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# Microscopic origin of the scattering pre-peak in aqueous propylamine mixtures: X-ray and neutron experiments *versus* simulations

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The structure of aqueous propylamine mixtures is investigated through X-ray and neutron scattering experiments, and the scattered intensities compared with computer simulation data. Both sets of data show a prominent scattering pre-peak, which first appears at propylamine mole fraction  $x \ge 0.1$  around scattering vector  $k \approx 0.2$  Å<sup>-1</sup>, and evolves towards  $k \approx 0.8$  Å<sup>-1</sup> for neat propylamine x = 1. The existence of a scattering pre-peak in this mixture is unexpected, specifically in view of its absence in aqueous 1-propanol or aqueous DMSO mixtures. The detailed analysis of the various atom–atom structure factors and snapshots indicates that significant micro-structures exist, which produces correlation pre-peaks in the atom–atom structure factors, positive for like species atom correlations and negative for cross species correlations. The scattering pre-peak depends on how these two contributions cancel out or not. The way the amine group bonds with water produces a pre-peak through an imbalance of the positive and negative scattering contributions, unlike 1-propanol and DMSO, where these 2 contributions compensate exactly. Hence molecular simulations demonstrate how chemical details influence the microscopic segregation in different types of molecular emulsions and can be detected or not by scattering experiments.

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## 1 Introduction

When radiation, whether it is visible light, X-rays or neutrons, is scattered off a liquid, it reveals the presence of the microscopic constituents through their density correlations.<sup>1,2</sup> These correlations are the result of the way these microscopic constituents interact.<sup>3</sup> Such constituents can be atoms or molecules, but also mesoscopic objects such as micelles and monolayers, for example. For mono-atomic liquids, the scattered intensity I(k) is a product of the form factor F(k) describing the shape of the particle and the structure factor S(k) describing the correlation between such particles: I(k) = F(k)S(k).<sup>4</sup> In this frequency representation, the main peak in I(k) positioned at  $k_{\rm M} = 2\pi/\sigma$  allows one to relate the mean size  $\sigma$  of the particles to the

particle correlation peak in *S*(*k*). This simple formula also holds for more complex systems, such as micelles. The reason is that micelles look just like meso-atoms floating in a structureless solvent, as usually explained in various textbooks. In this case, the form factor F(k) refers to the micelle shape, and S(k) to micelle-micelle correlations. Since micelles are composite objects, with an underlying atomic sub-structure, the corresponding I(k)will exhibit 2 scattering peaks, a main peak  $k_{\rm M}$  positioned at the mean atomic size, and a pre-peak at  $k_{\rm P} < k_{\rm M}$ , related to the micelle shape and size.<sup>5,6</sup> Pre-peaks are equally found in neat alcohols, as I(k) reveals, in addition to a main peak at  $k_{\rm M}$ , their existence at  $k_{\rm P} \approx 0.4$ –0.7 Å<sup>-1.7–9</sup> The origin of such pre-peaks has been traced back to the existence of short chain-like clustering of the hydroxyl head groups, with mean size  $d \approx 10$  Å. These experimental results have been confirmed by computer simulation, from both snapshot and cluster analysis and study of the atomatom correlation functions and the corresponding structure factors.<sup>10–12</sup> These analyses clearly demonstrate that the pre-peak  $k_{\rm P}$  is related to both the size of the chains formed in the neat liquids and their density. If one applies the same type of analysis to spherical micellar systems, for example, which are made of surfactant molecules immersed in a solution made of solvent, ions and counterions, the existence of a scattering peak around  $k_{\rm P} \approx 0.06 \text{ \AA}^{-1}$  is commonly interpreted in terms of spherical

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micelles of mean distance or size parameter  $d \approx 100$  Å.<sup>5,6</sup> Both these interpretations preserve the initial idea that a peak in I(k)is related to some specific geometrical structure in the complex liquid, such as chains and spheres. Recently investigated room temperature ionic liquids (RTIL) also have a scattering pre-peak.<sup>13-16</sup> Indeed, these liquids are made of complex ions, which contain both charged and neutral atomic groups, and the former tend to selfassociate, thus creating a mesoscopic separation between charged and neutral domains, and it is this pattern which is detected by radiation scattering. Therefore, it would appear that the sole existence of some micro-structure in a mixture is sufficient for a scattering pre-peak, and this micro-structure does not need to refer to any specific geometry in the self-assembled objects. However, D'Arrigo et al. have provided an exquisitely detailed investigation of aqueous binary mixtures of various short-chain alcohol molecules, such as diols and triols, some showing a pre-peak and others not.<sup>17–19</sup> This study does not suggest any systematic pattern between the appearance of such pre-peaks and the solute shape or atomic complexity. In this context, it seems necessary to examine the details of the atomic contributions to the scattering intensity, and the simple relation I(k) = F(k)S(k) is to be replaced by the very general Debye formula for I(k) (see below). In the present manuscript, we report the finding of a scattering pre-peak in aqueous 1-propylamine mixtures, from both small angle X-ray (SAXS) and neutron (SANS) scattering, which appears at propylamine mole fractions above  $x \ge 0.1$  at about  $k_{\rm P} \approx 0.2$  Å<sup>-1</sup>, and persists all the way to x = 1 into the neat solute, at about  $k_{\rm P} \approx 0.7$  Å<sup>-1</sup>. This pre-peak is unexpected, principally in view of the fact that aqueous mixtures of a similar molecule, namely 1-propanol, do not show any scattering prepeak.<sup>20</sup> Since 1-propanol and 1-propylamine differ only by the hydroxyl and amine groups, it is interesting to investigate this system in order to understand the exact origin of the scattering pre-peak, particularly in terms of any underlying micro-structure. Through the use of computer simulations, we compute all the atom-atom correlations and rebuild I(k), hence allowing one to understand the general origin of a pre-peak in terms of the atomic details of the molecular structure of the constituents. The study helps to clarify how individual atom-atom structure factors, which are the true reflectors of the underlying micro-structure, contribute to the total scattering intensity, and help or not to reveal the hidden complexity of the molecular organisation.

