuations increase with temperature and are dominant near the demixtion line. As a consequence this latter phenomenon suggests the following picture: the stability of the micelles decreases with increasing the temperature and can be related to the exchange of alcohol molecules between micelles.

In order to analyze, from a molecular point of view, the properties of such structures we have performed in the water-BE system a study of their anisotropic light scattering. As is well known light scattering is a powerful tool for the study of the structural and dynamical properties of materials. In particular, such studies give information on the translational and rotational motion as well as on the viscoelastic properties due to the interparticle interactions in complex fluid systems (such as supercooled liquids, micellar and polymer solutions, microemulsions and gels). Polarized and depolarized spectra can be used to study collective molecular motion in this class of systems. The information which can be extracted from the measured spectra is mainly related to the translational motion, as reflected by the density correlation function, and in the depolarized geometry to the rotational motion of the molecules as influenced by the presence of structural arrangements. On this basis, we show that depolarized scattering, being sensitive to the molecular rotational motion, can be used to probe the dynamics of water in the present complex liquids; giving, therefore, "local" information on the water properties in the neighborhood of micellar aggregates. Considering, in addition, that at present, great attention is devoted to the characterization of the structure and dynamics of water in confined geometries because of their fundamental and technological importance in many fields of physics, chemistry and biology [18], our objective is to study the properties of the water-BE solution. In particular, we hope that studying, by means of depolarized light scattering (anisotropic), the rotational dynamics of water molecules in presence of well defined micellar aggregates, we can obtain further information on the structural properties of the solution.

EXPERIMENTAL RESULTS AND DISCUSSION

The butoxyethanol used in this experiment was of high purity grade (99.99%) and was purchased from Jannsen Chemical. Triple distilled deionized gas-free water was used and the samples were prepared by weight in the proper quantity. Great care was taken to avoid contamination. All the samples were filtered before the measurements. Immediately after preparation, the samples were put into an optical cell. To avoid unwanted stray-light contributions at small forward angles we used a 27 mm diameter, high-precision optical round glass cell; we also used a refractive index matching bath continuously filtered in order to have flare-free measurements. In these conditions the

measured optical background in the scattered light was negligible. The scattering cell and the viscometer was thermostated, within ± 5 mK, in the range 0 — 49 °C, using a proportional temperature controller monitored by a calibrated platinum resistor connected to a high precision resistance bridge. The measurements were performed after a suitable time in order to ensure the thermodynamical equilibrium of the samples. The solutions studied in this work, together with the pure BE, have the following concentrations: $X = 0.015$, 0.035, 0.048, 0.052, 0.07 and 0.09. The depolarized Rayleigh scattering, was performed using a fully computerized double pass double monochromator (DMDP), SOPRA model DMDP 2000, with a half width at half maximum (HWHM) resolution of 700 MHz. All spectra are measured in the frequency range $-100 - +100$ cm^{-1} . The scattering geometry is the usual 90° arrangement with the incident beam vertically polarized with respect to the scattering plane. The scattered light was collected through a Glan-Thompson polarizer with an extinction coefficient better than 10^{-7} . The exciting source is the 5145 Å line from an Ar^+ laser (Spectra Physics 2020) operating at an average power of 1 watt.

Figure 3. Anisotropic spectra for pure BE (fig. 3a) and for a water-BE solution (fig. 3b).

It is well known that the nonshifted depolarized light scattering is caused by the fluctuations of the traceless part of the polarizability tensor [19]. The corresponding time correlation function $G^{\text{anis}}(t)$ and its Fourier transform $I_{\text{VH}}(\omega)$ can be characterized by various contributions, which depend on the different mechanisms involved in the scattering processes. Usually the depolarized intensity, or Rayleigh wing, is written in the form:

$$I_{\text{VH}}(\omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} \cdot \{ \langle \delta\alpha_{xy}^*(\vec{k},0) \delta\alpha_{xy}(\vec{k},t) \rangle \cdot \sin^2(\theta/2) + \langle \delta\alpha_{yz}^*(\vec{k},0) \delta\alpha_{yz}(\vec{k},t) \rangle \cdot \cos^2(\theta/2) \} \quad (1)$$

