Insignificant Effect of Temperature on the Structure and Angular Jumps of Water near a Hydrophobic Cation

Adyasa Priyadarsini and Bhabani S. Mallik*

ABSTRACT: The ambiguity in the behavior of water molecules around hydrophobic solutes is a matter of interest for many studies. Motivated by the earlier results on the dynamics of water molecules around tetramethylammonium (TMA) cation, we present the effect of temperature on the structure and angular jumps of water due to hydrophobicity using first principles molecular dynamics simulations. The average intermolecular distance between the central oxygen and four nearest neighbors is found to be the highest for water molecules in the solvation shell of TMA at 400 K, followed by the same at 330 K. The hydrogen bond (HB) donor–acceptor count, HB per water molecule, and tetrahedral order parameter suggests the loss of tetrahedrality in the solvation shell. Elevated temperature affects the tetrahedral parameter in local regions. The HB jump mechanism is studied for methyl hydrogen and water molecules in the solvation shell. Observations hint at the presence of dangling water molecules in the vicinity of the hydrophobic cation, and no evidence is found for the enhanced structural ordering of nearby water molecules.

1. INTRODUCTION

Understanding the ongoing debate on the structural arrangement of water around hydrophobic molecules can lead the path to comprehend the protein folding/binding, biomolecular solvation, and drug carriers.1–5 The properties of bulk water are interrupted by the presence of a hydrophobic molecule. The Frank & Evans “iceberg” model was the first attempt to provide a plausible explanation for the hydrophobic hydration, according to which within a specific range from the hydrophobic molecules, water experiences a higher degree of orientation in the form of an ice-like structure and forms a cavity around the same. The iceberg model as an effect of enhanced strength and number of hydrogen bonds has been supported.7–9 During the early stages of the conceptual development of hydrophobic hydration, it was believed that hydrophobicity is “entropy controlled”, and an increase in Gibb’s free energy results from a negative transition state entropy. Back then, this leads to the widely accepted enhanced ordering of liquid water close to the hydrophobic solute. The thermodynamic and entropic explanation creates a believable scenario for the iceberg model. Ben-Naim10 put forth the idea of the “structure of water” instead of local structural changes induced by a solute, hence, criticizing the use of entropy as a generic model to determine the solute-induced behavioral change of the entire solvent system. Adapting the solvent reorganization model,11–13 an alternate explanation for the change in Gibb’s free energy is provided by a set of studies, where in contrast to the iceberg model, hydrophobicity is explained to be a product of the free energy associated with cavity formation. Lee and Graziano14,15 extended the simple hydrated water model of Muller,9 which explains the existence of low energy and high energy hydrogen-bonded water in equilibrium. They put forth the idea of fewer but enthalpically stronger hydrogen bonds in the solvation shell than pure water. A few studies8,16–18 addressing the hydrophobic hydration and critically addressing the iceberg model,6 “flickering clusters”7,19 have been performed. However, later studies performed both experimentally and theoretically either support or deny the iceberg model depending on the size of the hydrophobes, such as the alkyl chain length,20–22 hydrophobic surface structure,23 ratio of the polar and apolar group,24,25 and temperature.26,27 Considering the size effect, water molecules are revealed to be more prone toward ordered arrangement in the near vicinity of small hydrophobic molecules such as methane.28 In contrast to the ordered arrangement, the neutron diffraction study of