### 2 Methodology

#### 2.1 The Debye expression

The radiation scattering intensity I(k) from a sample of volume *V* can be expressed through the Debye formula:<sup>21</sup>

$$I(k) = \frac{1}{V} \left\langle \sum_{i,j} f_i(k) f_j(k) \exp\left(i\mathbf{k} \cdot \left(\mathbf{r}_i - \mathbf{r}_j\right)\right) \right\rangle$$
(1)

where the functions  $f_i(k)$  are the atomic form factor for atom iand depend on the type of radiation which is scattered, and the sum runs over all pairs of scattering atoms i, j, which are at respective spatial positions  $\mathbf{r}_i$  and  $\mathbf{r}_j$ . The symbol  $\langle \cdots \rangle$  designates an average over all possible positions of these atoms, which could be either a thermal average in the case of experiments or a statistical ensemble average in the case of theory and simulations. Taking into account the fact that atoms are parts of molecular species, and introducing symbols i, j to designate the molecular species index, and  $a_i, b_j$  to designate the atoms of types a and b in respective molecules and using the definition of the atom-atom total structure factor:

$$\rho \sqrt{x_i x_j} S_{a_i b_j}^{(\mathrm{T})}(k) = \frac{1}{V} \left\langle \sum_{m_{a_i} m_{b_j}} \exp\left(i\mathbf{k} \cdot \left(\mathbf{r}_{m_{a_i}} - \mathbf{r}_{m_{b_j}}\right)\right) \right\rangle$$
(2)

where the sum runs over all atoms of type  $a_i$ ,  $b_j$ , and  $x_i = N_i/N$  is the mole fraction of molecular species *i*, one could cast the equation above into the final expression which will be used herein

$$I(k) = \rho \sum_{ij} \sqrt{x_i x_j} \sum_{a_i b_j} f_{a_i}(k) f_{b_j}(k) S_{a_i b_j}^{(T)}(k)$$
(3)

where  $\rho = N/V$  is the number density (*N* is the number of particles in the volume *V*). It is important to understand that the total structure factor appearing in these expressions contains the intramolecular atom–atom contributions as well as intermolecular atom–atom contributions, hence the superscript (T) for total. In the case of atoms rigidly bound inside a molecule, the intramolecular part is simply the Bessel function  $j_0(kd_{a,a_j}) = \sin(kd_{a,a_j})/kd_{a,a_j}$  where  $d_{a,a_j} = |\mathbf{r}_{a_i} - \mathbf{r}_{a_j}|$  is the distance between 2 atom sites  $a_i$ and  $a_j$  belonging to the same molecule of species *a*. The atom– atom structure factor  $S_{a,b_j}(k)$  is related to inter-molecular pair correlation function  $g_{a,b_j}(r)$  by the formula<sup>22</sup>

$$S_{a_i b_j}(k) = \delta_{ab} + \rho \sqrt{x_i x_j} \int d\mathbf{r} \left[ g_{a_i b_j}(r) - 1 \right] \exp(i\mathbf{k} \cdot \mathbf{r})$$
(4)

while the total structure factor is defined as

$$S_{a_i b_j}^{(\mathrm{T})}(k) = w_{a_i b_j}(k) + \rho \sqrt{x_i x_j} \int d\mathbf{r} \left[ g_{a_i b_j}(r) - 1 \right] \exp(i\mathbf{k} \cdot \mathbf{r})$$
(5)

where  $w_{a,b_j}(k) = j_0(kd_{a,b_j})$  is the intra-molecular correlation term, and the Kronecker  $\delta_{ab}$  serves to discriminate unlike-species contributions. In this work, the atom-atom structure factors  $S_{a,b_j}(k)$  are computed by the Fourier transform of the atom-atom correlation function  $g_{a,b_j}(r)$  obtained from the computer simulations, and through the use of eqn (3) and (5) are related to I(k), which is then compared with the experimental data obtained from X-ray and neutron scattering. As in ref. 23, we would like to emphasize that scattering expressions neglecting the intra-molecular contributions, such as in the often cited Pings–Waser paper,<sup>24</sup> can lead to severe underestimations of the small-*k* features of I(k). While it is customary to mask this discrepancy by plotting kS(k)*versus k*, such tricks do not really help in spotting differences resulting from the supra-structure between the calculated and the experimental I(k), which are particularly sensitive at small-*k* values.

#### 2.2 Experimental and computational details

SANS experiments have been carried out at the YuMO time of flight neutron spectrometer, operating at the IBR-2 pulsed reactor.<sup>25</sup> Mixtures of 1-propylamine (Sigma-Aldrich, 99% purity) with  $D_2O$  have been measured at 25 °C in quartz cells, and the

scattering data corrected for transmission, scattering of the empty cell and the incoherent background, and converted to absolute scale by comparing with scattering from vanadium, built in the instrument. The incoherent background was subtracted by measuring  $H_2O/D_2O$  mixtures with the same number density of H atoms as the studied propylamine solutions.

