Molecular Dynamics Simulation of the Hydration Structure and Hydrogen Bonding behavior of Phenol in Aqueous Solution

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Abstract: Molecular dynamics simulations are carried out to study the hydration structures and hydrogen bonding properties of phenol in aqueous solution with infinite dilution for several temperatures ranging from 273 to 363 K. The hydration structures of phenol are characterized by radial distribution functions and orientational ordering. There appears structured local distribution of water around phenol within the distance of 8 Å. Two hydration shells are defined to characterize the local structure. The orientation distribution of the water in the first hydration shell shows more ordered local structure than that in the second hydration shell. Increasing temperature leads to the disruption of the local structure. We mainly focus on the analysis of the hydrogen bonding interaction between phenol hydroxyl and water. The hydrogen bonds are identified based on the geometric criterion, which is defined according to analysis of radial distribution function and angle distribution. A definition of hydrogen bonding state $f(m, n)$ is proposed to characterize the hydrogen bonding structure of phenol in aqueous solution. Phenol in the hydrogen bonding state $f(m, n)$ means that the phenol hydroxyl forms m hydrogen bonds as donor and n hydrogen bonds as acceptor. At the different temperatures, the phenol hydroxyl prefers to stay in the hydrogen bonding state $f(1, 1)$. It is shown that the hydrogen bonding state $f(1, n)$ takes the dominant role. Thus phenol is proven to be a good hydrogen bond donor than acceptor. These findings help to further understand the hydration structure and hydrogen bonding behavior of phenol in aqueous solution.

Keywords: Phenol; Water; Hydrogen bond; Orientation; Molecular dynamics

28 simulation

29 **1. Introduction**

30 In recent years, there has been increasing interest in attempting to understand the
31 microstructure and behavior of aqueous binary mixture^[1-3]. In particular, the aqueous
32 binary mixtures of amphiphilic molecules, which contain both hydrophilic and
33 hydrophobic groups, exhibit non-ideal properties and are proven to be important in
34 chemistry. Thus considerable efforts have been devoted to investigate the
35 micro-structure and intermolecular interaction of the binary aqueous mixtures^[4-6]. The
36 existing knowledge advances the present study to make a further exploration on the
37 binary aqueous mixture of amphiphilic molecules.

38 Phenol known as carbolic acid is a typical amphiphilic compound, which has been
39 found worldwide in the industrial effluents of various chemical synthesis and
40 manufacturing processes. Phenol in wastewater is damage to organisms even at ppb
41 levels^[7], and it is difficult to degrade. Recently, there have been several methods for
42 efficient removal of phenol^[8-10]. Most of the treatment have been evaluated and
43 adopted in the aqueous environment. In order to improve the methods, it is important
44 to study the structure, dynamics and intermolecular interaction of the phenol/water
45 binary mixture. Thus, it requires a molecular level investigation of the phenol/water
46 binary mixtures for a variety of conditions.

47 Evidence on the amphiphilic behavior of phenol has been reported by
48 experimental^[11] and theoretical^[12, 13] studies. The hydroxyl group of phenol is apt to
49 form intermolecular hydrogen bonds with water in the aqueous solution. The
50 hydrogen bonds between phenol and water molecules have significant effect on the
51 hydrogen bonding network in the mixture. The aromatic group of phenol with
52 hydrophobic property is believed to be one of the many reasons for the anomalous
53 behavior of organic solvent^[14]. The aromatic structure of phenol represents weak
54 hydrogen bonding interaction with water, resulting in the formation of π -type
55 complex^[15]. Attention should be paid on the hydrogen bonding interaction between

water and phenol, which have effect to some extent on the structure and dynamics of the aqueous solution. Thus, the molecular associations of phenol and water are of significant importance to understand the structure of their binary mixture. At present, the structure of phenol/water mixture is usually characterized by the radial and spatial distribution functions, providing the information of the average and local distributions of water molecules around phenol^[15, 16]. However, it is impossible to observe the details of intermolecular configurations including the orientation of the water molecules relative to the phenol molecule, and the orientation angle of water as a function of position, etc.

