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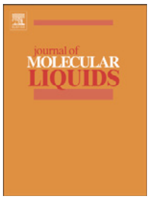

Hydration of OH radical in high temperature water

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Molecular dynamics simulation study on the hydration and hydrogen-bonding of the OH radical is presented for the 25 MPa isobar and the temperature ranging from 373 to 673 K. For the first time the water molecule and the radical have been described by the flexible three- and two-site models, respectively, which account for short-range interaction of the hydrogen atom. We have found that the mechanism of hydration and the degree of radical–water hydrogen-bonding are closely related to the structural transformations occurring in the hydrogen-bonded network of the solvent. Compact and ordered network, typical for the liquid phase, favours the cavity localization. Up to 573 K the decrease in the number of water–water hydrogen bonds has been associated with the increase in the number of radical–water H-bonds. Unlike the hydration in the condensed liquid phase the low density of supercritical water at 673 K stimulates the radical behaviour as a structure-maker. In the presence of •OH the structural inhomogeneity of the solvent has been noticeably reduced. Our work showed the importance of short-range interaction of hydrogen atoms in hydration and hydrogen bonding of •OH at high temperatures and proved that neglect of the angular condition greatly overestimates the number of radical–water H-bonds, mostly of the H-acceptor type.

1. Introduction

Compressed high-temperature water is widely used to safely destroy hazardous materials, such as organo-chlorine compounds, aromatics, pesticides or petroleum constituents, in the wet oxidation and supercritical water oxidation (SCWO) technologies [1–3]. Despite significant research activity in advanced oxidation processes (AOPs), still very little is known about the behaviour of the main oxidants in the high-temperature water at the molecular level. Study of the hydration of oxidising agents is crucial for understanding their transport properties and reactivity and, consequently, for developing industrial applications. By providing a direct insight into the structure and dynamics of hydration shells computer simulation is regarded as a valuable technique in addition to experimental methods.

Considering the roles of •OH in AOPs, simulation-based studies on its behaviour in high-temperature aqueous media are very limited [4,5]. Since both •OH and H_2O are associating species and complexation of the radical with one water molecule may change its reactivity [6] as well as transport properties, knowledge of the nature of hydrogen-bonding interactions is of primary interest. Taking into account that properties of the hydrogen-bonded network of pure water strongly depend on the thermodynamic conditions [1,2,7,8] one can expect differences in the behaviour of $•OH_{aq}$. However, with only crude estimation of the number of hydrogen bonds reported for several thermodynamic states [5] the radical–water bonding is far from being understood. The objective of the present molecular dynamic (MD) simulation work is to examine the influence of water density and temperature on the mechanism of hydration of the OH radical. It is also our aim to find out whether the presence of the radical affects the solvent structure and hydrogen-bonding of water molecules. Reliable analysis of hydration and hydrogen bonding at high temperatures requires usage of flexible models for the solvent components [9]. For this purpose a two-site model including short-range interactions of both the radical atoms has been developed and its applicability to the description of $•OH_{aq}$ has been proved for 310 K [10]. As previously this newly proposed model is employed here along with the compatible three-site flexible water potential [11].

2. Computational details

The NVE molecular dynamics simulations have been performed for the temperature ranging from 373 to 673 K and the densities corresponding to the 25 MPa isobar. All the thermodynamic states studied are listed in Table 1. In each simulation the system was modelled by the periodically repeated cubic box comprising one OH radical and 400 water molecules. Solvent components were described by the flexible model potentials: the three-site model for water [11] and the compatible two-site model for •OH [10]. The equations of motion were integrated using Verlet algorithm. To handle long-range Coulomb interactions we used Ewald summation [12]. For short-range non-bonding interactions the shifted-force shifted-potential method was followed [12]. The equilibration stage required $4 \cdot 10^5$ time-steps

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Table 1
Thermodynamic parameters for the simulated aqueous solutions. The average temperature T_{av} of each simulation and the corresponding standard deviation ΔT are provided in the last column.