SAXS measurements have been performed on a SAXSpace instrument of the Kratky system (Anton Paar, Austria), connected to a conventional X-ray generator (Seifert, 40 kV, 50 mA, Cu K<sub> $\alpha$ </sub>). Mixtures of propylamine with H<sub>2</sub>O have been measured at 25 °C in standard quartz capillaries of 1 mm outer diameter and 0.01 mm wall thickness and the scattering was recorded using an image plate for 30 min exposition time. The measured intensities were corrected for transmission, polarisation and the contribution of the empty capillary, and the data brought to absolute scale by comparing to scattering of water.<sup>26</sup> The data have not been corrected for the instrumental smearing.<sup>9</sup> The propylamine mole fraction range was 0.03–0.30 for SANS, and 0.0–1.0 for SAXS measurements.

The computer simulation data used in this work have been previously reported by some of us,<sup>27</sup> and we briefly give some details. All simulations were performed with the program package Gromacs,<sup>28</sup> with the forcefield Gromos53a6<sup>29</sup> for propylamine and the SPC/e<sup>30</sup> water. In order to properly describe the microstructure of the mixtures, a number of molecules of N = 2048 was found sufficient for propylamine concentrations above 50%, while  $N = 16\,000$  was found necessary for smaller propylamine concentrations. The box of neat propylamine contained 2048 particles, corresponding to a box length of 64.7 Å. As for the propylamine-water mixture, system sizes of both N = 2048 and  $N = 16\,000$  were considered, yielding an average box size of 54.6 Å and 108.4 Å, respectively. These box sizes ensure that the smallest k-vector value, for which our calculated structure factors are reliable, is about 0.1 Å<sup>-1</sup>. The systems were simulated in the isobaric-isothermal (constant NpT) ensemble, at a temperature of T = 300 K and pressure p = 1bar, using the Nose-Hoover thermostat<sup>31,32</sup> and Parrinello-Rahman barostat.<sup>33</sup> After energy minimization, the systems were equilibrated in the NVT and then NpT ensemble, for a total of 1 ns. The following production runs lasted 4 ns, in order to sample at least 2000 configurations for calculating site-site correlation functions  $g_{a,b_i}(r)$ , where  $a_i$ ,  $b_j$  represent any two atomic sites on the molecules and *i*, *j* correspond to the species index.

It seems important to clarify the problems of units for various types of I(k). Since the form factors have units of a distance, I(k) in eqn (3) has the dimension of an inverse length, and is usually expressed in cm<sup>-1</sup>. In the case of X-ray scattering, if one uses the form factors from crystallographic tables, these are expressed in units of electron radius ( $r_e \approx 2.8179$  fm), hence we use the prefactor  $r_e^2 \rho = r_e^2 (N/L^3)$ , where N is the number of molecules in a simulation box of size  $L_B$ . In the case of neutron scattering, the form factors are the scattering lengths, equally expressed in femtometers, hence the prefactor is just (1 fm)<sup>2</sup>(N/L<sup>3</sup>). All lengths are expressed in cm in order to obtain I(k) in cm<sup>-1</sup>.

## **3** Results

#### 3.1 Radiation scattered intensities

Fig. 1 shows the small angle X-ray scattered (SAXS) intensities (in  $\text{cm}^{-1}$ ) from experiments and simulations, and for the various propylamine mole fractions, including neat water and propylamine.

The first striking feature to be observed is the appearance of a scattering pre-peak in the overall k-range 0.2–0.7  $\text{\AA}^{-1}$ . The experiments show that the pre-peak appears for  $x \ge 0.1$ , starting at  $k \approx 0.2$  Å<sup>-1</sup>, and moving to higher k-values as x increases. The pre-peak amplitude has a non-trivial behaviour, first increasing until  $x \approx 0.2$ , then decreasing. The simulation data show exactly the same trends, in both peak positions and amplitude. But we see that the pre-peak exists even for the pure propylamine at  $k \approx 0.7$  Å<sup>-1</sup>, predicted from both experimental and simulated I(k). From this information, it is tempting to associate the scattering pre-peak in the mixture to a remnant of this neat propylamine pre-peak. We will see below that this is not the case, and that it also explains the non-monotonic behaviour of the pre-peak amplitude with x. In any case, since this pre-peak is a collective correlation effect, it is quite remarkable that the model based simulation I(k) should reproduce all the features of the real mixture spectra.

Concerning the main peak, which covers a wider range  $k_{\rm M} \approx 1.5$ –2.5 Å<sup>-1</sup>, we observe that the characteristic peakshoulder structure of the neat water I(k), at  $k \approx 2$  Å<sup>-1</sup> and  $k \approx 3$  Å<sup>-1</sup>, respectively, progressively changes into a single main peak feature as the concentration of propylamine is increased, as observed in both experimental and calculated spectra. This variation corresponds to consistently going from



**Fig. 1** X-ray and neutron scattering intensities for aqueous 1-propylamine mixtures with various propylamine mole fractions, from both experiments and computer simulations as obtained from eqn (3). Propylamine mole fractions are displayed in each graph, with color codes associated to their respective plotted curves.

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water molecule size  $\sigma \approx 3$  Å to propylamine average atomic constituent size  $\sigma_{\rm eff} \approx 4$  Å, through the use of the expression  $k \approx 2\pi/\sigma$ . We observe that the main peak positions are excellently reproduced by the simulation spectra. Interestingly, if we interpret the well known double peak structure of the X-ray spectra of pure water,<sup>34</sup> as corresponding to the water-water contact at  $k_{\sigma_{\rm W}} \approx 2 \text{ Å}^{-1} (\sigma_{\rm W} \approx 3 \text{ Å})$  and the hydrogen bonding distance at  $k_{\rm HB} \approx 3 \text{ Å}^{-1}$  ( $r_{\rm HB} \approx 2 \text{ Å}$ ), respectively, then the dual structure is seen to persist until  $x \approx 0.2$ , indicating the concentration range where the tetrahedral water hydrogen bonding holds. The observed differences in the main peak amplitudes between the experimental and the calculated intensities are a direct consequence of the united atom representation of the methyl/methylene groups of propylamine.<sup>23</sup> The model calculation leads to an overestimation of the carbon atom contributions, principally for the high propylamine mole fractions. While many previous investigations for several types of mixtures indicate that the agreement between simulation and wide angle scattering is generally excellent,<sup>35,36</sup> it is not obvious that this agreement should persist in the pre-peak region. Indeed, most realistic force field models capture well correlations at contact, which explains the large-k agreement. However, the pre-peak region corresponds to the meta-molecular aggregates' description, and it is not obvious that the simulations could well describe these features. The present results indicate that the microscopic details of the underlying micro-segregation are indeed well captured by model simulation, at least for this particular mixture.

