Journal of Molecular Liquids 248 (2017) 602–609

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Evolution of the micro-structure of aqueous alcohol mixtures with cooling: A computer simulation study

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ARTICLE INFO

Article history:
Received 13 June 2017
Received in revised form 26 August 2017
Accepted 8 October 2017
Available online 12 October 2017

ABSTRACT

We study by computer simulations aqueous ethanol and tert-butanol mixtures for temperatures below room temperature, from T=250 K to T=150 K, in order to monitor how concentration fluctuations and micro-segregation evolve with the lowering of temperature. Similarly to our recent study of aqueous-methanol mixtures [J. Chem. Phys. **145**, 144502 (2016)], we find that concentration fluctuations tend to decrease - as monitored by the lowering of the $k = 0$ value of the structure factors, while micro-segregation becomes more specific, in particular with a marked tendency of water to form short chain-like clusters, instead of large bulky nano-domains at higher temperatures. This clustering translates into a growing pre-peak in the water-water structure factors at $k \approx 0.5\text{Å}^{-1}$. The decrease of concentration fluctuations is also in agreement with the fact that calculated Kirkwood-Buff integrals tend to become ideal, in sharp contrast with the data for T=300 K, in particular for aqueous-tbutanol mixtures. This near-ideality is a consequence of water forming supra-molecular linear clusters. We conjecture that the cooling of nano-structured mixtures produces a "transfer" of $k = 0$ concentration fluctuation mode towards $k \neq 0$ mode, leading in particular to these supra-molecular water clusters.

1. Introduction

A naive picture of the cooling of micro-segregated mixtures would be that, because of the enhancement of the Boltzmann factor, the micro-segregation would increase, further increasing the concentration fluctuations. However, concentration fluctuations can occur differently at different k-vectors, as measured by the partial structure factors [1]. Macroscopic thermodynamic concentration fluctuations occur at $k = 0$ [2,3], which are not necessarily related to specific forms of local clustering - or micro-heterogeneity - which could occur at non-zero k-vectors [1]. This distinction is not immediately intuitive, but is a logical consequence of density correlations defined as $< \delta\rho_i(\mathbf{1})\delta\rho_j(\mathbf{2}) >$, where $\delta\rho_i(\mathbf{a}) = \rho_i(\mathbf{a}) - \bar{\rho}_i$ is the fluctuation of the density of species i at location $\mathbf{a}$ around the average density $\bar{\rho}_i$, and $< .. >$ designates a statistical ensemble average. Obviously, the first moment $< \delta\rho_i(\mathbf{a}) >= 0$ because of the macroscopic homogeneity, but the second moment depends on the relative position between two molecules, hence on all the associated k-vectors. Previous experimental and computer simulation studies of fluctuations in room temperature aqueous alcohol mixtures under ambient conditions, have shown that both concentration fluctuations - as measured through the Kirkwood-Buff integrals (KBI) [4,5], and micro-segregation - as observed through computer simulations [6,7], are notably increased, specifically with the increase of the number of methyl groups of the alcohol molecules [8]. In a recent study of the temperature dependence of aqueous methanol mixtures [9], we have found that these mixtures looked near ideal, as far as their KBI were concerned, while showing more specific micro-segregation than for room temperature, as witnessed by the increase of the structure-factor pre-peak.

In this study, we extend to very low temperature regions the simulations of two specific mixtures, namely when mixing water with ethanol or tert-butanol (subsequently abbreviated as tbutanol), with the aim to determine the respective status of concentration fluctuations and micro-segregation under these constraints. This is particularly relevant for the case of aqueous-tbutanol, for which several studies have pointed out the strong micro-segregation under ambient conditions [10–13], as well as the high concentration fluctuations as measured through the Kirkwood-Buff integrals, obtained through calorimetric measurements [14] as well as radiation scattering experiments [15,16]. The present simulation study clearly indicates that the KBI markedly decrease at lower temperatures,

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https://doi.org/10.1016/j.molliq.2017.10.039
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making these mixtures look nearly ideal. Yet, these mixtures still exhibit micro-segregation of the water and alcohol molecules.

Similarly to the previous one, the present study is strictly restricted to static properties, with the aim to relate configurational molecular properties to correlation functions and related KBI thermodynamical properties. The investigation of dynamical properties, in particular those related to lifetime of clustering, and in relation to spectroscopic properties and other experimental properties, will be developed in subsequent studies.

The picture which emerges from this study is that, lowering the temperature, which amounts to increase the various Boltzmann factors, selectively enforces water segregation with respect to the alcohol segregation, since water molecules form linear chain-like clusters, which wind through the mixture. It is this specific topological form of the aggregation of water which leads to the decrease of thermodynamic concentration fluctuations. This picture is more appealing when stated in the opposite direction: the increase of temperature melts/destroys the supra-molecular chain clusters of water, hence increasing the concentration fluctuations as well as making the segregated water domain larger and more disordered. Indeed, as the water clusters become larger, the Hbonding patterns become more diverse, and the linear clustering specificity of smaller cluster is lost.

Chain-like water clustering might appear at first as strange, since water is well known to be a tetrahedral liquid [17–19]. However, the tetrahedral connectivity would hold only in the optimal bulk conditions. Even then, it was recently proposed that pure water may be formed mostly of dimers instead of tetramers [20]. In any case, it is conceivable that, under dilution, that water molecules may not be able to group into tetramers, and would statistically achieve better H-bonding through chain-like patterns. This was found to be the case in aqueous mixtures of dimethyl-sulfoxyde [21], whereas in aqueous tbutanol mixtures water would form larger clusters with increased tetrahedral connectivity [22]. The fact that, under mixing conditions, water would decrease its number of hydrogen bonding with decreasing temperature is not obvious, and would probably depend on the nature of the solute. The behaviour of water in cold mixtures has been previously addressed by other authors [23–25]. For example, the behaviour of water in cryoprotectant mixtures is of genuine physical interest [24].

