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# Microstructure and concentration fluctuations in alcohol–Toluene and alcohol-Cyclohexane binary liquids: A small angle neutron scattering study

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ABSTRACT

The origin of concentration fluctuations in a series of binary liquids is examined by small angle neutron scattering in relation with H-bonded micellar clusters and the aggregation of alcohol-rich domains, which is also related to the well-known observation of a prepeak in diffraction spectra of alcohols. The results suggest that concentration fluctuations do not arise from size variation and re-arrangement of the mesoscopic domains but from the micellar-clusters themselves. We evaluate the scattering intensity at small angles and deduce the Ornstein–Zernike correlation lengths, the Bhatia-Thornton concentration fluctuations and the Kirkwood–Buff integrals. An alternative approach, based on the Guinier approximation was applied, indicating that the observed inhomogeneity could be related to spherical particles with diameter comparable to the H-bonded multimers. We compare the structure factor of different systems when varying the molecular interactions: the alcohol–solvent interaction has been tuned with Toluene and Cyclohexane aprotic solvents, and the amphiphilic character of the alcohol, by going from *Tert*-butanol to Ethanol and Methanol.

## 1. Introduction

Many binary liquids containing alcohol molecules display a strong deviation from the ideal mixture behavior. This deviation can be attributed to the incomplete mixing of the distinct interacting molecules at the microscopic level even though these liquids are often macroscopically miscible [1,2,3,4]. These original features are often observed for small-chains alcohols, also denoted hydrotropes, which exhibit an amphiphilic character but are too small to form ordinary micelles in solution [5]. Recent studies have linked the structural complexity of aqueous solutions of small H-bonded molecules to the interplay between concentration fluctuations and self-aggregation, the concept of molecular emulsions being introduced by Kezic and Perera [6,7,8,9]. It turns out that multiscale approaches are required for the structural characterization of H-bonded micelle-like clusters and their spatial organization during dilution in water or in an aprotic solvent, the latter acting as H-bond diluent, which modulates the molecular interactions [10,11,12,13,14].

Water–*Tert*-butanol (TBA) mixture is one of the systems that are the most debated currently, being considered as the prototypical system to advance our understanding of hydrotrope solubility in aqueous solution [5,8,9,15,16,17,18,19]. Analogous interest arises from studies on non-aqueous solvent–TBA mixtures. Distinct self-association and segregation processes have been examined in detail for *Tert*-butanol (TBA)–Toluene (TOL) and *Tert*-butanol (TBA)–Methylcyclohexane (MCY) systems [10]. For this purpose, two techniques were applied: Raman spectroscopy to quantify the size distribution of the H-bonded micellar multimeric clusters and neutron diffraction to investigate the spatial correlation between these clusters at larger distances [10]. According to the analysis of Raman results, TBA molecules mostly form H-bonded tetrameric units, which exhibit an exceptional stability [20,21]. They persist under conditions of high dilution, i.e. molar fraction $x$ of TBA as low as $x = 0.1$ in TBA-MCY mixtures. On the contrary, the spatial correlations between these neighboring micellar clusters seem much more sensitive to dilution. This phenomenon was revealed in the neutron diffraction structure factor by the suppression of a pre-peak, located at a momentum transfer $q_{PP} = 0.7$ Å$^{-1}$, which is a well-known signature of TBA intermediate range order and the existence of correlations between H-bonded units [10,22,23,24,25,26,27,28,29,30]. It was shown that the addition of a small amount of aprotic solvent is sufficient to turn off the prepeak intensity with a complete extinction for $x < 0.6$–$0.8$ for TBA–TOL and TBA–MCY [10]. Accordingly, it was suggested that the microstructure of these mixtures could be expressed in terms of non-interacting micellar TBA clusters for a broad range of compositions, while correlated clusters and diluted monomers were prevailing for high and low values of $x$ respectively (cf. Fig. 12 in ref. [10]).

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In this article, we extend the study of the segregation phenomenon towards a lower $q$-region. Small angle neutron scattering (SANS) is a complementary method to address the inhomogeneity of the mixtures in terms of concentration fluctuations, which are signatures of single-component-rich domains triggered by selective molecular interactions. Different hydrogenated/deuterated isotopic compositions are used to vary the scattering length density of the components of the binary liquids, and optimize the contrast between domains of different compositions. The characteristic correlation length of the inhomogeneities has been determined using the Ornstein–Zernike model [31]. An alternative approach, based on the Guinier approximation was applied, indicating that the observed inhomogeneity could be expressed in terms of weakly interacting spherical particles with diameter comparable to the H-bonded multimers [32]. The formalism of Bhatia and Thornton has been applied to decouple the different correlation functions related to density and concentration from the total neutron structure factor at zero-$q$ [33]. The fluctuations of the local composition have been quantified by the evaluation of the Kirwood–Buff integrals (KBI), which can be determined from the experimental forward scattering intensities [34].

The aim of this study is to shed light on the different phenomena, expressed in terms of self-association, multimers and concentration fluctuations that contribute to the complex microstructure of prototypical alcohols mixed with aprotic solvents. Different systems have been considered to vary their molecular interactions. First, the alcohol–solvent interaction has been tuned by comparing TBA–TOL and TBA–Cyclohexane (TBA–CYC) mixtures. The amphiphilic character of the alcohol has been then varied, going from TBA, to Ethanol (ETA) and Methanol (MEA). The overall assessment suggests that concentration fluctuations are primarily determined by the existence of H-bonded micellar-clusters with weak inter-cluster interaction rather than from fluctuations of the size and arrangement of mesoscopic alcohol-rich domains.

