Computer Simulation Study of tert-Butyl Alcohol. 2. Structure in Aqueous Solution

1 AUTHOR:

Peter G Kusalik
The University of Calgary

114 PUBLICATIONS **3,979** CITATIONS

SEE PROFILE

Computer Simulation Study of *tert*-Butyl Alcohol. 2. Structure in Aqueous Solution

Peter G. Kusalik

Department of Chemistry, Dalhousie University, Halifax Nova Scotia, Canada B3H 4J3

Alexander P. Lyubartsev, Dan L. Bergman, and Aatto Laaksonen*

Division of Physical Chemistry, Arrhenius Laboratory, Stockholm University, S-10691 Stockholm, Sweden

Received: May 23, 2000; In Final Form: July 6, 2000

MD simulations of *tert*-butyl alcohol (TBA), dissolved in water, are carried out. Two aqueous alcohol solutions are studied, a dilute 2 mol % and a more concentrated, 8 mol % solution. Two new potential models are used for TBA, a simple rigid three-site model and a flexible all-atom 15-site model. In solution, the flexible TBA model is dissolved with flexible SPC water molecules, while the rigid *tert*-butyl alcohol is simulated in rigid SPC/E water. This study principally focuses on the hydration structure around TBA and a possible self-association of TBA due to the strong amphiphilic character of this bulky molecule. In the more concentrated solutions and for both TBA models, small aggregates of a few alcohol molecules are formed spontaneously, persisting several tens of picoseconds. Tail-to-tail pairwise configurations of alcohols are preferred. In the dilute solution, little tendency to aggregation is observed during the simulation. The diffusion of the alcohols is reduced considerably as the concentration of the solution increases. Water structure is significantly enhanced upon the addition of TBA. The hydration structure of both models of TBA is markedly different from that of methanol, indicating that the steric bulk of a *tert*-butyl group can have large, though indirect, effect on hydrogen bonding.

Introduction

Besides having a long history,[24] interest in studies of aqueous solutions of alcohols is continuously increasing, driven by the growing industrial use of water−alcohol mixtures as solvents. The solvation of simple alcohols in water is also interesting on the molecular level, because they fit easily into the water structure by being able, in principle, to accept two hydrogen bonds and donate one. The problem is to make a suitable structural hole for the hydrophobic part of the molecule; moreover, because amphiphilic molecules alcohols will have an impact on hydration structure as well as aggregate.[2]

We have previously studied water−methanol mixtures to investigate the local hydration structure around the methanol molecule.[3] In that study it was shown that radial distribution functions (RDF), the traditional representation of liquid structure, were insufficient (and even misleading) in describing the local structure around these highly polar and strongly interacting molecules. Large structural changes were observed, although these were typically not manifested in the RDFs. Spatial distribution functions (SDF),[4,5] the three-dimensional analogues to RDFs were used to resolve fully the orientational space around each of the molecules and hence to provide complete information on the local structural environment. In our previous work,[3] we found that in methanol-rich solutions water−water correlations persisted to fairly large separations while the methanol structure was nearly the same as was found in the simulations of pure liquid methanol.[6] In water-rich solutions strong methanol-methanol correlations existed out at rather large separations and a highly localized H-bonded structure appeared around the OH group of the methanol, where all three of the H-bonding sites on the hydroxyl group were utilized.

tert-Butyl alcohol (TBA) differs from the other isomers of butyl alcohols (*n*-butyl, iso-butyl and *sec*-butyl) by being readily soluble in all proportions while the others are only sparsely soluble in water. Solutions of TBA in water show an anomalously large volume contraction, indicating that the bulky *tri*-methyl groups must be more readily accommodated into the water structure. At the same time the hydrophobic surface of the alkyl group is believed to enhance the water structure around it due to hydrophobic effects.[2]

Computer simulation studies of diluted TBA solutions have been reported previously. Nakanishi and co-workers carried out both Monte Carlo (MC)[7] and molecular dynamics (MD) simulations[8,9] of dilute aqueous solutions of TBA. In their MC study[7] of a dilute (215 H_2O + 1 TBA) solution they found two strong hydrogen bonds between the −OH group and water and a cooperatively connected hydrophobic structure around the $(CH_3)_3$-group. The ordering of water around TBA was even more pronounced than in their earlier simulation of methanol in water.[10] In their second study, they carried out MD simulations of a 3 mol % solution of TBA in water (209 H_2O + 7 TBA).[8] A clear association of TBA in water was observed, although no hydrogen bonds were formed between the TBAs. The self-diffusion of water was considerably slower than calculated for bulk water, consistent with its apparent increase in structure. Fornili and co-workers[11] used their quantum mechanically calculated TBA−water potential to perform MD simulations to investigate the hydration structure around TBA and compared it to that around trimethylamine-*N*-oxide, $(CH_3)_3$-NO. Bowron et al.[12] have used the method of empirical potential structural refinement as an aid to resolve their experimental structure factors into partial pair correlation functions.

In the preceding paper,[13] we have examined the structure in pure liquid TBA, and have explicitly compared two models, a

---

* Corresponding author. E-mail: aatto@tom.fos.su.se. Phone: +46 8 162372. Fax: +46 8 152187.