As stated in the beginning, a generic mean field argument, involving spherically averaged interactions, would predict the demixing of water and alcohol when lowering the temperature, and in particular it will predict the associated increase of concentration fluctuations. It is the opposite which is observed here. This is due to water giving up tetrahedral connectivity to prefer chain connectivity under crowding with the solute molecules. This failure of the mean field argument, seems to contradict the near ideal behaviour of these mixtures, demonstrating that mean field and low fluctuations are not necessarily collateral properties. This is possible precisely because water molecules can change their Hbonding topologies, hence allowing to transfer concentration fluctuations at $k = 0$ into a domain pre-peak at $k \neq 0$. This is an interesting illustration of the plasticity of water. Many aqueous mixtures, such as 2-butoxyethanol-water [26] or tetrahydrofuran-water [27] mixtures, exhibit lower critical solution temperatures (LCST), and subsequent demixing at high temperatures. The mechanism for remixing at lower temperature could reside in the property of water that we point out here, namely transfer $k = 0$ concentration fluctuations modes into $k \neq 0$ localized aggregates.

2. Simulation and theoretical details

We have simulated aqueous mixtures of ethanol and tert-butanol, under atmospheric pressure, in the temperature range between 250 K and 150 K. Since the melting temperature of pure water is 273 K, 159 K for ethanol and 298 K for tbutanol, it is quite possible that the chosen temperature range would correspond to supercooled metastable states for the real mixtures studied here. However, in computer simulations, it is possible to reach temperature usually experimentally inaccessible, such as for example in the case of pure water [28], in the quest for its second critical point in the so-called experimentally inaccessible “no-man's land” part of the phase diagram [29]. In addition, our simulations clearly indicate that all the reported states are liquid, as shown by the form of the correlation functions.

For each temperature, we have studied standard alcohol mole fractions of $x = 0.2$, 0.5 and 0.8. Additional simulations of neat ethanol within the temperature range mentioned above were performed as well. We have used the SPC/E model for water [30], the TraPPe model for tert-butanol [31] and TraPPe and OPLS models for ethanol [31,32]. The starting configurations were prepared with PACKMOL [33] and the molecular dynamics was performed with the Gromacs code [34].

We wish to particularly emphasize the choice of starting each simulation from an initial random distribution of molecules, as produced by PACKMOL. Indeed, a naive idea would be to start a lower temperature simulation from a previous high temperature one. If such protocol could be valid for random mixtures, it is certainly not so for a micro-heterogeneous one, such as these aqueous mixtures. Since these mixtures are micro-segregated, each segregated domain takes several hundred of picoseconds to relax, which is why nano-second scale simulations are required. In this condition, a quench in temperature will further increase the relaxation time, leading to quasi-frozen domains which would be stuck in the high temperature metastable basins. Conversely, starting from a random configuration allows the system to find its equilibrium state faster. In order to ensure independence from starting configurations, we test run some simulations from a PACKMOL configuration with species order exchanged.

The simulation protocol was identical for all systems. Initial configurations were first energy minimized, then equilibrated in the NVT ensemble for a couple of few nanoseconds. The NVT equilibrations were followed by lengthy NpT equilibrations that lasted 5 ns. Production runs lasted 10–15 ns, depending on the system. Temperature was maintained constant through the Nosé-Hoover thermostat [35,36], and pressure was maintained at 1 atm with the Parrinello-Rahman barostat [37,38] (both with time constant of 0.1 ps). The leap-frog integrator time step was fixed at 1 fs.

System sizes of $N = 2048$ particles were typically used for the mixtures, while simulation boxes of neat ethanol contained $N = 1000$ particles. These smaller systems have proven to be sufficient for neat alcohols, since these are homogeneous liquids. In addition, we observe small change of the box size with temperature. For example, the box size length for the equimolar ethanol-water mixture went from $L = 49.5$Å at 250 K to $L = 48.6$Å at 200 K and $L = 48.1$Å at 150 K. The compression effect was similar for the tbutanol-water mixture as well, where the box size length changed from $L = 56.4$Å at 250 K to $L = 55.6$Å at 200 K and $L = 55.1$Å at 150 K. In order to test that the system was not stuck in a frozen metastable configuration, specially at low temperatures, we look at snapshots 5 ns apart, and visually confirm that the system has evolved considerably. This is particularly obvious for micro-segregated and clustered systems, as in the present case.

We calculated site-site correlation functions $g_{a_i b_j}(r)$, where a_i, b_j represent any two atomic sites on the molecules of species i and j. Particular focus was on the oxygen-oxygen correlations, which are reported below. From the site-site function we have calculated the site-site structure factors $S_{a_i b_j}(k)$, defined as [2]:

$$S_{a_i b_j}(k) = \delta_{a_i b_j} + \rho\sqrt{x_i x_j}\int d\vec{r}[g_{a_i b_j}(r) - 1]\exp(-i\vec{k}.\vec{r}) \qquad (1)$$

where ρ is the number density and x_i the mole fraction of species i. The structure factors obtained are direct Fourier transforms of the correlation functions $g_{a_ib_j}(r)$, as per standard numerical methods [39]. Just like in our previous works, we show the cross structure factors by replacing $\delta_{a_ib_j}$ with 1 in the figures.