Received: January 6, 2021
Accepted: March 15, 2021
Published: March 19, 2021
methane—water$^{29}$ and methanol—water$^{30}$ solutions shows an inconsequential difference of the tetrahedral arrangement of water molecules in the distinct regions, a behavior assisted by several NMR$^{31−33}$ and theoretical studies.$^{34−37}$ Laage et al. proved that a lack of rapid exchange of hydrogen bond among the solvation shell water molecules around the hydrophobe increases the reorientation time, but this concept does not approve the iceberg model.$^{38}$ Highly ordered water molecules in the solvation shell than bulk water were reported by Galamba,$^{39,40}$ and the methodology adopted was later criticized by Graziano.$^{41}$ The analysis underscored that a subpopulation of water molecules in the hydration shell is more tetrahedral than those in bulk, but the other water molecules in the hydration shell are not more tetrahedral. Moreover, a theoretical study revealed a reduction in water formation.$^{42}$ Certain earlier attempts fail to prove the iceberg concept based on a decrease in the water—water entropy.$^{43,44}$ The theory postulated by Lum—Chandler—Weeks$^{45}$ deals with quantitative measurement of hydrophobicity encompassing the size effect, local concentration, chemical potential, and surface free energy that determines the drying effect. The liquid—vapor phase coexistence and striking difference in the solute—solvent/solvent—solvent interaction, which are affected by the length scale of hydrophobes, are the deciding factors for hydrophobicity.$^{46}$ Around the small apolar hydrophobic solute, such as moderate length alkane chains, water molecules get rearranged without significant loss of HB. This behavior, the elastic effect, is only applicable to the small hydrophobes. However, for large hydrophobes with nanoscale critical separation distance, the drying effect is observed when water trapped within parallel hydrophobic chains evaporates.$^{45,47−49}$

From the above discussion of the previously suggested theories, it can be concluded that the poor solubility of small hydrophobes like CH$_4$ and CH$_3$OH can be attributed to the large negative entropy resulting from inaccessible volume rather than HB rearrangement among water molecules. Detailed temperature-dependent statistical calculations$^{50}$ ranging from 0−100 °C, concretes the idea of “complete entropy—enthalpy compensation” due to HB rearrangement among water molecules in the vicinity of hydrophobes. This study also reveals that HB modification-induced enthalpic and entropic change turns positive in value after 4 °C and hence disproves heightened structural ordering and is also insignificant for hydrophobic hydration analysis. Cautious insight leads to two distinct contributors for a high negative entropic change, namely, change in entropy due to the direct rise of solvent-excluded volume in the presence of hydrophobes and entropy change due to stable repositioning of the solvent molecules. The mentioned contributions, sum to the entropy of cavity formation, are crucial for explaining Gibb’s free energy of hydrophobic hydration of small molecules.$^{50}$

Previously, we studied the water dynamic around symmetrical tetramethylammonium (TMA) ion using hydrogen bond dynamics, orientation autocorrelation function, time-dependent frequency correlation function, and hole propagation. We found the presence of a disordered water structure with a higher dangling lifetime, which was calculated following the Luzar—Chandler kinetic model,$^{51−53}$ inside the solvation shell defined within a distance of 5.5 Å as per N-O$_w$ radial distribution function (RDF) at 330 K. Studies defending the fact of dangling HBs and the less-ordered structure state that a significant fraction of water molecules around the hydrophobic solute tend to be dangling as it has been concluded in the previous study of the dynamics of water molecule around a TMA cation.$^{52}$ Also, the observations were confirmed from the dynamics of hydrogen bonds. In the current study, we primarily focus on the effects of temperature on the hydrophobicity of a TMA cation by calculating various properties like the hydrogen bond (HB) and dangling bond statistics, tetrahedral order parameter, and HB jump mechanism in the solvation shell. The first principles molecular dynamics simulations were performed at two different temperatures, 330 and 400 K. No evidence is found for the enhanced structural ordering of water molecules near the hydrophobe. The observations hint at the presence of dangling water molecules in the vicinity of the hydrophobe.