where $\langle \rangle$ denotes the thermodynamic averaging, $\delta\alpha_{ij}(\vec{k},t)$ indicates the traceless part of the polarizability tensor, θ the scattering angle in the usual scattering geometry. In the $I_{\text{VH}}(\omega)$ spectrum, contributions due to the coupling between rotational motion and collective hydrodynamic transport modes, if present, are also taken into account. In Fig. 3 are reported, the obtained spectra for pure BE (Fig. 3a) and for a water-BE solution (Fig. 3b). The depolarized Rayleigh scattering spectra in such conditions contain mainly two contributions: (i) the far contribution ($\omega \geq 30 \text{ cm}^{-1}$) and the narrow one ($\omega \leq 7 \text{ cm}^{-1}$) caused by molecular rotational motion. Such contributions are Lorentzian lines related to the exponential time decay of the local order. On this basis, our data were fitted to either a single or a double Lorentzian. As a result of such a procedure we obtain that the pure BE spectrum is well described by a single Lorentzian line plus the instrumental response function, while all other spectra can be fitted only in terms of two significant contributions. The HWHM and the relative intensity of each Lorentzian line are obtained directly by the fitting procedure. The true HWHM was obtained after subtraction of the instrument response function linewidth. In Fig. 3 the results of such a fitting procedure are shown as continuous lines. The pure alcohol exhibits a HWHM of about 1 cm^{-1} with a weak temperature dependence ($\sim 0.93 \text{ cm}^{-1}$ for $T = 0^\circ\text{C}$, and $\sim 1.1 \text{ cm}^{-1}$ for $T = 45^\circ\text{C}$), while the solutions show two contributions having respectively HWHM of about 3 and 40 cm^{-1} which are strongly dependent on T .

Considering the results of many studies performed in bulk water, in normal and supercooled regions, that show two Lorentzian lines a *fast* one, centered at about 40 cm^{-1} (nearly independent of T), and a *slow* one ranging from about 1.7 cm^{-1} ($T = -20^\circ\text{C}$) to about 8 cm^{-1} ($T = 50^\circ\text{C}$), we relate this two spectral contributions to the water dynamic in the solutions. In Fig. 4 and 5 we report, in a time representation, as a function of T for the different concentrations studied, the results of the *slow* and *fast* modes respectively; for comparison the results for pure water (coming from different experiments) [20,21] and for pure BE (fig. 4) are also shown. As it can be observed the alcohol rotational dynamics is slower in comparison with that one corresponding to water. Another quantity obtained from the spectra is the integrated area of the two different Lorentzian contributions that represent the number of scatterers for the respective modes. In Fig. 6 is reported the ratio of the area of the *fast* contribution with the total area for the several studied concentrations versus the temperature; as a result we have that the relative number of scatterers of the two distinct modes is independent of the concentration and the temperature. Looking Fig. 4 and 5 we have direct confirmation that the two contributions, *fast* and *slow*, observed from the measured spectra are due to the dynamics of water within the solutions. In particular we stress that the well known *slow* contribution ($1.7 \div 8 \text{ cm}^{-1}$) is related to the rotational dynamics of water molecules; more precisely to the hydrogen bond. In fact, the measured time follows an Arrhenius temperature

Figure 4. Temperature behavior of the *slow* relaxation time τ_s for the different studied solutions. Data for water refers to Ref. [20] (full dots) and Ref. [21] (full squares).

Figure 5. Temperature behavior of the *fast* relaxation time τ_f for the different studied solutions. Data for water refers to Ref. [21] (full dots).

dependence with an activation energy that corresponds to the hydrogen-bond energy [22]. The physical origin of the *fast* contribution ($\sim 40 \text{ cm}^{-1}$), observed very recently for the first time [21], is not clear and represents at present object of study. However, it can be related to the correlations of reorientational modes of water molecules [23], and the results of Fig. 6 agree with such an interpretation. The behavior of this mode, within the experimental error, is independent of the temperature in the range $-10 \div 20^\circ\text{C}$. (fig. 5) and is about the same of pure water; whereas a noticeable difference can be observed for $T > 20^\circ\text{C}$, in fact at these high temperatures an increase in the time τ_f is related to T increases; while the corresponding time for pure water remains constant.

Also the relaxation time τ_s , due to the *slow* Lorentzian contribution, shows two different behaviors for the two temperature intervals, $T < 20^\circ\text{C}$ and $T > 20^\circ\text{C}$ respectively. In fact, also in this case we observe that *slow* relaxation time behaves, with the temperature, in the same way of pure water; in particular, for $T < 20^\circ\text{C}$, τ_s , measured at the different water-BE concentrations, behaves as pure water showing the same Arrhenius temperature dependence (dotted lines in fig. 4). However, at the same temperature the relaxation time of the BE aqueous solution is higher ($\sim 30\%$) than that corresponding to the bulk water. For high temperatures, $T > 20^\circ\text{C}$, also for this mode we observe a remarkable difference with water: a sharper increase in τ_s increasing T . However, taking into account in the proper way the general findings of all the previous measurements in these solutions, and in particular the amphiphile character of BE molecules, we can rationalize the results of the present measurements.