Cluster size distribution probabilities were calculated with the Gromacs utility *g_clustsize*. Since the cluster calculations are done with respect to the geometric criteria, the choice of the cut-off distance was paramount. As customary, the cut-off was chosen to be close to the first minimum of the correlation function. In our case, that value was $r_{cutoff} = 3.7$Å for the alcohol's oxygen sites and $r_{cutoff} = 3.5$Å for the water's oxygen sites.

Among the calculated quantities are also Kirkwood-Buff integrals (KBI) [40], which are defined as:

$$G_{ij} = \int d\vec{r}[g_{a_ib_j}(r) - 1] \tag{2}$$

where $g_{a_ib_j}(r)$ is the site-site correlation function. Since the correlation functions $g_{a_ib_j}(r)$ do not go to the correct asymptote - a consequence of the nature of the finite size simulations - we employ the Lebowitz-Percus correction [41] in order to shift the tails of the correlation functions and thus obtain the proper value of the KBI. The procedure is mentioned in brief, as it is elaborated in previous papers [42,43].

The KBIs can be accessed via the thermodynamic route [3,5]:

$$G_{ij} = \left[k_BT\kappa_T - \frac{\bar{V}_i\bar{V}_j}{VD}\right](1-\delta_{ij}) + \left[G_{12} + \frac{1}{x_i}\left(\frac{\bar{V}_j}{D} - V\right)\right]\delta_{ij} \tag{3}$$

where κ_T represents the isothermal compressibility (k_B is Boltzmann constant and T the temperature), $\bar{V}_i$ the partial molar volume of species i, V the total volume and x_i the mole fraction of species i. The D is related to the concentration fluctuations through the expression [3,5]:

$$D = x_i\left(\frac{\partial\beta\mu_i}{\partial x_i}\right)_{TP} \tag{4}$$

where μ_i is the chemical potential of species i ($\beta = 1/kT$ is the Boltzmann factor). Eq. (3) can be reduced when several approximations are taken into account. Firstly, the compressibility term can be neglected since it's smaller in magnitude in comparison with other terms. Secondly, the partial molar volumes of the components can be replaced by the molar volumes of the neat components, for we can ignore the variations of excess volume with concentration (and the excess volume is at least one order of magnitude smaller than the volumes). In the end, the KBI from Eq. (3) can be connected to the component's mole fractions and volumes. The D term is dependent upon the chemical potential, which can be split into three different contributions (reference, ideal and excess parts): $\mu_i = \mu_i^{(0)} + k_BT\ln(\rho x_i) + \mu_i^{excess}$, and can be written as [3,5]:

$$D = 1 + x_i\left(\frac{\partial\beta\mu_i^{excess}}{\partial x_i}\right)_{TP} \tag{5}$$

If we can neglect the excess contribution and consider only the ideal part of the chemical potential, that corresponds to $D = 1$. When inserted into Eq. (3), it yields the ideal KBI, which is characteristic of non-interacting species.

3. Results

We present here the two key results, namely that, with decrease of temperature, micro-segregation becomes more specific for water, and that thermodynamic concentration fluctuations become ideal. The first results can be confirmed through the analysis of pair correlation functions, structure factors, cluster analysis and snapshots,

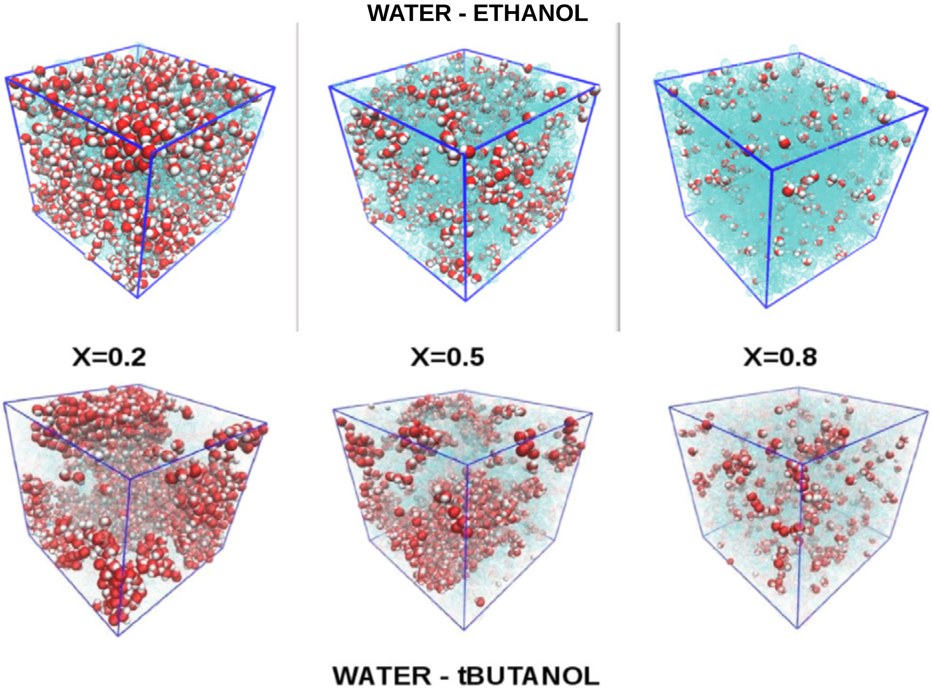

Fig. 1. Snapshots of the aqueous ethanol (upper row) and aqueous tert-butanol (lower row) systems at T=300 K. Three typical alcohol mole fractions are represented: 0.2 (left panel), 0.5 (middle panel) and 0.8 (right panel). Water molecules are represented with oxygens in red and hydrogens in white; alcohol molecules are shown in semi-transparent cyan color.