Fig. 1 equally shows the small angle neutron scattered (SANS) intensities from experiments and simulations. Once again, there are striking similarities between the experimental and calculated spectra, and the various pre-peak features are also consistent with SAXS results. In particular, pre-peak positions are the same. Concerning the main peak positions at  $k_{\rm M} \approx 1.14-2 \text{ Å}^{-1}$ , we can also note similarities between the two sets of data from simulations.

To close this section, we would like to point out that the very small-*k* behaviour of the calculated I(k) is not very accurate, and should not be taken into account. This is typically in the range  $0 \le k \le 4\pi/L_{\rm B}$ , where  $L_{\rm B}$  is the simulation box size. For the present simulations, this corresponds to an upper limit  $k_{\rm B} \le 0.1$  Å<sup>-1</sup>, and values below this range should not be considered as accurate.

#### 3.2 Snapshots

Since our simulations lead to qualitative agreement with the experimental I(k), we expect that they also represent the proper microscopic structure. Therefore, in order to understand the various origins for the pre-peaks, or their absence, we show in Fig. 2 typical snapshots of the water–propylamine mixtures, for four characteristic propylamine concentrations of 5% in panel (a), 20% in panel (b), 50% in panels (c and d), and 80% in panels (e and f). For 50% and 80%, propylamine and water are shown separately in the upper and lower panels, respectively. Through these snapshots, one might expect to observe a direct link between the micro-structure and the corresponding prepeak structure in I(k).



**Fig. 2** Snapshots of aqueous propylamine mixtures for various propylamine mole fractions *x* displayed near each panel. (a) x = 0.05 (for 16 000 molecules); (b) x = 0.2 (for 16 000 molecules); (c) and (d) for x = 0.5 (2048 molecules); (e) and (f) for x = 0.8 (2048 molecules). For these 2 latter concentrations, upper panels (c) and (e) highlight the amine groups, while lower panels (d) and (f) highlight the water molecules. Omitted atomic groups are shown as semi-transparent. In all snapshots nitrogen atoms are in blue, oxygen in red and hydrogen in white.

Fig. 2a and b indicate that water and propylamine form segregated domains, much like what has been reported in several of our earlier papers, for aqueous mono-ols<sup>37</sup> and other mixtures.<sup>38,39</sup> For higher propylamine concentrations, we have previously reported that water tends to form chain-like aggregates.<sup>27</sup> In order to show this more specifically, we have explicitly shown separately water molecules (lower parts) and propylamine nitrogen groups (upper parts) for the cases of 50% and 80%. One sees very clearly water chains, and less clearly the nitrogen dimer or trimer short chains. These snapshots would suggest that the pre-peak observed for x > 0.1 could originate from water chain clusters, much like in neat alcohols,<sup>10,11</sup> but also in neat propylamine.<sup>27</sup> But this conclusion does not apply to the 20% case, where it is clearly seen that water forms globular domains. However, a close investigation of such domains reveals that it is made of water chains juxtaposed to each other. This is entirely lost in Fig. 2a for x = 0.05. Although it might be tempting to associate chain-like water domains to the pre-peak, we will see in Section 3.4 that, while water-DMSO mixtures equally show waterchains,<sup>40</sup> there is no corresponding pre-peak in the scattered intensity.<sup>41</sup> It is therefore necessary to further investigate the correlations associated to the micro-structure, namely the atomatom structure factors.

#### 3.3 Structure factors

Since, as far as the simulations are concerned, it is the same structure factors which appear in eqn (3), and they differ only by the atomic form factors in SAXS and SANS scattering, it is instructive to trace back the differences in the upper and lower panels of Fig. 1 to features common to both of them.

To this end, we compare the various contributions of the underlying atom–atom structure factors  $S_{a_ib_j}(k) = \delta_{ij} + \rho \sqrt{x_i x_j} \tilde{h}_{a_ib_j}(k)$  for the neat propylamine in Fig. 3a, together with a scaled version of the SAXS intensity. One can see how the various individual atom– atom structure factors contribute to the pre-peak and the main peak, and how they get scaled down by the atomic form factors



**Fig. 3** (a) Atom-atom structure factors  $S_{a,a}(k)$  for neat propylamine from computer simulations. Like atom structure factors are shown by full lines with the following color codes: nitrogen in blue, hydrogen in red, first methyl group near the amine head in cyan, second methyl in orange and last terminal methyl in green. All cross correlations are shown by dashed lines with the respective atom colors. The black curve is the total X-ray *l(k)* scaled by a factor 250. (b) Selected atom-atom structure factors for the water-propylamine mixture for x = 0.2. Coloring method as in (a), with water oxygen in blue, nitrogen in green and second methyl in orange. All respective cross correlations are shown by dashed lines with the respective atom colors. The total X-ray *l(k)* is shown in black, scaled by a factor 20.

in eqn (3). We note that all structure factors give only positive contributions. In Fig. 3b, we compare the contributions of selected atom-atom structure factors for the 20% aqueous mixture, together with the corresponding  $I_{\rm X}(k)$ , scaled to match the vertical scale. This time around, we clearly see that most like species atomic contributions give a positive pre-peak, while the cross species contributions give exclusively inverse negative pre-peaks. All these contributions do not necessarily coincide at the same *k*-vector, but they are all about  $k \approx 0.2 \text{ Å}^{-1}$ . We also notice very clearly that it is the water structure factors which contribute mostly to the positive pre-peak. This latter finding is in stark variance with the suggestion that neat propylamine (from Fig. 3a) and the 20% mixture would share the same propylamine structural features. In turn, this remark led us to question the initial microscopic mechanisms, *i.e.*, the formation of short propylamine chains, that one would have in mind from the sole analysis of Fig. 3a.