2. RESULTS AND DISCUSSION

2.1. Structural Probe of Water Molecules around the TMA Cation. As our primary concern in this study is to determine the effect of elevated temperature on the hydrophobicity of a TMA on the surrounding water molecules, we start the analysis by calculating the center of mass—center of mass radial distribution function (RDF$_{COM-COM}$) between TMA and water molecules. RDF provides the distribution of the observed species around the reference species.$^{53,54}$ From our calculated RDF$_{COM-COM}$ as depicted in Figure 1, we obtain the first solvation shell distance from the center of mass of TMA, i.e., 5.5 Å; the curve flattens after the mentioned distance. The solvation shell criteria for 330 K match with the one obtained from the previously reported NTMA−O$_{H2O}$ RDF.$^{54}$ We obtain a minimum at 5.7 Å for 400 K. The coordination numbers (∼10) of water molecules corresponding to the maxima coincide with each other. The total number of water molecules in the first solvation shell sums to 23. For further calculations and analysis, the water molecules outside the solvation shell are expected to behave as bulk water, and the ones inside the solvation shell are considered under the influence of the hydrophobic TMA cation. A theoretical study$^{55}$ performed concerning TMA-Br/water and TBA-Br/ water system provides RDF and CN results, which harmonize with our results, with the first peak maxima around 4.5 Å. The structural variation-driven hydration of TMA$^+$ and TBA$^+$ studies using polarizable force fields also results in a similar solvation structure.$^{58}$

For both 330 and 400 K simulated trajectories, we have plotted the distance vs time correlation plot between COM of TMA$^+$ and fluoride ion, which is presented in Figure 2. The counter anion fluoride remains well separated from the TMA$^+$ as the average distance r[COM$_{TMA}$−F$^−$] for both the cases
varies between 4.0 and 6.5 Å. Hence, the fluoride ion is not expected to intervene in the effect of TMA⁺ on the surrounding water. We calculated the average number of water molecules common for the first solvation of both TMA⁺ and F⁻. We find only 3 water molecules out of 50, irrespective of the simulation temperature, following the condition [r[COM_{TMA}-COM_{H_2O}] < 5.5 Å and [r[F^-COM_{H_2O}] < 3.5 Å for 330 K and [r[COM_{TMA}-COM_{H_2O}] < 5.7 Å and [r[F^-COM_{H_2O}] < 3.5 Å for 400 K].

Then, we proceed toward exploring the configuration space of water molecules around TMA and the difference from the bulk water. The configurational space is calculated as a combined distribution of intermolecular O_w-H_w and O_w-O_w radial distribution, pictorially depicted in Figure 3a–d for solvation shell and bulk water at 330 and 400 K, respectively. Three dense regions can be identified on the configurational space, namely, regions I, II, and III embodying different O_w-H_w and O_w-O_w radial distribution pairs. Region I consists of [r[O_w-H_w] = 1.50 to 2.5 Å and [r[O_w-O_w] = 2.5 to 3.25 Å. Region II is spotted as the dense distribution comprising [r[O_w-H_w] = 2.75 to 3.5 Å and [r[O_w-O_w] = 2.5 to 3.0 Å. For both solvation shell and bulk water, we observe regions I and II to be identical to each other. In the case of region II, there is a slight decrease in the probability density hinting at the elevated statistics of dangling water molecules in the solvation shell at 330 K, but no such variation was observed for 400 K. Region III, which comprises [r[O_w-H_w] and [r[O_w-O_w]] ranging between 3.0–4.0 and 2.5–3.5 Å, respectively, has a higher probability in the case of bulk as compared to the solvation shell for both 330 and 400 K. These observations again disprove any major difference in the structural ordering of water around a hydrophobe irrespective of temperature change.

To have a further insight into the intermolecular distances between O_w-O_w and O_w-H_w, we calculated and compared the probability distributions of the same in the solvation shell and bulk. In Figure 4a, we have depicted the distribution of the average distance (P_{OH}) between the oxygen of the central water molecule and the oxygen atoms of the four nearest neighboring water molecules, which are further responsible for the formation of the hydrogen-bonded tetrahedral moiety. We observe a shift in P_{OH} toward a higher value of average distance in the solvation shell, which can be attributed to the structurally less-coordinated water around TMA. Previous studies involving water around monatomic cations and anions put forth the idea of varying HB count, which depends upon the size of the concerned ionic solute. In the case of TMA⁻–like apolar hydrophobic solutes, the tetrahedral orientation of local water molecules is distorted due to the tangential orientation of water molecules toward the solute.