TABLE 1: Some Characteristic Parameters and Results from the Simulations of the Different Water Solutions of TBA: W and T Denote Water and TBA, Respectively[a]

quantity	c model I		model II	
no. of (CH₃)₃CH molecules	4	20	4	20
no. of H_2O molecules	252	236	252	236
temperature (K)	300	300	300	300
ρ (g/cm³)	0.99	0.95	0.99 ± 0.001	0.9349 ± 0.001
cutoff (Å)	10.0	10.0	10.0	10.0
$\langle U_{TOT} \rangle$	-44.9 ± 0.6	-42.3 ± 0.5	-48.2 ± 0.01	-73.0 ± 0.04
$\langle U_{WW(ES)} \rangle$	-53.7 ± 0.8	-50.4 ± 0.6	-60.6 ± 0.4	-57.0 ± 0.3
$\langle U_{WW(LJ)} \rangle$	8.8 ± 0.6	8.3 ± 0.5	9.7 ± 0.01	9.5 ± 0.02
$\langle U_{WT(ES)} \rangle$	-31.0 ± 5.3	-33.8 ± 3.0	-69.5 ± 3.2	-46.9 ± 1.1
$\langle U_{WT(LJ)} \rangle$	-14.0 ± 3.0	-8.5 ± 1.4	-30.2 ± 0.2	-17.7 ± 0.1
$\langle U_{TT(ES)} \rangle$	0 ± 0.4	-0.8 ± 0.6	0.3 ± 0.3	-1.3 ± 0.3
$\langle U_{TT(LJ)} \rangle$	-0.3 ± 0.3	-2.0 ± 0.3	-1.3 ± 0.1	-9.0 ± 0.1
$D_v(T)$[b] ($\times 10^{-9}$ m²/s)	2.54	2.05	1.0[c]	0.77[d]
$D_v(W)$[e] ($\times 10^{-9}$ m²/s)	2.63	2.50	2.15[f]	1.87[g]
simulation (ns)	0.4	0.4	0.6	0.6

[a] All energies are in kJ/mol. The potential energies for these pairs of molecular types are given as the total quantities, divided by the number of water molecules (water−water) or the number TBA molecules (water−TBA and TBA−TBA). Note that for model II there is a large intramolecular contribution to the potential energies. [b] Tanaka et al.[8] 1.70×10^{-9} m²/s at 298.15 K with MCY water as solvent. Noto et al.:[11] 2.64×10^{-9} m²/s at 300 K with MCY water as solvent. [c] 0.84×10^{-9} m²/s at 5 mol% and 301 K,[22] 0.49×10^{-9} m²/s at 2 mol% and 298 K for *t*-BuOD.[23] [d] 0.54×10^{-9} m²/s at 10 mol% and 301 K,[22] 0.30×10^{-9} m²/s at 7 mol% and 298 K for *t*-BuOD.[23] [e] Tanaka et al.:[8] 0.65×10^{-9} m²/s at 298.15 K with MCY water as solvent Noto et al.:[11] 1.19×10^{-9} m²/s at 300 K with MCY water as solvent [f] 1.28×10^{-9} m²/s at 5 mol % and 301 K.[22] [g] 0.89×10^{-9} m²/s at 10 mol % and 301 K.[22]

TABLE 2: Coordination Numbers Extracted from the Radial Distribution Functions by Integrating to the First Minimum[a]

	model I		model II	
	2 mol %	8 mol %	2 mol %	8 mol %
		quantity		
O_w around O_t	1.8	1.4	2.0	1.7
O_w around H_t	0.45	0.52	0.65	0.60
O_t around H_w	0.8	0.6	0.7	0.6
O_w around O_w	4.4	4.5	4.3	4.1
O_w around H_w	1.9	1.9	1.8	1.8

[a] Water oxygen: O_w. Water hydrogen: H_w. Hydroxyl oxygen: O_t. Hydroxyl hydrogen: H_t.

with an anharmonic O−H stretching potential. The details of the potentials are given in the preceding paper.[13] Both models have been used to simulate pure TBA as a liquid, where the 15-site model gave clearly superior results.

For the molecular model for water, we use the three-site simple point charge model (SPC/E) of Berendsen and co-workers[14] together with the three-site model for TBA, and the flexible SPC potential by Toukan and Rahman[15] together with the 15-site TBA model. In the model of Toukan and Rahman, the O−H stretching is made anharmonic,[15] and thus the dynamical behavior of hydrogen bond donors should be equally well described in both potential models (water and TBA).

Unlike the other three butyl alcohols, i.e., normal, *iso* and secondary, *tert*-butyl alcohol is readily soluble in water. In this work we have studied two concentrations, a dilute, roughly 2 mol % (4 TBA and 252 water molecules), and a more concentrated, 8 mol % solution (20 TBA and 236 water molecules). In our discussions below we will refer to these as "dilute" and "concentrated" solutions, respectively. As in our simulations of pure liquid TBA, all solutions were studied at room temperature.

A standard simulation setup, cubic periodic boundary conditions with the minimum image convention, was employed. Simple combination rules were used for cross-interactions and the long-ranged electrostatic interactions are calculated by means of the Ewald method.[16] Some simulation characteristics and the temperature and the density used in our simulations are given in Table 1 along with some standard results. A more detailed description of the simulation details is given in our preceding paper.[13]

The simulations were carried out on a Fujitsu VX vector parallel supercomputer at the Center for Parallel Computers at the Royal Institute of Technology (KTH) in Stockholm and on the departmental parallel Linux pc cluster[17] at the division of Physical Chemistry, Stockholm University.

Results and Discussion

Structure around *tert*-Butyl Alcohol. In Figure 1 we present a set of RDFs about the TBA oxygen, while in Figure 2 we report a similar set of $g(r)$ functions now centered on the water oxygen. In each case results for both potential models at both concentrations are shown. Coordination numbers for water oxygens and water hydrogens around the TBA hydroxyl group and around water have been collected in Table 2.