State	Temperature T [K]	Density ρ [g cm^{-3}]	$T_{av} \pm \Delta T$ [K]
A	373	0.969	373.5 ± 6.9
B	473	0.881	471.2 ± 8.7
C	573	0.74	575.8 ± 9.1
D	673	0.167	669.4 ± 10.2

of 0.1 fs. After equilibration the data were collected for 20 ps (states *A*–*C*), and for 50 ps (state *D*). More details of the simulation method can be found elsewhere [10].

We calculated partial radial distribution functions (RDFs) g_{ij} for radical–water sites (*O*r–*O*w, *O*r–*H*w, *H*r–*O*w, *H*r–*H*w) and for water–water sites (*O*w–*O*w, *O*w–*H*w, *H*w–*H*w) in solution. The corresponding hydration and coordination numbers n_{ij} have been computed using Eq. (1).

$$n_{ij} = 4\pi\rho_j \cdot \int_{r_{ij}^{o}}^{r_{ij}^{min}} r^2 g_{ij}(r)dr \qquad (1)$$

where the integral limits match the left-end of the first peak and the first minimum, whereas ρ_j is the number density of the *j*-th site.

Evaluation of the number of H-bonds formed by the OH radical depends on a set of requirements assumed in a definition of hydrogen bond. These requirements may include the separation-condition, relative orientation of the pair, or its interaction energy. In this work hydrogen bonding has been characterised in terms of definitions *D*1, *D*2, and *D*3, specified in Table 2. *D*1 only specifies the allowable separation r_{HdOa} between the hydrogen atom of the H-donor molecule and the oxygen atom of the H-acceptor. It provides a crude evaluation of hydrogen bonding. More precise *D*2 controls r_{HdOa} along with the angle α_{HdOdOa} between the O−H bond of H-donor and the line connecting the two oxygen atoms. In addition to *D*2 definition *D*3 examines the donor–acceptor interaction energy E_{da}. The hydrogen bonding requires the separation r_{HdOa} to be smaller than 2.7 Å being the sum of van der Waals radii of the hydrogen and oxygen atoms. The allowable values for r_{HdOa}, α_{HdOdOa}, and E_{da}, 2.5 Å, 30°, and −8 kJ mol^{-1}, respectively, have been assumed the same as for H-bonds in pure water [7]. Using *D*1, *D*2, and *D*3 we distinguished between H-donor and H-acceptor roles played by the radical.

To examine how the presence of •OH influences the structure and hydrogen-bonding of the solvent we referred to the results obtained from the NVE simulations of pure water for the thermodynamic conditions listed in Table 1[8]. In these simulations, like here, we used the three-site flexible model of water [11].

3. Results and discussion

The investigated states *A* and *B* correspond to the pressurised high temperature liquid far above the coexistence curve. State *C* occurs close to the subcritical region, whereas state *D* represents the supercritical water of very low-density. Latest simulation study of pure solvent at states *A* and *B* showed existence of continuous hydrogen-bonded network comprising extended patches of four-bonded molecules and less ordered regions [8]. In-between states *B* and *C* breakage of the continuous network into a variety of hydrogen-bonded clusters associated with a disappearance of patches have been reported [8]. Simulation of pure solvent at state *D* indicated significant non-homogeneity of the water structure [7] evidenced by X-ray inelastic scattering [13] and NMR spectroscopy [14]. The characteristic feature of state *D* is coexistence of empty regions and branched-chain clusters of hydrogen-bonded molecules. Apart from the hydrogen-bonded clusters there is also an abundance of monomers, i.e. molecules forming no H-bond to others.

Table 2
Definitions of the radical–water hydrogen bond followed in this work.

Definition	Required conditions[a]		
*D*1	$r_{HdOa} \leq 2.5$ Å		
*D*2	$r_{HdOa} \leq 2.5$ Å	$\alpha_{HdOdOa} \leq 30°$	
*D*3	$r_{HdOa} \leq 2.5$ Å	$\alpha_{HdOdOa} \leq 30°$	$E_{da} \leq -8$ kJ mol^{-1}

[a] Subscripts H_d, O_d, and O_a refer to the H-donor hydrogen, the H-donor oxygen atom, and the H-acceptor oxygen atom, respectively; r_{HdOa} and α_{HdOdOa}, denote the H-bond length and angle; and E_{da} is the interaction energy of H-bonded molecules.