In the case of 400 K, the difference in the average O4 distance in the bulk and solvation shell is higher as compared to that of 330 K. The distribution of the intermolecular distance between the nearest pair of oxygen of water molecules is depicted in Figure 4b. A little shift in the maximum probable distance between intermolecular oxygen pairs is observed for both 330 and 400 K. Then, we calculated the same for oxygen to the first and second nearest intermolecular hydrogens and present them individually in Figure 4c,d, respectively. Both in the bulk and solvation shells, the r_OH1 distribution is indistinguishable, which can be attributed to the effect of higher simulation temperatures of 330 and 400 K. However, in the case of r_OH2 probability distribution, we observe a peak at 2.8 Å for the solvation shell, which is missing in the case of bulk. This observation is evident in the presence of two intermolecular hydrogens around the same O_w in the proximity of 1.5 to 2.7 Å. However, due to the hydrophobicity of TMA in the solvation shell, a significant proportion of the second closest H_w are at a distance higher than 2.45, the water–water hydrogen bond limiting distance. Hence, the pieces of evidence indicate the presence of dangling bonds in the solvation shell.

2.2. Hydrogen Bond Statistics. For the formation of a hydrogen bond (HB) between water molecules, certain distance and angle criteria are needed. For our observations, we have considered the HB criteria to be the r_{O-H} < 2.45 Å and the angle H-O_donator-O_acceptor < 30°. From the probability distribution of different nearest neighbor distances, it is obvious that hydrophobicity affects the HB count in its vicinity; but the question arises up to what extent. To obtain a quantitative idea of the former question, we calculated the HB donor and acceptor numbers. We obtained the total number of HBs donated and accepted and the total number of HB donor and acceptor water molecules, hence obtaining the average number of HBs per donor (HB-D) and acceptor (HB-A) water molecules.

The graphical presentation is provided in Figure 5a, which reflects that the number of HBs (donated and accepted) in the solvation shell is less than in bulk, hence assuring the
hydrophobic effect. Our results are in line with the previously reported HB donor/acceptor count around hydrophobic solutes,\textsuperscript{39} according to which, at room temperature, the HB donor/acceptor count decreases modestly in the solvation shell region of aliphatic and aromatic hydrocarbons. For both 330 and 400 K, the difference in the water–water average HB-D and HB-A count is equivalent for bulk, whereas, in the solvation shell, there is a visible difference as HB-D is higher than the HB-A count. The observations follow the effect of methyl species acting as HB donors for certain water molecules.\textsuperscript{62} Totaling the HB donor/acceptor count in the solvation shell, we obtain the $N_{\text{HB}} = 3.47$ and 3.42 for 330 and 400 K, respectively. Bulk water with the perfect tetrahedral arrangement is known to form 4 HBs with its nearest neighbors. To solidify our previously obtained results, we proceed toward calculating the number of HBs per water molecule, presented as a probability distribution in Figure 5b. The distribution represents the probability of formation of $n$ HBs per water molecule in the solvation shell and bulk. In the two distinguished regions, the formation of four HBs is most probable, with varying contributions from 2, 3, and 5 HBs per water molecule. $P(N_{\text{HB}})$ peaks for four HBs per water molecule, and the probability of formation of 2 and 3 HBs significantly increases in the solvation shell as compared to the bulk. The distribution pattern is similar for 330 and 400 K, with the average numbers of HBs per water molecule of 3.38 and 3.37 for the solvation shell and 3.68 and 3.64 for bulk, respectively. Integrating the HB donor/acceptor count and averaging HB per water molecule, we obtained close values for solvation shell water $N_{\text{HB}} = 3.47$ and 3.42 at 330 K and $N_{\text{HB}} = 3.42$ and 3.37 at 400 K, respectively. A decrease in the $N_{\text{HB}}$ is observed in the solvation shell as compared to bulk. Similar effects were also observed in the study of water around hydrophobic alkyl chains with varying chain lengths.\textsuperscript{63} Not so different values of the $N_{\text{HB}}$ in the distinct regions can be attributed to the relative structural ordering of the water molecules to compensate for the loss of HB, which is caused by cavity formation, in the vicinity of the hydrophobes. Similar differences in the values were observed for the neopentane molecule,\textsuperscript{64} which has comparable symmetry as our studied molecule.