In order to investigate this matter further, we show in Fig. 4a for SAXS and Fig. 4b for SANS, the various partial contributions



**Fig. 4** Partial species – species contributions to X-ray I(k) calculated from computer simulations, as defined in eqn (6) (see text), for various propylamine concentrations *x* indicated in the panels. (a) For X-ray scattering and (b) for neutron scattering.  $I_{vww}(k)$  shown in blue,  $I_{pp}(k)$  in magenta and  $I_{wp}(k)$  in green. The dashed line is explained in the text.

of the species–species contribution to I(k). To this end, we rewrite eqn (3) with obvious notations as

$$I(k) = I_{ww}(k) + I_{pp}(k) + I_{wp}(k)$$
(6)

and in Fig. 4a and b we show the 3 contributions,  $I_{ww}(k)$  for water in blue,  $I_{pp}(k)$  for propylamine in magenta, and the waterpropylamine cross term  $I_{wp}(k)$  in green, together with the total intensity I(k) in black. In addition, we show by a dashed dark green line the negative sum  $-I_{ww}(k) - I_{pp}(k)$  of the like species contributions, with the idea in mind to see how these compensate the cross species contribution  $I_{wp}(k)$ . We plot these contributions for 4 typical propylamine concentrations of 5%, 20%, 50% and 80%. Only the pre-peak k-range is highlighted. In each of these cases, we observe that the like species contribution is always positive, while the cross species contribution is always negative. Comparing the light and dashed dark green curves, we see that the like species/cross species compensation is incomplete for x > 0.2, near complete for x = 0.2 and exactly compensated for x = 0.05. This happens for both SAXS in Fig. 4a and SANS in Fig. 4b, albeit with different magnitudes. These plots help to understand the origin of the pre-peak in the final scattered intensities: it is the incomplete cancellation of like species and cross species contributions. However, this information by itself does not help much to understand the physical origin of the pre-peak, specifically in terms of the underlying micro-structure. The only common structural feature we have found so far is the water chain cluster pattern, that one could eventually associate to the pre-peak. To confirm or disprove if this is true, we now compare with other aqueous mixtures we have investigated in previous works.

#### 3.4 Other aqueous mixtures

In recent works, some of us have investigated aqueous 1-propanol<sup>23</sup> and aqueous DMSO mixtures.40,41 1-Propanol is chemically more similar to propylamine than DMSO, having the same alkyl part with a hydroxyl OH head instead of an amine NH<sub>2</sub> head. However, our previous investigation of aqueous 1-propanol revealed very large micro-segregation, with very large domain correlation pre-peaks, positive for like species atom correlations and negative for cross species correlations, but which tend to cancel exactly to lead to a total absence of scattering pre-peaks in the X-ray and neutron scattering I(k), and consistent with experimental data.<sup>42,43</sup> We named this phenomenon domain ordering correlation, by analogy with charge ordering.<sup>44</sup> On the other hand, our computer simulation of aqueous DMSO mixtures revealed pre-peaks in water-water structure factors, which we could attribute to the existence of chainlike water aggregates.<sup>40</sup> Such water aggregation appears because of the strong water-DMSO pairing, detected by many previous studies with various methodologies, which leave water molecules unable to maintain their usual tetrahedral ordering, hence enforcing chain ordering. However, this chain ordering was found not to lead to any scattering pre-peak, consistent with X-ray data, and even near excellent agreement between the computed and measured scattering intensities I(k).<sup>36,41</sup>

Both results are illustrated in Fig. 5, where we show the various contributions of the scattering intensities of the 50% aqueous DMSO mixture in panel (a) and 30% aqueous 1-propanol in



**Fig. 5** Partial species–species contributions to *I(k)* calculated from computer simulations for X-ray scattering, (a) for the equimolar aqueous DMSO mixture and (b) for the 30% water 1-propanol mixture.

panel (b), in a way similar to that shown in Fig. 4. The intensities are shown in absolute (or electron) units  $(I(k)/\rho)$ , as in ref. 34, 41 and 45. The final scattering shows no pre-peak in both cases, despite the existence of clear positive and negative pre-peaks in like and cross correlations. This result is very astonishing, mainly in view of the fact that chain clusters of the hydroxyl groups lead to a scattering pre-peak in neat alcohols and neat propylamine. This discrepancy is not currently understood and we propose an interpretation in the next section. The results of the present paper on aqueous propylamine are consistent with both aqueous alcohol and aqueous DMSO mixtures, while at the same time producing some results difficult to interpret. Indeed, we find that no scattering pre-peak is found in the domain ordering low propylamine concentration region, which is also consistent with aqueous 1-propanol results. At the same time, for propylamine concentrations higher than x = 0.1, we find water chain ordering, but with a scattering pre-peak, which is not consistent with what is found in aqueous DMSO mixtures, and which also show water chains. In view of the contradictory results found in neat alcohols, aqueous DMSO and aqueous propylamine, it is quite tempting not to relate the scattering pre-peak to some underlying water chain ordering.