Structural transformations in the hydrogen-bonded network due to the increasing temperature and the decreasing density are expected to affect the hydration of •OH. First insight into in the closest vicinity of the solute is provided by the radical–water RDFs. In Figs. 1 and 2 the functions g_{OrOw}, g_{HrOw}, g_{OrHw}, and g_{HrHw} calculated for the states *A*–*D* are presented along with the respective water–water RDFs in solution: g_{OwOw}, g_{OwHw}, and g_{HwHw}. In addition to Figs. 1 and 2, Table 3 provides information about the peak-positions of the radical–water RDFs. The respective hydration numbers and water–water coordination numbers are also given. A comparison between the radical–water RDFs and the intermolecular parts of the water–water functions reveals that the arrangement of solvent molecules in the hydration shell depends on the thermodynamic state. At states *A* and *B* the *O*r–*O*w and *H*r–*H*w peaks coincide with the minima of g_{OwOw} and g_{HwHw}, respectively, whereas the g_{HrOw} and g_{OrHw} peaks are mostly placed in-between two intermolecular peaks of g_{OwHw}. The minimum of g_{OrOw} is well-pronounced and coincides with the remnant of the second peak of g_{OwOw}. These features indicate that, like it has been found for the dilute solution at 310 K [10], the OH radical occupies cavities in the H-bonded network of water. The hydration numbers calculated from Eq. (1) and listed in Table 3 show that there are 12 ÷ 13 molecules in the closest vicinity of the radical at state *A*, and 11 ÷ 12 at state *B*. These numbers are only slightly lower compared to 13 ÷ 14 molecules reported for 310 K [10]. More significant reduction in the hydration number is associated with a breakage of the continuous hydrogen-bonded network at state *C*. Smaller degree of connectivity of the solvent molecules results in a noticeable build-up of the shoulder shown by both g_{HrOw} and g_{OrHw} at ca. 2 Å. Such behaviour suggests the increasing role of hydrogen-bonding interaction with the neighbouring water molecules. The cavity-like hydration shell observed for states *A*, *B*, and *C* disappears in the low-density supercritical water. At state *D* all radical–water RDFs are clearly wider and almost encompass the intermolecular parts of water–water RDFs. Taking into account that the hydration number, n_{OrOw} ~ 4, is close to the coordination number for the water molecule at ambient conditions the water molecules seem to gather in the vicinity of the radical. It indicates different mechanism of hydration compared to the condensed states *A*–*C*. The compact gel-like structure forces the radical to seek distortions in the hydrogen-bonded nets. In the low-density fluid the radical acts as a structure-maker rather than a structure-seeker. To support this conclusion we have examined how the solvent structure is influenced by the presence of •OH. The water–water RDFs calculated in this work for the diluted solution have been compared with those obtained from the simulations of pure water at states *A*–*D* [7,8]. Within the statistical uncertainty the RDFs obtained for the condensed states *A*, *B* and *C* showed no difference whereas the influence of •OH on the solvent structure has been found for state *D*. The g_{OwOw} and g_{OwHw} functions computed for pure water and solution at state *D* are compared in Fig. 3, in panels (a) and (b), respectively. Fig. 3(c) presents the relative local density δ_{Ow} around the oxygen atom of the water molecule in solution and in pure solvent:

$$\delta_{Ow}(R) = \frac{n_{OwOw}(R)}{\frac{4}{3}\pi R^3 \rho_{Ow}} = 3\cdot\int_0^R r^2 g_{OwOw}(r)dr. \qquad (2)$$

According to Eq. (2)$\delta_{Ow}(R)$ represents the ratio of the cumulative oxygen–oxygen radial distribution function to the number of molecules