2.3. Tetrahedrality of Water Molecules around the TMA Cation. Water tetrahedrality is affected by the orientational arrangement and is an important factor for the HB network. Initially projected by Chau and Hardwick,\textsuperscript{65} the tetrahedral order parameter is later explored and scaled by Errington and Debenedetti.\textsuperscript{66} The tetrahedral order parameter

![Figure 4](image_url)

**Figure 4.** Probability distribution of different intermolecular distances at 330 (black) and 400 K (magenta), such as (a) the average distance between the oxygen of the central water molecule from the four nearest neighbors, (b) the average distance between the two nearest oxygen pairs in the solvation shell (solid line) and bulk (dotted line), and the intermolecular distance between (c) OW and the first nearest HW and (d) OW and the second nearest HW in the solvation shell (solid line) and bulk (dotted line).

![Figure 5](image_url)

**Figure 5.** (a) Average numbers of the donor (HB-D) and acceptor (HB-A) HBs in the bulk (blue) and solvation shell (red) at 330 (top panel) and 400 K (bottom panel), (b) distribution of hydrogen bonds per water molecule in the solvation shell (solid line) and bulk (dotted line), (c) pictorial representation of a perfect tetrahedral arrangement of water molecules hydrogen bonded to each other, and (d) tetrahedrality distribution $P(q_{\text{tet}})$ of water molecules in the solvation shell (solid line) and bulk (dotted line) at 330 (black) and 400 K (magenta).
is provided by $q = 1 - \frac{3}{8} \sum_{i=1}^{3} \sum_{j=i+1}^{4} (\cos \theta_{ij} + \frac{1}{3})$, where $q$ is the tetrahedrality, $\theta_{ij}$ is the angle between the $i^{th}$ central and $j^{th}$ water molecule, and $i$ & $j$ are closest neighbors to the central water molecule as depicted in Figure 5c. The value of $\cos \theta_{ij}$ can be any value between 0 and 1 corresponding to completely random and perfectly tetrahedral arrangement, respectively. In Figure 5d, we have presented the probability distribution of $q_{\text{tet}}$ of water molecules in the solvation shell and bulk, where the most probable $q_{\text{tet}}$ acquires the probability 1. An important deciding factor for $q_{\text{tet}}$ is the temperature. In bulk, we observe the maximum to be at 0.8, which is the usual behavior for pure water at ambient temperature. Also, a high peak at 0.5 is consistent with the previously reported results for pure water.66 The probability of the heightened peak at $q_{\text{tet}} = 0.5$ is higher at 400 K as compared to 330 K for bulk water, signifying the inflated deviation of the water molecules from the tetrahedral structure. For the solvation shell, we observe a further shift of the distribution plot to lower values of $q_{\text{tet}}$ due to an increase in disorientation and dangling of the water molecules, which is equivalent for 330 and 400 K. A combined effect of temperature as well as hydrophobicity of the TMA ion contributes to the observed high probable lower tetrahedral order of 0.5 for the solvation shell. A marginal difference in the $P(q_{\text{tet}})$ in the solvation shell and bulk fits with the previously reported results for water around hydrophobic amino acid solutes.67

The classical molecular dynamics simulations of water molecules reported a higher structural ordering around small uncharged non-polar hydrophobes, and the cited reason being the heightened tetrahedral ordering around the subregions of the hydrophobic molecule.39,60 However, Graziano31 criticized the findings based on the fact that small structural arrangements leading to the entropic alteration are not enough to explain the hydrophobic hydration observed for small hydrophobes. The solvation enthalpy is a combined contribution10,41 from both solute—solvent interaction energy and the enthalpy of rearrangement. The enthalpy of rearrangement of the solvent system for a small hydrophobic molecule such as methane, ethane, and hence effectively TMA+, is rather positive in value culminating in the reduced structural ordering of the water molecule. From our reported distance distribution of r(O4), we find a shift of 0.3 Å toward the higher value for solvation shell water molecules, which is again reflected in the probability distribution of $q_{\text{tet}}$ through a reduction in the tetrahedral ordering. In a recent study68 of the water structure around different localities of tert-butanol, an undercoordinated water layer with reduced tetrahedral ordering was observed.