The TBA oxygen−water oxygen RDF is given in Figure 1a. We would expected that the first peak in this function should be sensitive to the nature of the H-bonding between water and TBA. Interestingly, both potential models give comparable curves, although the first peaks of the two curves for model I are shifted slightly to larger separations compared to those obtained with model II. This behavior together with lower peak heights suggest stronger H-bonding for model II. For both
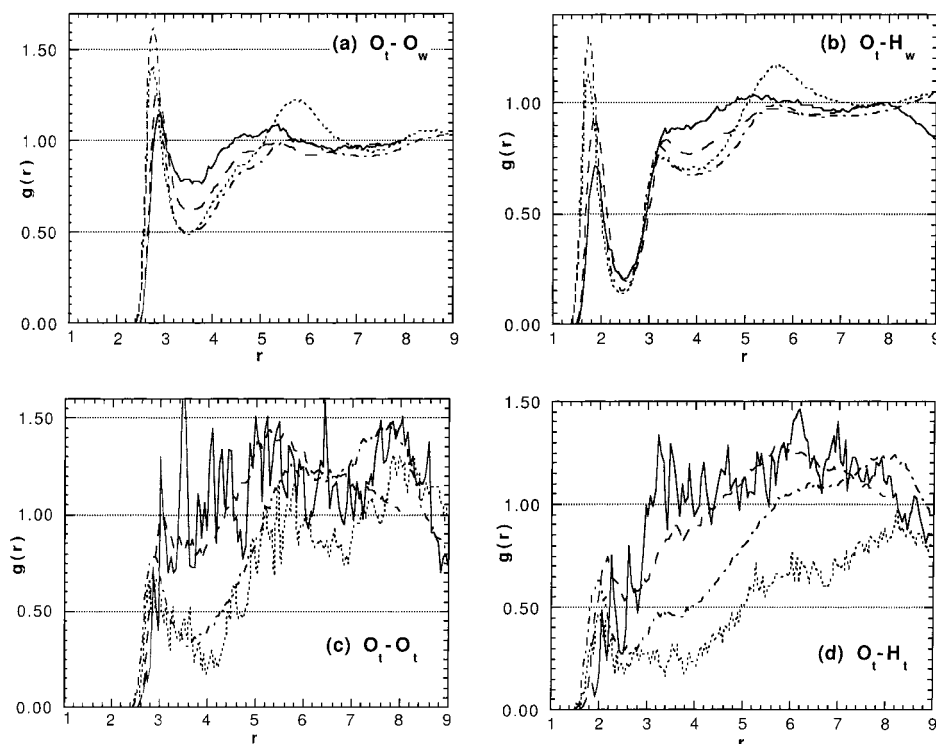
simple three-site model where the entire hydrophobic *tert*-butyl group is represented as a single LJ sphere, and a flexible all-atom 15-site model. In the present work we now extend our examination of these same two potential models to dilute aqueous solutions of *tert*-butyl alcohol. As in our preceding article,[13] the structure in the solutions is examined and compared in detail with the aid of both radial and spatial distribution functions.

This paper is outlined in the following way: in the next section we give details of our computational approach. In section III, we discuss our results concerning the radial and spatial analysis of the structure and the observed self-association in aqueous TBA solutions. Finally, our conclusions are given in section IV.

Computational Details

The results of our simulations of TBA in aqueous solution might be expected to be sensitive to the choice of the potential models and hence it is important that this selection should be made carefully. For example, an all-atom model should contain all the various internal modes of motion, including the degrees of freedom resulting from the four different internal rotations. A comparable water model should be chosen for balanced cross-interactions between the two molecules.

In our preceding paper,[13] we describe the development two very different potential models for TBA: a simple three-site model, analogous to that for methanol by Haughney et al.,[6] and a fully flexible all-atom 15-site model. The latter was equipped

Figure 1. Radial distribution functions about the TBA oxygens in aqueous TBA solution. (a) TBA oxygen−water oxygen, (b) TBA oxygen−water hydrogen, (c) TBA oxygen−TBA oxygen, (d) TBA oxygen−TBA hydrogen. Solid line corresponds to model I, 2 mol% solution; dashed line is model I, 8 mol%; dotted line is model II, 2 mol%; and dash−dotted line is model II , 8 mol% solution.
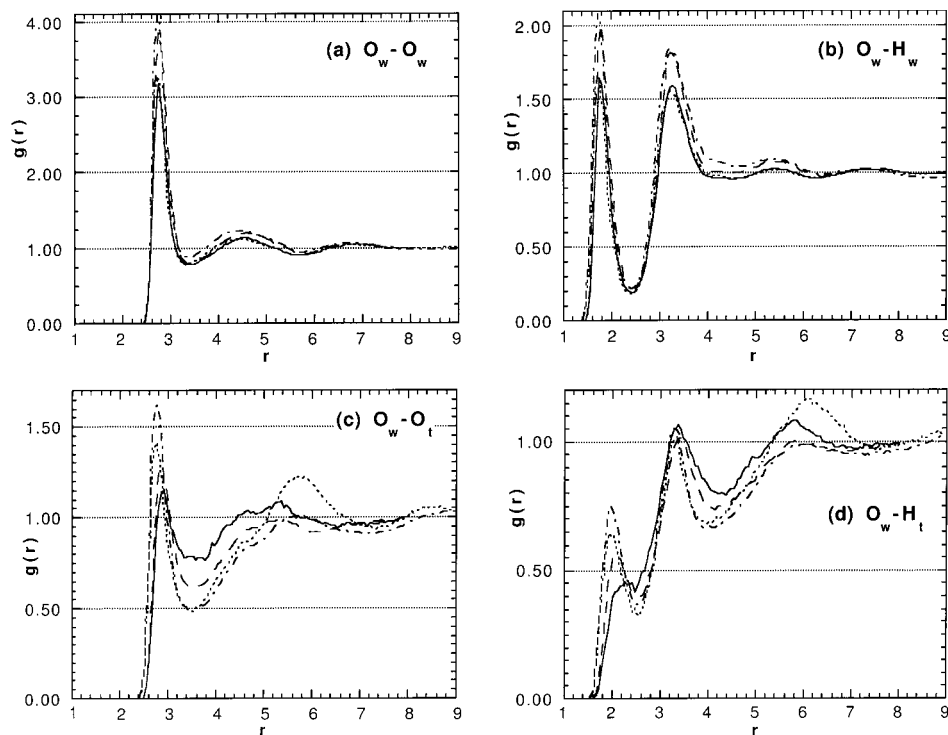