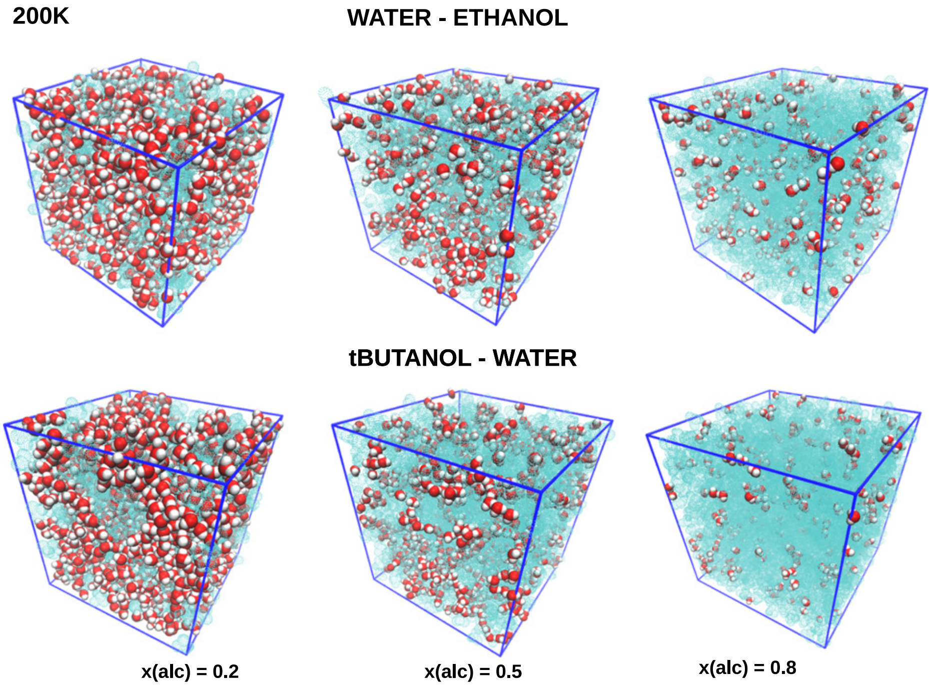

Fig. 2. Same as Fig. 1, but at T=200 K, highlighting water clustering. Alcohol molecules are shown in semi-transparent cyan color.

while the second results are obtained through the analysis of the Kirkwood-Buff integrals.

3.1. Snapshots

As a reminder, we show in Fig. 1 snapshots of room temperature aqueous-ethanol (top row) aqueous-tbutanol (bottom row) mixtures for three specific alcohol mole fractions x, which cover low, middle and high concentration ranges, namely $x = 0.2, 0.5$ and 0.8. As can be seen, water shows pronounced bulky domains, particularly apparent for $x = 0.2$ and $x = 0.5$.

Fig. 2 shows snapshots at lower temperature T=200 K of both aqueous ethanol and tbutanol mixtures, with the water molecules highlighted, and the atoms of the alcohol molecules shown as cyan semi-transparent spheres. This representation allows a more clear view of the behaviour of the water domains. The chain-like appearance of water clusters is apparent for $x = 0.2$ and 0.5, and smaller such clusters can be seen for $x = 0.8$. The most important point

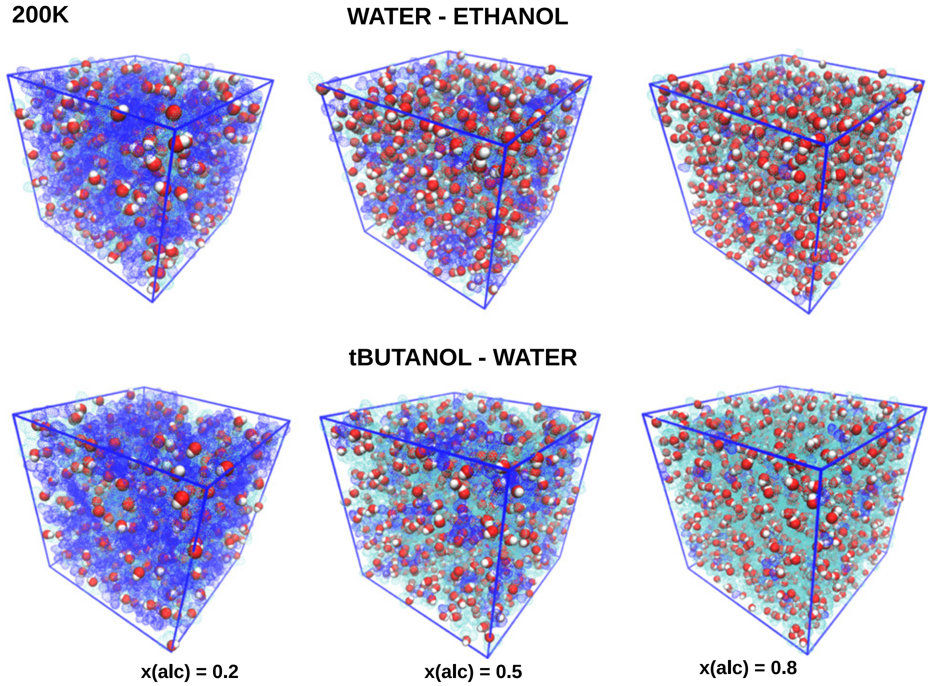

Fig. 3. Same as Fig. 2, but highlighting alcohol hydroxyl groups. Water molecules shown in semi-transparent blue and alcohol methyl groups in cyan.

is the dramatic difference in micro-segregation with the similar room-temperature snapshots as shown in Fig. 1. The difference is principally due to the change in clustering of the water molecules with temperature, which affects greatly the spatial distribution of the domains.