## 4 Discussion

The challenge posed by the present work is to understand the exact origin of the unexpected scattering pre-peak, seen in both SAXS and SANS as well as in the corresponding simulated spectra. We have convincingly shown that this pre-peak could not be unambiguously associated to the water chain formation witnessed in aqueous propylamine mixtures, despite the coincidental appearance of this pre-peak with the chain formation for x > 0.1. As mentioned in the Introduction, in scattering experiments, it is customary to associate pre-peaks with some underlying supra-molecular structure. But our previous studies have also demonstrated that, while a supra-molecular structure indeed produces pre-peaks in the atom-atom structure factors, these pre-peaks come in various shapes, positive ones and inverted negative ones, associated with different types of correlations, and that their final contribution to the scattering intensity can be exactly cancelled, leading to no pre-peak. In other words,

as observed in aqueous 1-propanol<sup>23</sup> and more recently in aqueous *tert*-butanol,<sup>46</sup> the absence of a scattering pre-peak in  $I(k)^{20,47,48}$  does not necessarily imply the absence of micro-heterogeneity and associated structure factor pre-peaks in  $S_{a,b_j}(k)$ . Conversely, some types of micro-structure, such as chain aggregates, sometimes produce a pre-peak, as in neat alcohols, and sometimes not, as in aqueous DMSO. These differences are certainly due to the differences between the various types of solutes, which we try to rationalise now.

When comparing Fig. 4 to Fig. 5, one striking feature is that the water-water blue curve is below the solute-solute magenta curve for the case of no pre-peak scenario (Fig. 5), whereas the ordering is reversed in Fig. 5 for the cases where a pre-peak is found. We follow here the assumption that it is this inversion which is the key to explain the origin of the scattering pre-peak, and we propose a molecular picture for it. The elements provided by the simulations are that water forms chains in aqueous 1-propylamine and DMSO, while it forms large globular domains in aqueous 1-propanol. Since both 1-propanol and 1-propylamine have a similar number of methyl groups, we deduce that the amine group allows a better water hydrogen bonding than the hydroxyl group, which in turn allows water to segregate much less in the latter mixture, by forming short chains instead of globular domains. This should explain why the water-water scattering contribution shows this specific inversion in these 2 mixtures, in the following way. When both species are fully micro-separated, then the species-species scattering contributions compensate exactly, whereas when the micro-separation is incomplete, the species that segregates the most (here water forming chains) contributes excedently. As to DMSO, which is known to be a rather hydrophilic molecule, the dominant solute contribution to the scattering is principally due to the large form factor of the sulfur atom. Indeed, the X-ray form factors are Gaussian-like functions<sup>49</sup> which start at the atomic number at k = 0, and this number is 16 for the sulfur atom, whereas it is 8 for oxygen, 7 for nitrogen and 6 for carbon. It is this dominance which explains why the solute-solute contribution to the scattering is above that of water. It is interesting to compare these explanations to the usual criteria for molecular hydrophobicity and hydrophilicity. Accordingly, one would select both 1-propanol and 1-propylamine as rather hydrophobic molecules (because of the dominance of the methyl groups), while DMSO would be hydrophilic.<sup>50,51</sup> However, these criteria alone cannot explain the inversion of the scattering curves and the existence or not of a scattering pre-peak. In addition, we note that hydrophilicity does not imply the traditional watersolute dimer picture, widely popularised in the case of aqueous-DMSO,<sup>50,51</sup> since we find that water forms chains in both aqueous DMSO and aqueous 1-propylamine. In order to highlight the specific behaviour of water in the case of aqueous 1-propylamine, which cannot be explained either by hydrophobicity or by hydrophilicity, we introduce the concept of water "mingling" for this type of mixture. 1-Propylamine has two hydrogens attached to the nitrogen atom, thus leading to more possibilities to water to bind to this molecule. We argue here that it is this mingling of water with the amine head group which leads to both water chain formation and the dominant water-water scattering contribution in I(k),

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hence leading to incomplete cancellation of like and unlike species domain correlations in favour of the like correlation, and hence the pre-peak. This argument is further supported by the fact that, a certain amount of propylamine is required for the incomplete cancellation to happen, in other words for the water-amine mingling to occur, which is seen to happen from x > 0.1 in both real and simulated systems.

In order to illustrate the concept of water mingling with the solute, we show in Fig. 6 selected atom-atom correlation functions between hydrogen bonding atoms, namely water oxygen O<sub>w</sub>, propylamine nitrogen N and 1-propanol oxygen O. The resulting pair correlation functions are compared for the 20% solute mixtures in panels (a) and (b), and for the 50% mixtures in panels (c) and (d). All 4 panels show that the water oxygenoxygen correlations  $g_{O_{0}O_{0}}(r)$  are above 1, indicating that water tends to self-segregate in the distance range shown of about 1 nm or so. This self-segregation is more pronounced for the water 1-propanol (panels (b and d)) than for water propylamine mixtures. Conversely, the comparison of the green curves shows that the solute hydrogen bonding sites are more correlated at contact for the alcohol ((b) and (d)) than for the amine ((a) and (c)). This clearly illustrates that the alcohol hydroxyl groups tend to form chain-like clusters, indirectly proving that they form separated pockets. Indeed, as illustrated in our previous studies, neat alcohols tend to form better defined chains than neat propylamine.<sup>11,52</sup> But the most interesting features are seen in the cross correlations (in magenta). The water oxygen and propylamine nitrogen sites are clearly more correlated than the water and alcohol oxygen sites, and this holds for the entire range shown. This is definitive proof that water mingles more with the amine nitrogen than with the alcohol oxygen. In addition, this mingling happens while water tends to form segregated pockets in both mixtures and for all concentrations for which a pre-peak is seen. Interestingly, the water-solute first