In the low temperature region the two relaxation times behave, on changing T , in a way similar to the corresponding times for pure water. More precisely, while τ_f is nearly the same of the bulk water at all concentrations studied, τ_s is the same only for $X = 0.015$. For the other concentrations this latter time is larger (30%) than the corresponding one in water, but shows the same Arrhenius temperature dependence. In such a case, as shown by the surface tension data, the concentration X is above the C.M.C. and, as verified by S.A.N.S. [16], well defined micellar structures, with a gyration radius corresponding to the length of the alcohol molecule, are present in the system. Such a behavior for τ_s can be explained if we take into account the results of recent studies (X-ray [24] and Raman [25] scattering) on the aqueous suspension of a long chain amphiphile (C_{10}E_5). For these analyses it is clearly shown that water molecules interact with the hydrophilic groups of the amphiphile molecules and more precisely that water is partially bound to the oxyethylene groups of the amphiphile, forming a layer that surrounds the micellar structure. In addition, the structure of such bound water presents a local, low dense, four coordinated environment typical of the supercooled water. A behavior verified in many experiments for transport properties of water in confined geometries (water in confined geometries at room temperature has a behavior similar to the supercooled bulk water). In particular, this latter fact is reflected in the OH stretching vibrational modes with a behavior that corresponds to water at a lower temperature than the actual one in which the measurements is performed the measurement [25]. Being this phenomenon analogous to those observed in the actual results for τ_s , and considering that the T behavior (Arrhenius) of this rotational relaxation time is the same of the corresponding one in bulk water, we can assert that the data of the present analysis confirms, thought the study of the water (hydrogen bond) dynamics, the results of many other experiments: micellar structures are present in water-BE suspensions. Additional confirmation of this is given by the results on both the relaxation times at the concentration $X = 0.015$ (below the C.M.C.). In fact, being the system unable to build-up alcohol structures at this concentration value (as verified also from S.A.N.S. data [15]), the observed dynamics corresponds (within the experimental uncertainty) to the hydrogen bonds dynamics in bulk

water.

As far as the high temperature behavior ($T > 20^\circ\text{C}$) in the two characteristic times is concerned, we observe noticeable increases, increasing T , showing a water-dynamics in the BE solutions very different respect to the pure bulk water. This behavior in both τ_s and τ_f is related to the demixing phenomenon that takes place in the system which behaves as a critical one. Light and neutron scattering data [10,11,16] give information, in this temperature range, of an increase in the long range correlation length ξ of the fluctuations. This quantity, as shown by light scattering data [26], obey to the laws for critical phenomena showing the well known characteristic divergence, approaching the critical temperature T_c as $\xi = \xi_0 \epsilon^{-\nu}$, where $\epsilon = |T - T_c|/T_c$ is the reduced temperature and ν is the critical exponent. In addition, whereas in the low temperature region the S.A.N.S data are well fitted with a modified Guinier form, for the present temperatures a perfect fit is obtained only with the use of the simple Ornstein-Zernike relation [16]. Both these scattering results give, therefore, the information that the onset of the critical phenomenon can be detectable at temperatures near 20°C . The increase with temperature in the correlation length ξ has been ascribed [16] to the presence in the system of concentration fluctuations together with the spherical micelles; these fluctuations increase with temperature and are dominant when approaching the demixtion curve. This implies that the stability of the micelles decreases with increasing the temperature, and can be partly due to a possible exchange of alcohol molecules between micelles. In such a case, as shown by X ray [24] and Raman [25] scattering data in water solution of a long chain amphiphile (C_{10}E_5), the isolated alcohol molecules are hydrated in the oxyethylene group with an average number of bound water molecules for group n_w larger than that for amphiphile molecules aggregated in the micellar structure. More precisely, $n_w > 2$ for free alcohol molecules and $n_w \simeq 1$ for molecules within the micelles. The structure of such bound water presents a local, low dense, four coordinated environment typical of the supercooled water.

Figure 6. Ratio of the area of the *fast* Lorentzian mode with the total area for the several studied water-BE concentrations versus the temperature.

Another possible explanation of this high temperature dynamics can be due to a clustering of the micelles in the critical region with ordering effect in water outside the micellar structure. The increase in ξ approaching T_c can be

connected to a percolation-like phenomenon, similar to that observed in micremulsion systems [27] with a LCST. By using this model one explains the critical behavior of the shear viscosity and the relaxation rate in the density-density correlation function measured by dynamic light scattering in the present mixture. Such data can be analyzed in terms of the mode-coupling theory only if background effects (due to a persisting presence of micellar aggregates) on the transport coefficient are taken into account [26]. Both these two possibilities for the explanation of the physical origin in the increases of the two observed rotational times, are accounted for by the results represented in Fig. 6 for the ratio of scatterers involved in both the relaxational processes. We conclude with the suggestion that additional measurements of surface tension, and of small angle X ray scattering, can lead to a definitive explanation of the high temperature behavior in the structural and dynamical properties of the water-BE system.

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