Fig. 3 shows the same snapshot as Fig. 2, but with the O and H atoms of the alcohols highlighted, and methyl groups show in semi-transparent cyan and water shown in semi-transparent blue. This way, we can see how alcohol molecules cluster, when compared with water. The chain-like bonding of ethanol is more apparent in the 80% picture, while for tbutanol, the fact that the OH groups bind into small inner micelles-like clusters make them harder to see. It is clear that the coherence of water self-binding - as observed in Figs. 1 and 2, overwhelms that of the alcohols, which can be trivially explained by the larger partial charges on the O and H sites.

Snapshots at T=150 K are quite similar to T=200 K. In fact the largest configuration change is for going from T=300 K to T=200 K. this similarity between T=200 K and T=150 K is equally confirmed in the KBI, as shown below.

3.2. Kirkwood-Buff integrals

Fig. 4 shows the KBI for both mixtures, aqueous ethanol and aqueous tbutanol, respectively, and temperatures 200 K and 150 K. KBI obtained through the simulations as well as ideal KBI, as calculated following procedures that we have previously detailed [1,44], are shown. It is obvious that the KBI obtained in simulations are near ideal, confirming that, despite non-random mixing and strong directional interactions witnessed by chain-like water clustering, these mixtures have very little concentration fluctuations. This would namely correspond to $D(x) \approx 1$ in Eq. (5). This is a very strong non-intuitive finding, which enforces the idea that concentration fluctuations should be analysed through their entire *k*-vector dependence. The KBI at T=250 K (not shown here) exhibits non-ideal behaviour, particularly at small alcohol content, just like for the room temperature case.

3.3. Cluster distributions

Fig. 5 and Fig. 6 show the cluster analysis for each of the mixtures. The cluster distributions of the oxygen atoms of the alcohol (top) and water (bottom) are shown, each plot corresponding to alcohol concentrations $x = 0.2$, 0.5 and 0.8 from left to right. It is seen that all the cluster distributions look strictly monotonous as function of cluster sizes, and that they show no specific peak and little temperature dependence. A notable exception is the cluster distribution of tbutanol at $x = 0.8$ in Fig. 6-right panel, which shows a pronounced plateau for cluster sizes from 1 to 10, and even a tiny peak for T=250 K. This is explained by referring to the cluster distribution of the pure alcohol reported in Ref. [45,46]. This distribution shows a pronounced cluster peak around cluster size 5, which concerns the micelle-like clusters observed in the snapshot. Clearly, from the results here, we see that that 80% tbutanol retains some of such clusters, which explains the plateau feature noted here in Fig. 6. This plateau is not observed for 80% ethanol in Fig. 5, despite the fact that pure ethanol has also a specific cluster peak [47]. Specific features for aqueous ethanol appear only at higher ethanol contents. Another notable exception is the water oxygen distribution for aqueous ethanol at 20% ethanol content (lower left panel of Fig. 5), which shows strong temperature dependence. This is in contrast with the corresponding 20% tbutanol cluster distribution in Fig. 6. Our interpretation is that it is water clustering which shows the stronger temperature dependence than the alcohols. 20% tbutanol aqueous mixture contains less water than 20% aqueous ethanol mixture, which explains the respective temperature dependence. It also demonstrates indirectly the sensitivity to temperature of the water clustering.

The present analysis shows that the cluster distributions of low temperature aqueous alcohol mixtures are rather trivial, just like in a random mixture such as Lennard-Jones mixtures [48,49]. This result was previously observed in room temperature mixtures [50].