**Fig. 6** Illustration of water "mingling" through comparison of hydrogen bonding sites for the case of water 1-propylamine 20% (a) and 50% (c) with water 1-propanol 20% (b) and 50% (d), respectively.  $g_{O_wO_w}(r)$  shown in blue,  $g_{O_wN}(r)$  and  $g_{O_wO}(r)$  in magenta, and  $g_{NN}(r)$  and  $g_{OO}(r)$  in green.

peak is slightly higher for the water alcohol mixtures than for the corresponding water propylamine mixture. This is an indirect proof of the nature of the "interface" between the 2 components: it is more "sharp" for the water alcohol than for the water amine mixtures. These notions associated to an "interface" are to be considered with caution, since the interface has a proper meaning only for a mesoscopic system, which is not the case here. Nevertheless, it helps to characterise differences in the looseness of the segregation between different types of mixtures, hence justify the wording "water mingling" that we introduce here.

This explanation can be exported to other systems as well. For example, in neat alcohols, there are no cross species correlations, and thus there is no pre-peak compensation mechanism. A very similar explanation holds also for RTILS; since the uncharged groups are attached to charged ones, the negative domain contributions are diminished. The extension of this picture to micellar systems is more involved and will be reported elsewhere. But the general idea remains the same: it is the solutionmicelle "interface" which contributes mostly to the pre-peak.

A simple model can further help to explain the above argument.53 We consider a model binary mixture which microsegregates. The pair interactions between like species 1 and 2 are simple Lennard-Jones interactions  $v_{11}(r)$  and  $v_{22}(r)$ . The segregation can be implemented by a negative well in the cross species pair interaction  $v_{12}(r)$ , positioned at some large distance between the adverse molecules 1 and 2. This distance sets the domain separation. In this scenario, the positive and negative domain correlation pre-peaks are exactly compensating, because of the homogeneity of the segregation throughout the system. Now, one can break this homogeneity by allowing for a mixing of species close to contact. This can be achieved by an additional attractive well in  $v_{12}(r)$  superimposed on the short range interaction at contact. The effect of this well would be to increase the contact correlations, hence producing a corresponding increase of the small-k behaviour of the cross structure factor  $S_{12}(k)$ . This increase will counter the negative domain pre-peak, hence leading to the net positive pre-peak in the sum of the 2 contributions.

## 5 Conclusions

In the present study, we have studied, by both traditional X-ray and neutron small angle scattering techniques, aqueous propylamine mixtures, and found the existence of a scattering pre-peak, which appears for propylamine concentrations x > 0.1and persists until pure propylamine. This pre-peak is also observed in the computer simulation results, and is in qualitative and near quantitative consistency with scattering experiments. The same simulations reveal the existence of chain-like water clusters for concentrations above x > 0.1, suggesting a link between this supra-structure and the scattering pre-peak. The detailed analysis of the atom–atom structure factor contributions reveals that this attribution is not justified, mainly in view of contradictory information obtained in other aqueous mixtures, such as aqueous 1-propanol or aqueous DMSO mixtures. We propose that it is the presence of the amine group in propylamine which allows water to

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mingle with the solute, hence producing a net imbalance in the like species and cross species domain correlations, leading to a net positive pre-peak in the scattering function. This way, radiation scattering appears as a probe of the mixing behaviour of the molecular constituents. Furthermore, the explanation provides a potential unification of the various types of scattering pre-peak in very different types of mixtures, in terms of the water–solute "interface" instead of the usual micro-structural shape explanation.

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 C. Raman, Nature, 1923, 111, 185.
- 2 B. Berne and R. Pecora, *Dynamic Light Scattering: With Applications to Chemistry, Biology, and Physics*, Dover Publications, 2000.
- 3 J. A. Prins, Nature, 1929, 123, 908-909.
- 4 H. Fischer, A. Barnes and P. Salmon, *Rep. Prog. Phys.*, 2006, **69**, 233.
- 5 M. Teubner and R. Strey, J. Chem. Phys., 1987, 87, 3195-3200.
- 6 Y. Chevalier and T. Zemb, Rep. Prog. Phys., 1990, 53, 279.
- 7 A. Narten and A. Habenschuss, J. Chem. Phys., 1984, 80, 3387-3391.
- 8 S. Sarkar and R. N. Joarder, J. Chem. Phys., 1994, 100, 5118-5122.
- 9 M. Tomšič, A. Jamnik, G. Fritz-Popovski, O. Glatter and L. Vlček, *J. Phys. Chem. B*, 2007, **111**, 1738–1751.
- 10 I. Bakó, P. Jedlovszky and G. Pálinkás, *J. Mol. Liq.*, 2000, **87**, 243–254.
- 11 L. Zoranić, F. Sokolić and A. Perera, J. Chem. Phys., 2007, 127, 024502.
- S. Bellissima, S. De Panfilis, U. Bafile, A. Cunsolo, M. González, E. Guarini and F. Formisano, *Sci. Rep.*, 2016, 6, 39533.
- 13 H. Annapureddy, H. Kashyap, P. De Biase and C. Margulis, *J. Phys. Chem. B*, 2010, **114**, 16838–16846.
- H. K. Kashyap, C. B. Santos, H. V. R. Annapureddy, N. Murthy, C. Margulis and E. Castner, *Faraday Discuss.*, 2012, 154, 133–143.
- 15 A. Triolo, O. Russina, H.-J. Bleif and E. Di Cola, *J. Phys. Chem. B*, 2007, **111**, 4641-4644.
- 16 Y. Wang and G. A. Voth, J. Am. Chem. Soc., 2005, 127, 12192-12193.
- 17 G. D'Arrigo, R. Giordano and J. Teixeira, *Eur. Phys. J. E: Soft Matter Biol. Phys.*, 2003, **10**, 135–142.
- 18 G. D'Arrigo, R. Giordano and J. Teixeira, Eur. Phys. J. E: Soft Matter Biol. Phys., 2009, 29, 37–43.