Figure 2. Radial distribution functions about the water oxygens in aqueous TBA solution. (a) water oxygen−water oxygen, (b) water oxygen−water hydrogen, (c) water oxygen−TBA oxygen, (d) water oxygen−TBA hydrogen. The lines are as defined in Figure 1.

models in Figure 1a there are roughly two water molecules in the first peak (see Table 2), assumed to be hydrogen bonded to the hydroxyl group of TBA, where model II has consistently larger values. Figure 1b shows the TBA oxygen−water hydrogen RDF. We find evidence again for reasonably strong hydrogen bonding between water and TBA with model II, with slight strengthening with increased concentration. From Table 2 we find that both models predict somewhat less than one

H-bond being donated from water to TBA. The results in both Figure 1a and b for model II are in good agreement with the RDFs and their concentration dependence obtained from empirical potential structure refinement of Bowron et al.[12] Figures 1c and (d) reveal that there is little direct H-bonding between TBA molecules in these dilute aqueous solutions with either model I or II. This is also in accord with the results of Bowron et al.[12] at their lowest concentration.
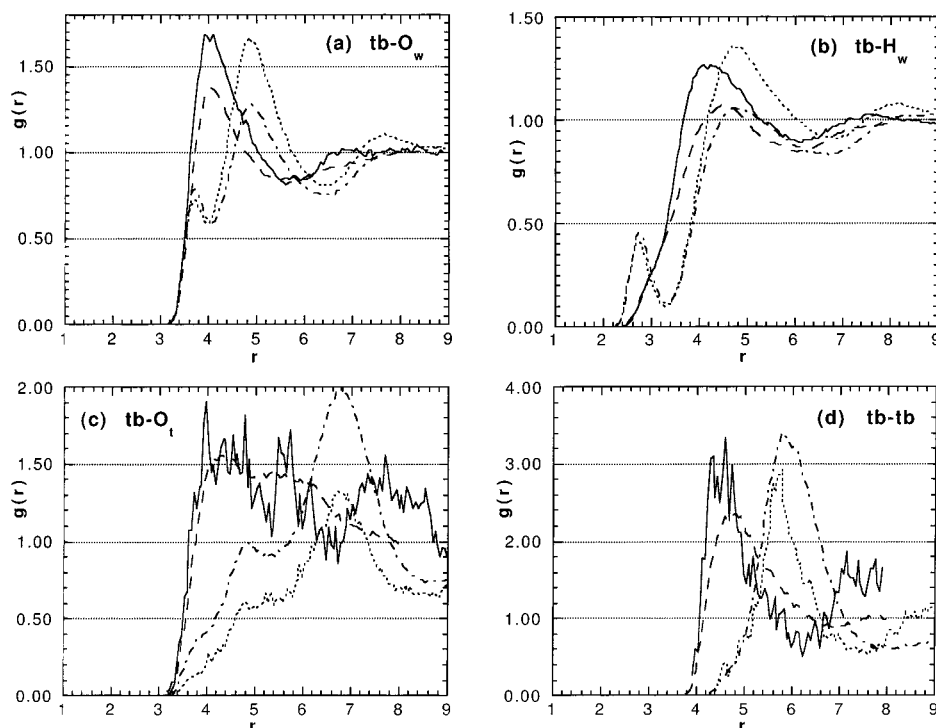
Figure 3. Radial distribution functions about the *tert*-butyl group (tb) in aqueous TBA solution. (a) tb−water oxygen, (b) tb−water hydrogen, (c) tb−TBA oxygen, (d) tb−tb. The lines are as defined in Figure 1.

The H-bond structure in Figure 1 can be compared with that apparent in Figure 2. Again we have evidence that TBA engages in relatively weak H-bonds with water, with model I consistently exhibiting weaker behavior. Examination of Figure 2a,b clearly shows that water prefers to hydrogen bond to itself in these aqueous solutions. Comparison of Figure 2c,d with Figures 1c,d indicates that TBA is a stronger H-bond acceptor than H-bond donor to water. Again this observation is consistent with the findings of Bowron et al.[12] The coordination numbers for water oxygens around the TBA hydrogen are somewhat less than one for the both concentrations and models when integrated to 2.5 Å, indicating that not all TBA hydroxyl groups donate a (strong) H-bond to water. Yet it is also clear that TBA only accepts (at most) one H-bond from water, despite have potentially two H-bond accepting sites. We recall that water is a symmetric H-bond donor and acceptor (i.e., it can both donate and accept two hydrogen bonds). It is perhaps not surprising then to see that, in the hydration of the hydroxyl group of TBA, water chooses to enforce a similar balance.