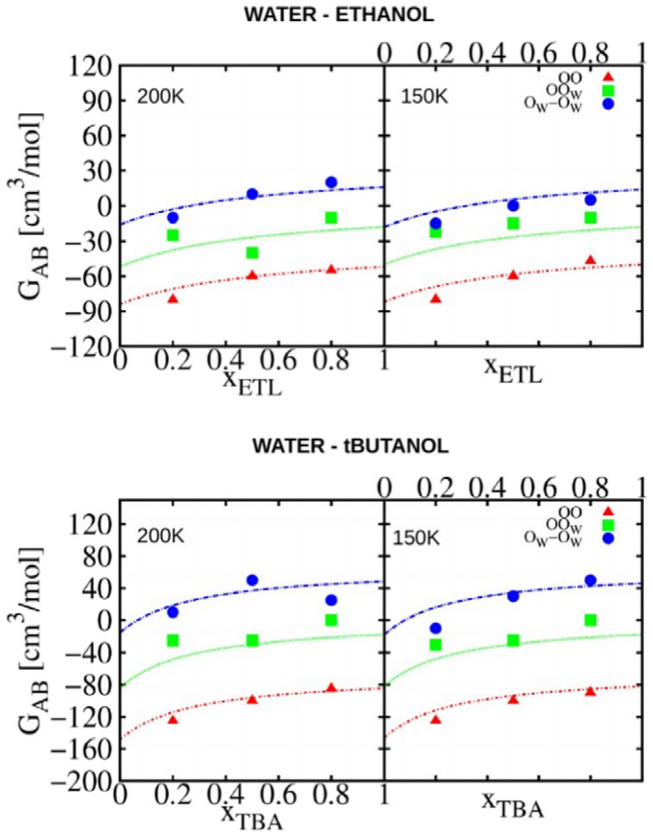

Fig. 4. Kirkwood-Buff integrals of the aqueous-ethanol (top) and aqueous-tbutanol (bottom) mixtures, and for two temperatures: 200 K (left panel) and 150 K (right panel). Color code is as follows: red for ethanol-ethanol, blue for water-water and green for the cross KBI. Symbols correspond to KBIs from present simulations, while dashed lines represent ideal KBI.

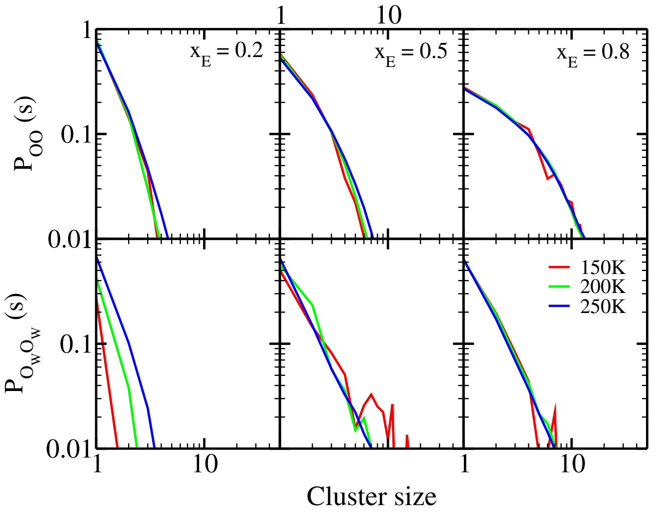

Fig. 5. Cluster size distribution probabilities versus cluster size for the aqueous ethanol system. The cluster size distributions for ethanol oxygen sites (upper row) and water oxygen sites (lower row) are depicted for various temperatures (color code is in the legend). Three typical alcohol mole fractions are represented: 0.2 (left panel), 0.5 (middle panel) and 0.8 (right panel).

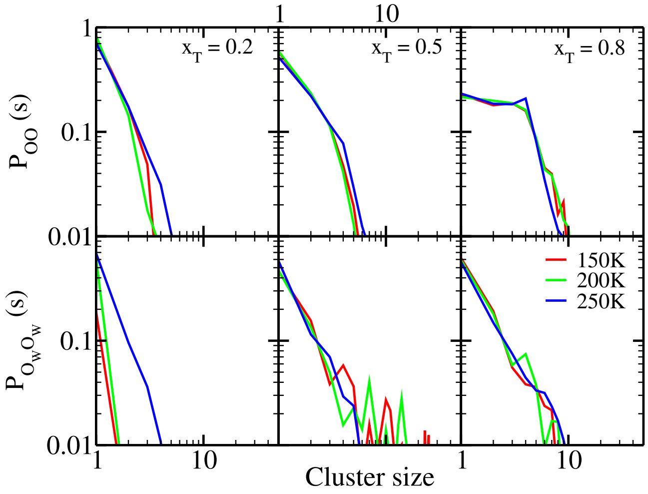

Fig. 6. Same as Fig. 5, but for aqueous-tbutanol mixtures.

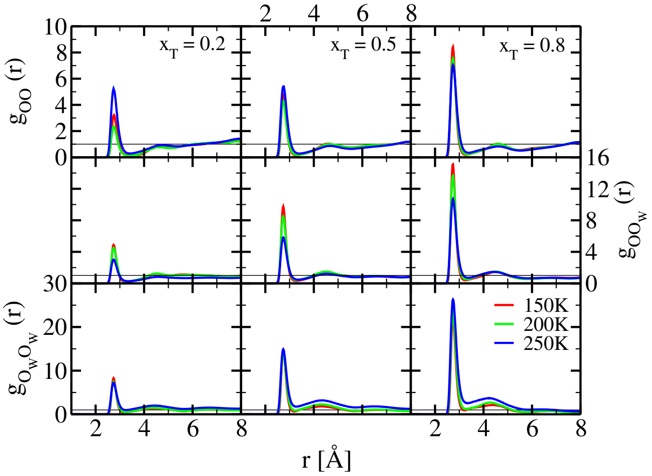

Fig. 8. Same as Fig. 7, but for aqueous-tbutanol mixtures.

It indicates that cluster analysis is not the most adequate tool to study micro-segregation. Indeed, we have previously argued that pair correlation functions and structure factors contain more specific information about clusters [50].

3.4. *Pair correlation functions*

Fig. 7 -for aqueous ethanol, and Fig. 8 -for aqueous-tbutanol, show pair correlation functions between the oxygen sites, at various temperatures and for specific concentrations. One sees the two typical features previously noted in many other cases under ambient conditions, namely that the first peak of the water-water correlations increases with decreasing water content, while it is the opposite trend for the solutes - namely the first peak of the solute-solute correlations decrease with decreasing solute content. As stated before [50], these results are simply the consequence of the higher partial charges on water oxygen and hydrogen sites, that on similar sites of the alcohol molecules. The cross oxygen atom correlations of both mixtures (middle rows) show a trend similar to that of alcohol, in particular what concerns the first peak. This is an indirect indication that there is an appreciable cross binding, despite the domain segregation. The fact that these first peaks are generally intermediate between that of water and alcohol, indicates that water could preserve tetrahedrality by binding with the oxygens of the alcohol molecules, while chain-binding with itself.