## 2. Experimental

Small-angle neutron scattering experiments were performed on the PAXY diffractometer (LLB, Saclay). The sample detector distance chosen was 1.6 m and the neutron wavelength used was 3.5 Å allowing the measurement of the diffracted intensity in a momentum transfer range ($0.04 < q < 0.5$ Å$^{-1}$). The samples were prepared from hydrogenated *Tert*-butanol TBA(H) mixed with deuterated Toluene TOL(D) or with Cyclohexane CYC(D) as well as their opposite isotopic compositions: the four types of mixtures are latter denoted TBA(H)–TOL(D), TBA(H)–CYC(D), TBA(D)–TOL(H) and TBA(D)–CYC(H), respectively. Methanol and Ethanol hydrogenated samples were also prepared with deuterated Toluene i.e. MEA(H)–TOL(D) and ETA(H)–TOL(D) mixtures. The bulk samples were prepared in volume fraction covering the concentration range $x = 0$–$1$ ($x$ being the volume fraction of the alcohol). The measurements were conducted at room temperature with a thermal bath regulator set to 22 °C. The solutions were prepared in advance so the mixtures are thermodynamically at equilibrium. The solutions were filled in 1 mm quartz Hellma cells. The intensities were corrected from empty cell contribution by subtraction of the filled and empty samples spectra, divided by their own measured forward transmission. The correction of the systematic variation of the detector efficiency and normalization of $I(q)$ to absolute unit were performed with respect to the measured intensity of hydrogenated water filled in the same cell, having a flat signal with a known value of its incoherent cross section ($\Sigma(H_2O)/4\pi = 0.445$ cm$^{-1}$).

## 3. *Tert*-butanol–Toluene and *Tert*-butanol–Cyclohexane systems

### 3.1. Experimental results

The neutron scattering profile shows an increase of the scattering intensity at low $q$ for all the binary mixtures (Figs. 1 and 2), which firmly indicates that the molecular distribution in the liquid is heterogeneous. In the $q$-range covered by the SANS instrument, albeit a prominent maximum intensity centered at $q = 0$, the scattered intensity does not exhibit any measurable peak at finite $q$-value.

Teubner and Strey have introduced a phenomenological approach to interpret the scattering intensity of microemulsions [35]. The theory has been later discussed for aqueous solutions of short-chains amphiphilic molecules, including TBA and discussed in the frame of so-called molecular emulsions [6,7,8,9,36]. According to Teubner–Strey approach, the scattering function is expressed as the inverse four-order polynomial in $q$. The microstructure is defined by two characteristic lengths corresponding to the domain size $d$ (i.e. periodic repeat distance) and the correlation length $\xi$. A distinct prediction of this theory is the appearance of a prepeak located at $q = 2\pi/d$, that reflects the pseudo-periodic organization of the domains. The absence of a diffraction peak in the present SANS measurement suggests that on the length scale probed there is no observable microstructure with pseudo periodic order. We remind that the correlations between micellar clusters show up as a prepeak at $q = 0.7$ Å$^{-1}$ which is then related to smaller (near-molecular) repeat distances. In addition, it was shown that this prepeak rapidly vanishes with dilution, which is at variance with the small angle scattering intensity that readily increases [10]. This suggests that the intercluster correlations are effectively lost by dilution. The Debye–Bueche model is an alternative model which is often used to describe phase separated binary systems [31]. The scattering intensity is a squared Lorentzian function $I(q) \propto \frac{1}{(1+q^2\xi^2)^2}$ introducing a unique correlation length $\xi$. It is indeed a special case of the Teubner–Strey model for $\xi \ll d$. In practice, it was observed in other studies that this is reduced to an Ornstein–Zernike function (single Lorentzian form) if the four-order term $(q\xi)^4$ is not detectable, which turns out to be the case in the present study, given that $q\xi < 1$ [37]. This is analyzed quantitatively in the following.

### 3.2. Ornstein–Zernike analysis

The scattered intensity was modeled by a Lorentzian function according to the Ornstein–Zernike theory [38]. Extending the case of phase separating systems [39,40], this formalism is also known to accurately reproduce the scattering intensity of many non-ideal binary mixtures [41,42,43] and can be defined as:

$$I(\mathrm{q}) = \frac{A}{1 + q^2\xi^2} + B \tag{1}$$

where the first term comprises the $q$-dependent coherent scattering, the second term represents the $q$-independent background and $\xi$ is the correlation length characterizing the spatial extension of the scattering length density fluctuations. This formalism can be applied to describe the scattering intensity at zero angle which can originate from domains with distinct scattering length density caused by density and/or concentration fluctuations. Experimentally, the coherent forward scattering intensity $I_{\mathrm{coh}}(0)$ can be obtained via extrapolation to zero-$q$. The first term $A$ arises from the $q$-dependent coherent scattering. The second term $B$ comprises the coherent scattering arising from the isothermal compressibility and the incoherent scattering, which do not depend on $q$, according to

$$A = I_{\mathrm{coh}}(0) - \rho^2 k_B T \kappa_T \overline{b}^2 \approx I_{\mathrm{coh}}(0) \tag{2}$$

$$B = \frac{\sigma_{inc}}{4\pi} + \rho^2 k_B T \kappa_T \overline{b}^2 \approx \frac{\sigma_{inc}}{4\pi} \tag{3}$$

where $\rho$, $k_B$, $T$, $\kappa_T$ $\sigma_{inc}$ are the molecules number density, the Boltzmann constant, the temperature, the isothermal compressibility, and the average incoherent cross section per volume, respectively. The average molecular scattering length $\overline{b}$ is defined as $\overline{b} = x_1 b_1 + (1 - x_1) b_2$, where $x_1$ is the aprotic solvent molar fraction, $b_1$ and $b_2$ are the sums of the coherent scattering lengths of the atoms constituting the aprotic and the alcohol molecules. The isothermal compressibility of