Nakanishi et al.[7] also found roughly two water molecules hydrogen bonding to the hydroxyl group of TBA in their early work with the same solution. We can also compare our results with the work of Tanaka et al.[8] They observed very strong hydrogen bonds; this is evident from the first minima of their $g(r_{OH})$ which goes essentially to zero. In the present work, the intensity at the first minimum is around 0.2 for water hydrogens binding to the TBA oxygen and 0.4 for TBA hydrogens binding to water oxygen. The relatively small diffusion coefficients Tanaka et al.[8] obtained for TBA in aqueous solution also suggests a very firmly attached hydration shell around the hydroxyl group of TBA (see Table 1). As we might expect then, we see from Table 1 that model I tends to overestimate the self-diffusion coefficient for aqueous TBA, while model II gives substantially better agreement with experiment, suggestion that it may be giving a more accurate description of H-bonding in solution. If we compare the present results with those of Noto et al.,[11] they show great similarity; their RDF curves are quite

comparable to ours. Of course, this behavior must depend strongly on the atomic charges which are the same in the two studies. Unfortunately, the OPLS model has not been, to our knowledge, used to simulate TBA in aqueous solutions.

A set of RDF functions around the *tert*-butyl group are shown in Figure 3 for both models. As was the case in pure liquid TBA, these "tb" points do not exactly correspond to the same point in the molecule; in model I it corresponds to the center-of-mass of the *tert*-butyl group, while in model II it is represented by the central-carbon site. Despite this difference, it is clear from Figure 3 that the two models predict somewhat different structure around the *tert*-butyl group. Model I shows a closer approach of the neighboring oxygen (water and TBA) sites and tb groups. Model II shows a characteristic short-range shoulder peak on the tb−O$_w$, tb−H$_w$, and tb−O$_t$ RDFs, once again in agreement with the empirical potential structural refinement results of Bowron et al.[12]

Figure 4 displays the water oxygen SDF around the TBA oxygen for the 8 mol % solution of model II. The isosurface threshold has been set to 1.6 times the average bulk density. This figure has been shaded by separation, darker shading indicating a smaller distance between the oxygens. We can see the typical hydrogen bond (red) features in Figure 4, although the acceptor feature is somewhat obscured. As in pure liquid TBA, we see that both H-bond acceptor and donor structures are slightly elongated. In addition, we can see four distinctive secondary (orange) features. There is a second neighbor feature that can be seen as a half ring around the acceptor cap in front of the hydroxyl hydrogen. This half-ring almost joins the H-bond feature behind the TBA oxygen. The H-bond donor neighbor also has a secondary structure associated with it in the form of a narrow band of density appearing below and behind it. Yet, another second-neighbor structure can be seen above the donor feature. This secondary feature grows into a broad elongated cap upon decreasing the threshold further. Finally, directly above the TBA oxygen we find a fourth second-neighbor feature at relatively short separations. This feature, which eventually joins
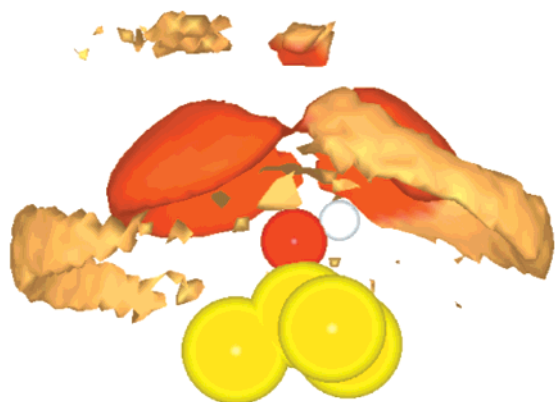
Computer Simulation Study of *tert*-Butyl Alcohol. 2

J. Phys. Chem. B, Vol. 104, No. 40, 2000 **9537**

Figure 4. Water oxygen density around the TBA oxygen in the 8 mol % solution for model II of TBA. The threshold is set to 1.6 times the average bulk density. The red (orange) surfaces shown have been shaded by their distance from the TBA oxygen; darker shading indicates a smaller separation between the oxygens.
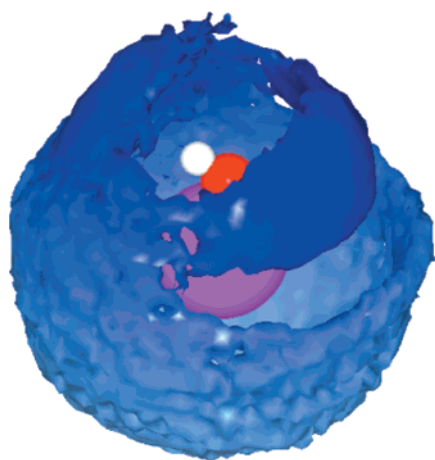

Figure 5. Water oxygen density around the TBA oxygen for the 2 mol % solution using model I at the threshold of 1.6. The blue surface is again shaded by separation.

Figure 6. Spatial density of (a) TBA oxygen around water oxygen at the threshold of 1.55 and (b) the same TBA oxygen SDF now overlayed with the *tert*-butyl function at a threshold of 1.35 times the average bulk density. Results for a the 2 mol % solution using model I are shown. Shading is again by separation, where blue surfaces represent TBA oxygen density and green surfaces *tert*-butyl density.

both edges of the surrounding half-rings, is very suggestive of a bridging water second neighbor.