All these correlation functions show a similar feature: a sharp first peak - witnessing strong Hbond induced O-O association, followed by very small second and higher neighbour correlations, indicating that Hbond induced pairing is the principal mechanism at low temperatures. First peaks are higher for water than for the alcohol, and higher for the higher alcohol. Since the charges are the same for both alcohols, this latter features can be explained only by the bulkiness of the tbutanol alkyl group, as compared with that of ethanol. It would seem that higher neutral groups spatial constraints, enforce the Hbonding between the oxygen atoms.

There are, however, important differences between aqueous ethanol and aqueous tbutanol mixtures, in what concerns the behaviours of second and higher neighbour correlations of the alcohol oxygen-sites. This can be seen by comparing upper rows of

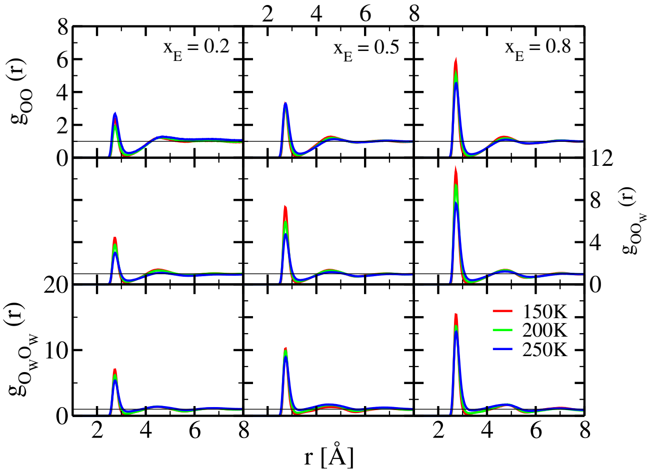

Fig. 7. Site-site correlation functions between the oxygen atoms of aqueous ethanol mixtures. Ethanol oxygens (upper row) and water oxygens (lower row) and cross correlations (middle row). The corresponding temperatures are shown in the figure legend. Three typical alcohol mole fractions are represented: 0.2 (left panel), 0.5 (middle panel) and 0.8 (right panel).

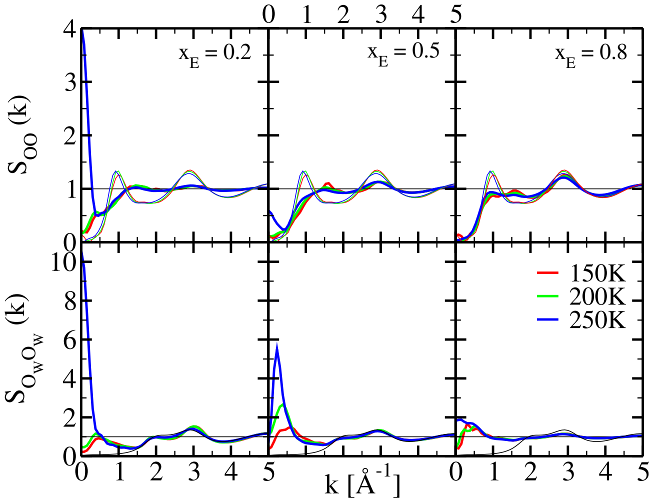

Fig. 9. Site-site structure factors of aqueous ethanol, calculated from the correlation functions in Fig. 7 (cross structure factors not show), with the same organization of rows, panels and temperature color codes. The thinner lines in the upper panel are oxygen-oxygen structure factors of neat ethanol, for same 3 temperatures. The thinner black line in lower panel is for pure water at T=300 K.

Fig. 7 with that of Fig. 8. The higher order neighbour correlations of aqueous-tbutanol mixtures appear depleted, being lower than 1 for a large spatial range. As explained in Ref. [50], this is a signature of lower oxygen Hbonding beyond first neighbour. It can be achieved by chain-like Hbonding, or simply by predominance of dimers or trimers of oxygen aggregates. This was apparent in the snapshots of Fig. 3. Again, this difference with ethanol is attributable to the bulkiness of the tbutanol non-polar part, which takes more room in the liquid, and hence constrains the bonding topology of alcohol. Since water has its own bonding pattern, whose supremacy is dictated by stronger Coulomb charges and interactions, the hydroxyl groups of tbutanol must fit in between these two constraints, which explains the choice of reduced bonding as the simplest choice. The decrease of temperature removes thermal agitation and helps select simpler bonding patterns.

3.5. Structure factors

Fig. 9 and Fig. 10 show the structure factors corresponding to the correlation function of Fig. 7 and Fig. 8. We want to track two important features. Firstly, the decrease of concentration fluctuations at the $k = 0$ part of the structure factors. Note that, for aqueous-tbutanol, the high temperature structure factors have, in addition to the $k = 0$ part, a sharp pre-peak at $k \approx 0.17\text{Å}^{-1}$, which is related to the large segregated domains. And secondly, the appearance of domain pre-peak at $k \approx 0.5\text{Å}^{-1}$, associated to the formation of various domains, as seen in the snapshot of Fig. 2 and Fig. 3. In order to facilitate interpretations, we plot in thinner lines the oxygen-oxygen structure factors of neat alcohols (upper panels) and water (lower panels). This way one can compare the evolution of the pre-peak part of the alcohols (about $k_P \approx 0.8 - 1\text{Å}^{-1}$), as well as the main peak (about $k_M \approx$ 2.8-3Å^{-1}) with concentration and temperature. Incidentally, the temperature dependence of the neat alcohol structure factor can be seen to be very small (shown for ethanol only), indicating the relative cluster robustness of alcohols.