### 2.4. Hydrogen Bond Jump Mechanism

We expect that there could be weak hydrogen bonding between TMA and water molecules because methyl groups are bonded to a positively charged nitrogen atom in TMA. We calculated the RDF of oxygen atoms of water molecules around methyl carbon atoms (C$_{\text{TMA-Ow}}$) and hydrogen atoms (H$_{\text{TMA-Ow}}$) of the TMA ion as depicted in Figure 6a,b, respectively. For C$_{\text{TMA-Ow}}$ RDF, we observe the first maximum at 3.8 Å and the first minimum at 4.5 Å for 330 K, which remains unchanged for 400 K. However, the H$_{\text{TMA-Ow}}$ RDF does not show a proper first maximum and minimum. To get proper cutoff distances to define the solvation shell, we calculated the combined distribution function (CDF) for these two RDFs. The CDF is shown in Figure 6c,d for 330 and 400 K. We find that the combined distribution of these two distances has the maximum probability at 3.5 and 2.5 Å for the corresponding RDFs, suggesting that there is a weak hydrogen bonding between TMA and water molecules irrespective of the temperature. The first minimum for C$_{\text{TMA-Ow}}$ RDF is observed at 4.5 Å, and for H$_{\text{TMA-Ow}}$ RDF, it is found to be 3.5 Å. We consider 4.0 and 3.0 Å as the distance cutoffs for weak HB according to the definition. Using these distance cutoffs, we

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*Figure 6. RDFs of oxygen atoms (Ow) of the water molecules (a) around carbon atoms of TMA (C$_{\text{TMA}}$) and (b) around hydrogen atoms of TMA (H$_{\text{TMA}}$). (c, d) CDF of C$_{\text{TMA-Ow}}$ and H$_{\text{TMA-Ow}}$. (e) Hydrogen bond angle (<Ow-C$_{\text{TMA}}$-H$_{\text{TMA}}$) distribution between water and TMA. (f) Schematic representation of different geometrical parameters concerning hydrogen bond jump.*
calculated the HB angle \(\angle O_a-C_{TMAC}-H_{TMAC} \) distribution, which is shown in Figure 6e. The probability of HB angle peaks appears within 30° for both 330 and 400 K.

We have calculated the hydrogen bond jump mechanism of water around TMA. The Laage-Hynes approach was used to calculate the jump mechanism, which was successfully used in reorientational dynamics of water around different solutes like monoatomic anions \((F^-, Cl^-, and I^-)\) \(^{71,72}\) oxyanions \((\text{nitrate, carbonate, and perchlorate})\) \(^{73-75}\) hydrophobic molecule \((\text{tetramethylurea})\) \(^{76}\) and protein.\(^{77}\)

This approach was also used in reorientational jumps of acetamide molecules in neat molten acetamide and later in deep eutectic mixtures made of acetamide and lithium salts.\(^{78}\) Using this approach, we calculated the hydrogen bond jump dynamic are calculated, including all the four TMA methyl groups. A total of 134 and 104 switch events are captured for 330 and 400 K, respectively, and averaged with a common point where the hydrogen bond switch happens defined by \(\theta = 0°\). Time dependence of distances \(R_{C^*=O_a} \) and \(R_{C^*=O_b} \) before and after hydrogen bond jump is shown in Figure 7a.d. In contrast to pure water, \(C^*\) is not equidistant from the initial and final hydrogen bond acceptors \(O_a\) and \(O_b\).