Figure 5 gives the corresponding solvation structure for the 2 mol% solution using model I, also at a isosurface threshold of 1.6. We can again see a fairly well defined H-bond donor feature. The other distinct feature is the bowl appearing below the TBA molecule, which results from hydrophobic association (not apparent at this threshold with model II). The H-bond acceptor feature, however, is not well defined, but rather appears to be an extension of the bowl (non-hydrogen bonded) structure from below. The lighter shading of the H-bond acceptor structure indicates that it occurs at somewhat larger separations (as was also evident in the $g(r)$ in Figure 1b). Clearly water is having some difficulty acting as (or is otherwise reluctant to be) a H-bond acceptor for model I.

Structure around Water. Model I is used in Figure 6a,b where we begin to examine the spatial structure around water. These figures show the TBA oxygen density (blue) around the water molecule at a threshold of 1.55 (Figure 6a) and same TBA oxygen isosurfaces now overlayed with the *tert*-butyl SDF (green) at 1.35 times the average bulk density (Figure 6b). Shading by separation again is used to help to reveal details. These SDF results are also useful to explore further the water structure around a TBA molecule in aqueous solution. Particularly striking is the fact that no hydrogen-bonded donor peak is observed below the oxygen in Figure 6a. Even when the
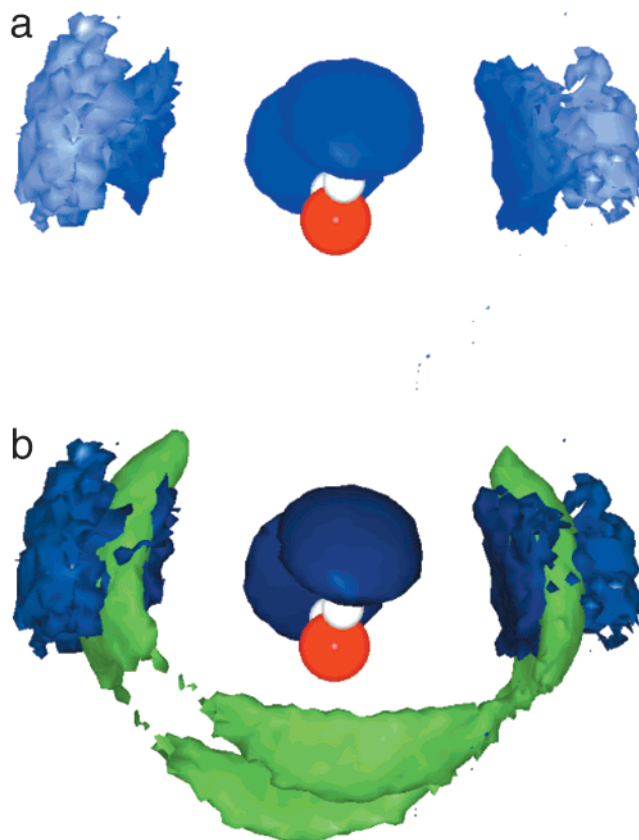
threshold is reduced no donor peak appears as a distinctive feature. Clearly we have confirmation that our model *I* is a rather weak hydrogen-bond donor (to water). However, typical symmetric caps appear due to H-bond accepting neighbors. Also prominent in Figure 6a are the two equatorial out-of-plane features. The dark shading of the inside surfaces closest to water oxygen correspond to separation less than 3.5 Å, indicating that these inner surfaces represent TBA H-bond donors, where the water (turned somewhat away from the TBA hydroxyl group) is preferring to make a weak bifurcated H-bond with the TBA molecule thus allowing it to H-bond more readily to the immediate hydration. Figure 6b adds the neighboring *tert*-butyl density (green) around water. The appearance of *tert*-butyl density at larger separation than the nearest out-of-plane oxygens provides further evidence that these must be (weakly) H-bonded neighbors. The four distinct equatorial features in the *tert*-butyl density otherwise represent the tendency of a water molecule to lie flat to the hydrophobic surface, as we have seen in previous work.[3]

TBA is known to be a strong structure-maker in water. In Figure 2a,b we show the water oxygen−oxygen and oxygen− hydrogen RDFs calculated for the solvents in the simulation with models I and II. It is obvious from these curves that at lower concentrations, TBA does not significantly affect the water structure. However, in the higher 8 mol % solution there is about a 25% increase in the intensity of the first peaks. Similar observations can be made from the corresponding hydrogen− hydrogen RDF curves (not shown), although much of this effect could be biased by the rather large excluded volume of our TBA solute.

Figure 7. Water oxygen−oxygen spatial distribution functions at a threshold of 1.65 for model II and a concentration of 8 mol % TBA. Shading of the red (orange) surfaces is again by separation, with the green features representing density due to third-neighbors.
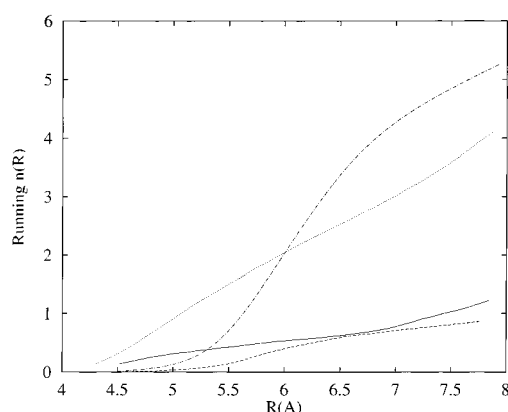

Figure 8. Coordination numbers from the *tert*-butyl RDFs. Solid line: model I, 2 mol % solution. Dotted line: model I, 8 mol %. Dashed line: model II, 2 mol %. dash−dotted line: model II, 8 mol % solution.