Fig. 9 and Fig. 10 show the dramatic decrease of concentration fluctuations as temperature is decreased from T=250 K to lower ones, as seen by the decrease of $S(k = 0)$ for water and ethanol oxygen atoms, particularly visible for $x = 0.2$. There is an important difference with higher alcohol contents, for which this value diminishes strongly. The reason concentration fluctuations are suppressed at higher alcohol content is explained the following way. Neat alcohols naturally suppress their concentration fluctuations by forming specific clusters. In a way, these clusters "lock" fluctuations into supra-molecular entities. This transfer of the k-dependent fluctuations from small-k to k_P can be seen very clearly in the case of ethanol, by comparing the concentration dependence of the structure factors with that of pure ethanol (upper row in Fig. 9): at low alcohol concentrations S(k) is nearly structureless, and progressively acquires a structure similar to that of the neat alcohol as the concentration is increased.

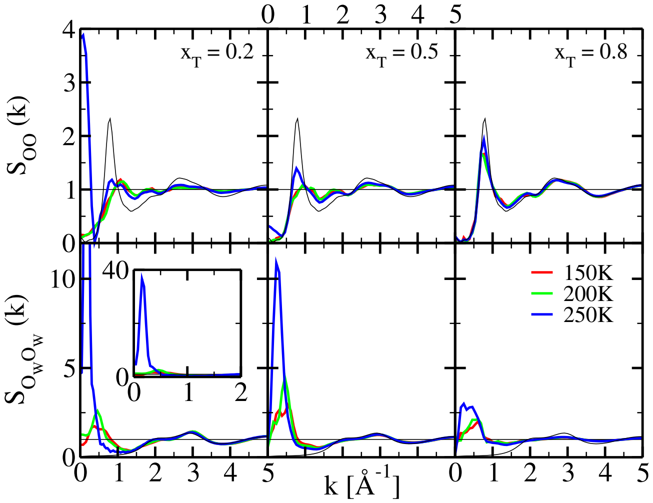

Fig. 10. Site-site structure factors of aqueous tert-butanol, calculated from the correlation functions in Fig. 8, with the same organization as in Fig. 9. The thinner black line in upper and lower panel is for pure tbutanol and pure water (T=300 K), respectively. The inset in lower left panel is a closeup of the small-k behaviour.

For water (lower rows) it is seen that S(k) develops a pre-peak around $k_P \approx 0.5\text{Å}^{-1}$, which is still much higher than the room temperature domain pre-peak ($k_D \approx 0.17\text{Å}^{-1}$). Unlike alcohol molecules which form cluster under neat condition water cannot seem to be able to do that, which could be attributed to the larger degrees of freedom of bonding, due to missing neutral groups. This is obviously the most important difference between Hbonding in water and alcohols. In the presence of adverse solute, water has many ways of forming pockets, which tends to increase $k = 0$ part of the structure factor, because of the associated long range correlations. As more solute is added and water rarefied, water molecules can form supramolecular linear clusters, hence in a way act just like alcohol molecules as far as bonding topologies are concerned. This explains the lower $S(k = 0)$ for water oxygens for $x = 0.5$ and $x = 0.8$. However, if water forms such domains, then it should equally show a pre-peak similar to neat alcohols. We indeed observe such pre-peaks at $k_P \approx 0.17\text{Å}^{-1}$in the lower part of Fig. 10 for aqueous-tbutanol, although at a lesser extent for aqueous ethanol in Fig. 9. A look at the snapshots in Fig. 1 shows that the water domain is more bulky for aqueous tbutanol, which could explain that the pre-peak appears as shifted to smaller k-values for this mixture, particularly for T=250 K.

The ideality of the KBI as T is decreased, which means lesser concentration fluctuations in the $k = 0$ mode of the structure factors, conjugated with the appearance of a pre-peak at $k \neq 0$ in the water-water structure factors, could be indicative of the general mechanism which is responsible for the occurrence of LCST in many binary aqueous mixtures. The small water aggregates responsible for the pre-peak structure permit re-entrant miscibility of water in cold solutes.

4. Conclusion

The present study confirms what we have found in previous simulations of aqueous methanol simulations, namely that lowering the temperature in aqueous alcohol mixtures renders them near ideal as far as Kirkwood-Buff integral based concentration fluctuations are concerned. In addition, the origin of this near ideality can be traced back to the fact that water forms linear clusters, which meander through the system. It would seem that water transforms into a supra-molecular entity of chain-like aggregate in appearance. This formation suppresses the fluctuations corresponding to the distribution of water in large pockets, which are predominant at high temperatures, as is the case for aqueous tbutanol mixtures, for example. These findings demonstrate a remarkable plasticity of the water molecules under cold conditions. This type of auto-organisation of water could have appreciable consequences for the preservation of organisms and water filled materials at low temperatures.

Acknowledgements

This work has been partially supported by the Croatian Science Foundation under the project 4514 "Multi-scale description of meso-scale domain formation and destruction". M. Požar thanks the French Embassy in Croatia for the financial support through "bourse du Gouvernement Français".

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