This can be observed when the hydrogen bond strength of the initial acceptor \(O_a\) is involved in a weak hydrogen bond with another water molecule, all the specific properties associated with the HB jump dynamic are calculated, including all the four TMA methyl groups. A total of 134 and 104 switch events are captured for 330 and 400 K, respectively, and averaged with a common point where the hydrogen bond switch happens defined by \(\theta = 0°\). Time dependence of distances \(R_{C^*=O_a} \) and \(R_{C^*=O_b} \) before and after hydrogen bond jump is shown in Figure 7a.d. In contrast to pure water, \(C^*\) is not equidistant from the initial and final hydrogen bond acceptors \(O_a\) and \(O_b\).

The jump angle \(\langle \theta \rangle \) and its distribution before and after hydrogen bond jump is shown in Figure 7c.f. A jump angle of \(-27°\) to \(+23°\) is observed corresponding to a jump amplitude of \(50°\) for 330 K, whereas, \(\theta \) for 400 K is found to be \(-23°\) to \(+23°\), and hence a jump amplitude of \(46°\) is observed. We calculated other angular parameters \(\psi\) and \(\varphi\) relevant to the jump mechanism depicted in Figure 7b.e. \(\psi\) is defined as the angle between the \(C^*\)–\(H^*\) bond and its projection on the \(O_a\)–\(C^*\)–\(O_b\) plane, whereas \(\varphi\) is defined as the angle between vectors \(C^*\)–\(O_a\) and \(C^*\)–\(O_b\). The angle \(\varphi\) is observed to be \(66°\) throughout the hydrogen bond jump for both temperatures. We have scaled the values as \(\psi-60°\) in Figure 6b,e. The average value for the angle \(\psi\) is observed to be 21 and 19° for 330 and 400 K, respectively, which is found to be more compared to the values observed in hydrogen bond jump in pure water.

3. CONCLUSIONS

Here, we present the study of the hydrophobicity of TMA in a relatively dilute aqueous solution by probing the hydrogen bond formation and jump mechanism in two different simulation temperatures above ambient conditions. We find no significant difference in the intermolecular distance distribution of the first pairs of \(O_a\)–\(O_a\) \([P(t_{OH})]\) and \(O_a\)–\(H_g\) \([P(t_{OH})]\), irrespective of the solvation region or temperature. In the case of the second nearest hydrogen, we observe an extended peak of \(P(t_{OH})\) at the region outside the allowed \(O_a\)–\(H_g\) distance for H bond formation for the solvation shell, whereas the same peak is missing in the case of bulk. This gives an expression that a significant number of second nearest hydrogens do not participate in HB formation. This is further confirmed by the HB count. The HB donor and acceptor counts are equivalent for bulk water, but a difference is observed for solvation shell water, as the HB acceptor count is less than that of the donor due to the interference of methyl groups acting as HB bond donors. We observe a little reduction in the HB donor and acceptor number for 400 as compared to 330 K. From the probabilistic presentation of the number of HBs per water molecule, it is confirmed that the formation of 2 and 3 HBs per water molecule is notably high inside solvation shell as compared to the bulk water. The tetrahedral order parameter obtained for the distinct regions also follows the previous results, as the probability of a lower \(q_{tet}\) value is higher in the solvation shell. Also, at 400 K, the \(P(q_{tet})\) peaks are higher at 0.5 for bulk water due to loss of ordered arrangement at a higher temperature compared to 330 K. We studied the HB jump mechanism around methyl hydrogens as there is apparent participation of methyl groups in the HB donation to the water molecules. We observed an increase in the equivalent distance between \(C^*\) and \(O_a\) and \(O_b\) from 3.7 and 3.85 Å for 330 and 400 K, respectively, in the hydrogen bond with other water molecules before the jump happens. Both acceptors become equidistant (3.7 and 3.85 Å for 330 and 400 K, respectively) before the jump happens, where the incoming acceptor forms a hydrogen bond with another hydrogen atom of TMA. An increase in the equivalent distance between the \(C^*\) and initial and final acceptors during the HB transfer event from 330 to 400 K is understandable as atomic jiggle increases at a higher temperature, hence disrupting the structural orientation. Then, there will be a rotation of the methyl group of the TMA cation, which transfers the hydrogen bond from the initial acceptor \((O_a)\) to final acceptor \((O_b)\).