Figure 7 shows the spatial distribution of water oxygens around a water molecule at an isosurface threshold of 1.65 for model II and at a concentration of 8 mol% TBA. We can see familiar features in the local water structure, the darker nearest-neighbor and the lighter second H-bonded neighbor features. The interstitial density feature characteristic of the pure liquid[4] is conspicuously missing, while at the same time the secondary (network) structure, including a third neighbor feature, is already well resolved in the SDF at a density threshold of 1.65. This is a clear indication that the local water−water (tetrahedral) correlations are enhanced in this solution compared to that of pure water. This is in agreement with the conclusions of the experimental study of dilute aqueous alcohol solutions of Harris and Newitt.[18]

Association of *tert*-Butyl Alcohol in Water. Because of its strong amphiphilic character, TBA might be expected to associate in aqueous solution. In Figure 8 we give the running coordination numbers from the RDFs between the *tert*-butyl groups for both of the models and concentrations; the corresponding RDFs are shown in Figure 3d. It is clear from the coordination numbers that there is virtually no association at the lower concentration (2 mol %) with either of the two potential models. At the higher concentration (8 mol%), however, significant association is evident. This associative behavior appears spontaneously (out of a random mixture) only after a short simulation run and persists throughout the simulation. This association is more modest for model I, while the

Figure 9. The SDF of the central carbon of the tributyl group of TBA at the threshold of 4.5 times the average density (green) overlayed with the oxygen density at 6.0 times the average value (red). The results are for model II in a 8 mol % solution.

15-site model appears to favor groups of 3−4 TBA molecules in this aqueous solution. Two of these associated molecules appears to form contact configurations with their bulky *tert*-butyl groups "tail-to-tail". This observation is consistent with the solute−solute orientational correlations extracted by Bowron et al.[12] The lifetime of these pairs has been calculated (from configurational analysis) to be in the range 20−30 ps, excluding possible reformations. A small degree of hydrogen bonding can be observed among the TBA molecules in the solution from an analysis of the RDFs between the TBA hydroxyl groups. We did not analyze if some of the associated molecules were also H-bonded, however we would expect that the likelihood of this would increase with cluster size, or concentration, in accord with the results of Bowron et al.[12,19]

Figure 9 shows the SDF for the central carbon of the *tert*-butyl group at an isosurface threshold of 4.5 times the average density for model II and a concentration of 8 mol %. The neighboring TBA oxygen density (red) around the TBA molecule at 6.0 times its bulk value has been added to Figure 9. These high thresholds clearly show how strong the association of TBA molecules is in this more concentrated solution. Bowron et al.[12] have observed a similarly strong tendency of association. We note that the preferred areas of association appear to follow the form of the *tert*-butyl group. The two central carbon features appearing above and on either side of the TBA molecule should represent H-bonded TBA neighbors that are also maximizing the contact of their *tert*-butyl groups. Once again, this agrees with the analysis of Bowron et al.[12] where "broader distributions" were found in the solute−solute orientational correlations at higher concentration (where larger clusters would be expected).

The associations described above resemble the so-called "microheterogeneities", observed in a number of other binary liquid mixtures, for example, in the water-poor aqueous mixtures with acetonitrile.[20,21] In that system, however, the small complexes (groupings) were formed by water rather than acetonitrile. An instantaneous arbitrary snapshot of our TBA solution showing only the TBA molecules (the water are removed for visibility) is shown in Figure 10. We can clearly see that the TBA molecules form small islands of a few
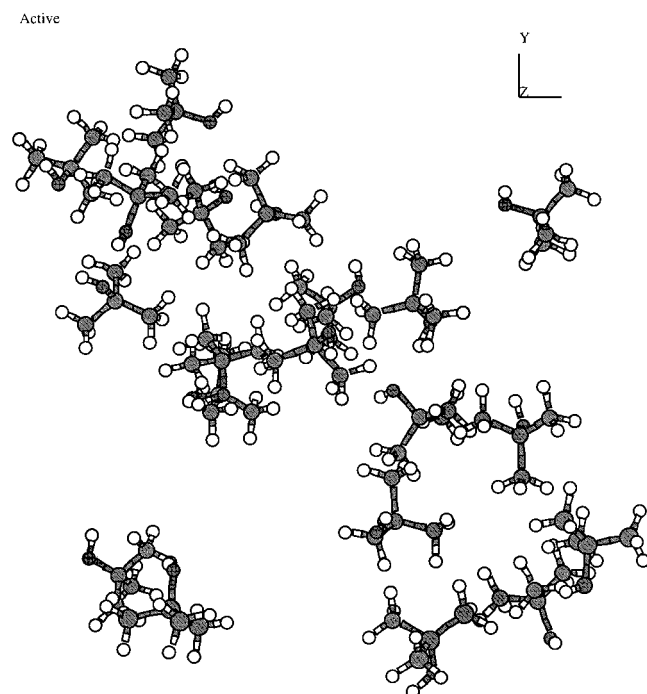
Computer Simulation Study of *tert*-Butyl Alcohol. 2

J. Phys. Chem. B, Vol. 104, No. 40, 2000 **9539**

Figure 10. An arbitrarily chosen snapshot from the simulation with model II at 8 mol %. The waters have been removed to show the associations of the TBA molecules.

molecules in this aqueous solution. Yet by observing another snapshot of this same system somewhat later, it is also clear that these islands are continuously changing.