- 19 G. D'Arrigo, R. Giordano and J. Teixeira, *Langmuir*, 2000, 16, 1553–1556.
- 20 T. Takamuku, H. Maruyama, K. Watanabe and T. Yamaguchi, *J. Solution Chem.*, 2004, **33**, 641–660.
- 21 P. Debye, *The collected papers of Peter J. W. Debye*, Interscience Publishers, 1954.
- 22 J.-P. Hansen and I. McDonald, *Theory of Simple Liquids*, Academic Press, Elsevier, Amsterdam, 3rd edn, 2006.
- 23 A. Perera, Phys. Chem. Chem. Phys., 2017, 19, 28275-28285.
- 24 C. J. Pings and J. Waser, J. Chem. Phys., 1968, 48, 3016-3018.
- 25 A. I. Kuklin, D. V. Soloviov, A. V. Rogachev, P. Utrobin, Y. Kovalev, M. Balasoiu, O. Ivankov, A. Sirotin, T. Murugova, T. Petukhova, Y. Gorshkova, R. Erhan, S. Kutuzov, A. Soloviev and V. Gordeliy, *J. Phys.: Conf. Ser.*, 2011, **291**, 012013.
- 26 D. Orthaber, A. Bergmann and O. Glatter, J. Appl. Crystallogr., 2000, 33, 218–225.
- 27 M. Požar and A. Perera, J. Mol. Liq., 2017, 227, 210-217.
- 28 S. Pronk, S. Páll, R. Schulz, P. Larsson, P. Bjelkmar, R. Apostolov, M. R. Shirts, J. C. Smith, P. Kasson, D. van der Spoel, B. Hess and E. Lindahl, *Bioinformatics*, 2013, 29, 845–854.
- 29 C. Oostenbrink, A. Villa, A. Mark and W. van Gunsteren, *J. Comput. Chem.*, 2004, **25**, 1656–1676.
- 30 H. J. C. Berendsen, J. R. Grigera and T. P. Straatsma, J. Phys. Chem., 1987, 91, 6269–6271.
- 31 S.-U. Nosé, Mol. Phys., 1984, 52, 255-268.
- 32 W. G. Hoover, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1985, 31, 1695–1697.
- 33 M. Parrinello and A. Rahman, J. Appl. Phys., 1981, 52, 7182–7190.
- 34 G. Hura, J. M. Sorenson, R. M. Glaeser and T. Head-Gordon, J. Chem. Phys., 2000, 113, 9140–9148.
- 35 I. Akiyama, M. Ogawa, K. Takase, T. Takamuku, T. Yamaguchi and N. Ohtori, *J. Solution Chem.*, 2004, **33**, 797–809.
- 36 E. Galicia-Andrés, L. Pusztai, L. Temleitner and O. Pizio, J. Mol. Liq., 2015, 209, 586–595.
- 37 A. Perera, L. Zoranić, F. Sokolić and R. Mazighi, J. Mol. Liq., 2011, 159, 52–59.
- 38 M. Požar, J.-B. Seguier, J. Guerche, R. Mazighi, L. Zoranić, M. Mijaković, B. Kežić-Lovrinčević, F. Sokolić and A. Perera, *Phys. Chem. Chem. Phys.*, 2015, 17, 9885–9898.
- 39 M. Požar, B. Lovrinčević, L. Zoranić, T. Primorac, F. Sokolić and A. Perera, *Phys. Chem. Chem. Phys.*, 2016, 18, 23971–23979.
- 40 A. Perera and R. Mazighi, J. Chem. Phys., 2015, 143, 154502.
- 41 A. Perera and B. Lovrinčević, Mol. Phys., 2018, 116, 3311-3322.
- 42 H. Hayashi, K. Nishikawa and T. Iijima, *J. Phys. Chem.*, 1990, **94**, 8334–8338.
- 43 L. Almásy, G. Jancsó and L. Cser, *Appl. Phys. A: Mater. Sci. Process.*, 2002, **74**, s1376–s1378.
- 44 A. Perera, Phys. Chem. Chem. Phys., 2017, 19, 1062-1073.
- 45 Y. Koga, Y. Kasahara, K. Yoshino and K. Nishikawa, *J. Solution Chem.*, 2001, **30**, 885–893.
- 46 S. Kaur and H. K. Kashyap, J. Chem. Sci., 2017, 129, 103–116.
- 47 K. Iwasaki and T. Fujiyama, J. Phys. Chem., 1977, 81, 1908–1912.
- 48 K. Nishikawa, Y. Kodera and T. Iijima, *J. Phys. Chem.*, 1987, **91**, 3694–3699.

- 49 E. Prince, H. Fuess, T. Hahn, H. Wondratschek, U. Müller, U. Shmueli, A. Authier, V. Kopsky, D. Litvin, M. G. Rossmann, E. Arnold, S. Hall and B. McMahon, *International Tables for Crystallography, Vol. C: Mathematical, Physical and Chemical Tables*, IUCR, 2006.
- 50 A. Luzar and D. Chandler, J. Chem. Phys., 1993, 98, 8160-8173.
- 51 B. Kirchner and M. Reiher, J. Am. Chem. Soc., 2002, 124, 6206–6215.
- 52 A. Perera, F. Sokolić and L. Zoranić, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2007, 75, 060502(R).
- 53 A. Baptista and A. Perera, J. Chem. Phys., 2019, 150, 064504.