The jump angle \(\langle \theta \rangle \) and its distribution before and after hydrogen bond jump is shown in Figure 7c.f. A jump angle of \(-27°\) to \(+23°\) is observed corresponding to a jump amplitude of \(50°\) for 330 K. Whereas, \(\theta \) for 400 K is found to be \(-23°\) to \(+23°\), and hence a jump amplitude of \(46°\) is observed. We calculated other angular parameters \(\psi\) and \(\varphi\) relevant to the jump mechanism depicted in Figure 7b.e. \(\psi\) is defined as the angle between the \(C^*\)–\(H^*\) bond and its projection on the \(O_a\)–\(C^*\)–\(O_b\) plane, whereas \(\varphi\) is defined as the angle between vectors \(C^*\)–\(O_a\) and \(C^*\)–\(O_b\). The angle \(\varphi\) is observed to be \(66°\) throughout the hydrogen bond jump for both temperatures. We have scaled the values as \(\psi-60°\) in Figure 6b,e. The average value for the angle \(\psi\) is observed to be 21 and 19° for 330 and 400 K, respectively, which is found to be more compared to the values observed in hydrogen bond jump in pure water.
transition state before the complete rotation of the methyl group and transfer of HB. Also, a reduction in the total count of HB jumps for methyl hydrogen from one solvation shell to another is observed. From the properties discussed above, such as the intermolecular distance distributions, HB counts, and tetrahedral order parameters, it is obvious that in the close vicinity of the hydrophobe, there is a negligible reduction in the structural ordering. Thus, refraining the water molecules from forming four HBs each, which is a tangible nature of bulk water, is hence incompatible with the iceberg model. The ramification of simulation temperature is the most conspicuous from $P(r_{23})$, tetrahedral order parameter, and averaged number of jump count. The results are in confirmation with the previously obtained dynamics properties of water inside the solvation shell of TMA.$^{44}$

4. COMPUTATIONAL METHODS

We performed first principles molecular dynamics (FPMD) simulations to understand the effects of temperature on the hydrophobicity of the TMA cation by considering a relatively dilute aqueous solution. For our calculations, we simulated a system containing 1 tetramethylammonium ion, 50 water molecules, and a fluoride ion to maintain neutrality. The initial geometry of the system was obtained from classical molecular dynamics (CMD) simulations, which is performed by using TraPPE$^{87}$ and SPC/E$^{82}$ force fields for TMAF and water, respectively. The FPMD simulations were performed using the quickstep (QS) module available within the CP2K software suite.$^{89}$ The QS method$^{24}$ follows the Gaussian plane wave approach using dual-centered Gaussian-type orbitals to solve the self-consistent Kohn–Sham equations.$^{35}$ We used Becke–Lee–Yang–Parr (BLYP) exchange-correlation functionals with a TZV2P basis set.$^{36–88}$ The core electrons were explained using the Goedecker–Teter–Hutter (GTH)$^{89}$ pseudopotentials with a plane wave cutoff of 600 Ry. To include van der Waal’s interaction, Grimme’s 3rd order dispersion (D3)$^{90,91}$ is used, which is essential for properly defining water density and other physical properties. Two different TMA–water systems are simulated 330 and 400 K, and the temperature was maintained using the Nose–Hoover thermostat.$^{72}$ Initially, 15 ps of NPT simulation provided the average box length of 11.65 Å for the cubic box. Following which, 50 ps of NVT and NVE simulations were performed with a time-step of 0.5 fs. The periodic boundary condition was applied in all three directions. The trajectories generated after the NVE simulations were used for further calculations. All the plots are prepared using XMGRAVE. The combined distribution function (CDF) in the form of configurational space is calculated using TRAVIS$^{93}$ and is plotted using GNUPLOT.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge financial support (EMR/2016/004965) for this work from the Department of Science and Technology, India, and Sathish Dasari for the help on jump mechanism analysis. A.P. likes to acknowledge the Ministry of Education, Government of India, for her Ph.D. fellowship.

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