These observations are consistent the diffusion coefficients calculated for TBA in these solutions (see Table 1). For both models the diffusion coefficients are considerably lower in the more concentrated solutions, as is also the case in the experimental data included in Table 1. We would expect the aggregates move slower due to their effectively larger mass. Similar behavior was observed by Tanaka et al.[8] We point out that the reduction of the diffusion coefficients for water (see Table 1) at the higher concentration can be accounted for by the increase in water structure.

Conclusions

We report MD computer simulations to investigate in detail the local spatial structure in aqueous TBA solutions, using a simple rigid three-site model and a flexible all-atom 15-site potential for TBA. Two aqueous solutions representing mixtures containing 2 and 8 mol % TBA were studied. The analysis was carried out by using a combination of radial distributions functions (RDF) and spatial distribution functions (SDF).

Our examination of the local structure in our two model aqueous TBA solutions revealed the hydrogen bonding to the surrounding water is not as pronounced as proposed previously for both model systems. Particularly the three-site model is found to be a weak H-bond donor to water, again revealing some of the deficiencies of this simplified model. Although some secondary H-bonded structures is apparent, including a bridging water molecule, the hydration structure around TBA appears to lack the very specific and localized H-bonded character observed in aqueous solutions of methanol.[3] This is particularly interesting since model I closely resembles the models used for methanol except for the size of its hydrophobic alkyl group. Clearly, the bulk of the *tert*-butyl group is helping to interfere with water's ability to H-bond to the hydroxyl group of the TBA molecule. However, comparison of results from the three-

site and 15-site models also shows that the details of the shape of the hydrophobic group can noticeably effect its hydration. We do find that the water (network) structure is significantly enhanced in the presence of TBA, particularly as the concentration is increased. We find that water molecules surrounding the *tert*-butyl group prefer to lay flat against its hydrophobic surface. While little self-association is observed in our dilute solutions, in more concentrated aqueous solution (8 mol % TBA), it occurs spontaneously within a few ps. Clusters of three or four TBAs are formed but also undergo continual change on times scales of tens of picoseconds. A tail-to-tail type of configurations with the bulky hydrophobic groups in contact is a preferred arrangement of two TBA molecules. The translational motion of the TBA and water molecules in these aqueous solutions was also studied and correlates well with the local structural behavior we have identified and with experimental data.

References and Notes

(1) Mendeleev, D. I. Compounds of Alcohol with Water. Ph.D. Thesis, St. Petersburg University, St. Petersburg, 1865.

(2) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry;* VCH: Weinheim, 1988.

(3) Laaksonen, A.; Kusalik, P. G.; Svishchev, I. M. *J. Phys. Chem. A* **1997**, *101*, 5910−5918.

(4) Svishchev, I. M.; Kusalik, P. G. *J. Chem. Phys.* **1993**, *99*, 3049.

(5) Kusalik, P. G.; Laaksonen, A.; Svishchev, I. M. Spatial Structure in Molecular Liquids. In *Theoretical and Computational Chemistry Series;* Elsevier: Amsterdam, 1999.

(6) Haughney, M.; Ferrario, M.; McDonald, I. R. *Mol. Phys.* **1986**, *58*, 849−853.

(7) Nakanishi, K.; Ikari, K.; Okazaki, S.; Touhara, H. *J. Chem. Phys.* **1984**, *80*, 1656−1670.

(8) Tanaka, H.; Nakanishi, K.; Touhara, H. *J. Chem. Phys.* **1984**, *81*, 4065−4073.

(9) Tanaka, H.; Nakanishi, K. *Fluid Phase Equilib.* **1993**, *83*, 77−84.

(10) Okazaki, S.; Nakanishi, K.; Touhara, H. *J. Chem. Phys.* **1983**, *78*, 454.

(11) Noto, R.; Martorana, V.; Emanuele, A.; Fornili, S. L. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3803−3808.

(12) Bowron, D. T.; Finney, J. L.; Soper, A. K. *Mol. Phys.* **1998**, *93*, 531−543.

(13) Kusalik, P.; Lyubartsev, A. P.; Bergman, D. L.; Laaksonen, A. *J. Phys. Chem. B* **2000**, *104*, 9526.

(14) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. *J. Phys. Chem.* **1987**, *91*, 6269−6271.

(15) Toukan, K.; Rahman, A. *Phys. Rev. B* **1985**, *31*, 2643.

(16) Allen, M. P.; Tildesley, D. J. *Computer Simulations of Liquids;* Oxford Science: Oxford, 1985.

(17) For the Hälge−A Linux cluster, see: http://www.fos.su.se/physical/aatto/helge/.

(18) Harris, K. R.; Newitt, P. J. *J. Phys. Chem. B* **1998**, *102*, 8874.

(19) Bowron, D. T.; Finney, J. L.; Soper, A. K. *J. Phys. Chem. B* **1998**, *102*, 3551.

(20) Kovacs, H.; Laaksonen, A. *J. Am. Chem. Soc* **1991**, *113*, 5596.

(21) Bergman, D. L.; Laaksonen, A. *Phys. Rev. B* **1998**, *58*, 4706.

(22) Kipkemboi, P. K.; Easteal, A. J. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2956.

(23) Mayele, M.; Holz, M.; Sacco, A. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4615.

(24) Already more than 100 years ago, young Mendeleev studied the nonideal behavior of the ethanol−water mixtures as a topic of his doctoral thesis of ref 1. As a byproduct of these scientific efforts is his recommendation that the ideal alcohol concentration in Vodka should not exceed 40 wt %, still followed in Russia.