In the present work, we report molecular dynamics (MD) simulation of phenol/water binary mixtures with infinite dilution for the temperatures ranging from 273 to 363 K. It is important to study the behavior of the dissolved phenol in water in order to understand the structural property of the phenol/water mixture at the molecular level. Temperature is adjusted to study its effect on the hydration structure and hydrogen bonding statistics of phenol in aqueous solution under constant pressure. We will focus the discussion on the analysis of the structure and the hydrogen bonds between phenol and water, the structure and orientation of phenol in the vicinity of water. The results will deepen the understanding of the effects of temperature on the spectra, structure and other properties of phenol in aqueous environment.

2. Details of Simulation

MD simulations of phenol in water have been performed by the NAMD package^[17] developed by the joint collaboration of the Theoretical and Computational Biophysics Group and the Parallel Programming Laboratory at the University of Illinois at Urbana-Champaign. The mixtures of phenol and water have been simulated in the isobaric-isothermal (NpT) ensemble at the pressure of 1 atm and five temperatures (i.e. 273, 298, 323, 343 and 363 K), which were controlled by the Langevin dynamics and Langevin piston Nosé-Hoover methods^[18], respectively. Each simulation box was built with one phenol molecule solvated in 500 water molecules. The non-bonded

atoms i and j were described by Lennard-Jones (LJ) and Coulomb potentials with the parameters ε , σ , and q as follows:

$$U_{ij} = \sum_i \sum_j 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} e^2 \quad (1)$$

where $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$ and $\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$. In the binary mixtures, water molecules were modeled using the model of SPC/E^[19], and the LJ parameters for the phenol molecule were described with the OPLS potential functions proposed by Jorgensen and Nguyen^[20]. The atomic charges for phenol were fitted from B3LYP/6-311++G(d, p) calculation by Guedes and coworkers^[16]. The geometric and interaction parameters of phenol have been validated by comparing the hydration enthalpy of one phenol molecule in water^[16]. The LJ parameters for the water and phenol molecules are listed in Table 1. The atom names of phenol and water are referred to the snapshots of phenol and water, shown in Fig. 1.

Table 1. Lennard-Jones parameters and partial charges of water and phenol

Molecule	Atom	ε (kcal/mol)	σ (Å)	q (a.u.)
Water	OW	0.155	3.166	-0.8476
	H1, H2	0.000	0.000	0.4238
Phenol	C1	0.070	3.550	0.5667
	C2	0.070	3.550	-0.4090
	C3	0.070	3.550	-0.0214
	C4	0.070	3.550	-0.2304
	C5	0.070	3.550	-0.0952
	C6	0.070	3.550	-0.2910
	H2	0.030	2.420	0.1900
	H3	0.030	2.420	0.1157
	H4	0.030	2.420	0.1394
	H5	0.030	2.420	0.1281
	H6	0.030	2.420	0.1680
	OH	0.170	3.070	-0.7613
	HO	0.000	0.000	0.5004

For each simulation, all molecules were constrained to the nominal length with the SHAKE algorithm. The particle mesh Ewald (PME) method^[21] was used to solve full

electrostatic interaction, and the grid spacing was set 1.0 Å. The Lennard-Jones (LJ) potential was switched and truncated from 10 to 12 Å. The shifting function was adopted to separate the long and short electrostatic interactions with the cut-off distance of 12 Å. The contributions of PME and LJ potential to intermolecular force and energy were evaluated at every time step. A cubic cell with periodic boundary conditions was adopted in order to reduce the edge effect. Each system was totally run for 10 ns with initial energy minimization for 1000 time steps. The first simulation run for 5 ns was used for equilibration, and the subsequent run for 5 ns was performed for structure and hydrogen bonding analysis. A time step of 2 fs was adopted and the coordinates of all atoms were sampled every time step. The initial configuration for each simulation was generated randomly.

Fig. 1 The chemical structures of phenol and water with atom labeling.

3. Results and Discussion

3.1. Structural properties around the benzene ring

3.1.1. Radial distribution function

The first focus of the paper is on the RDFs for the water molecules in the vicinity of phenol. Radial distribution function (RDF) $g(r)$, where r is the distance between two sites, is the fundamental property characterizing the averaged spatial structure and the local molecular distribution. The study on the RDFs directly provides the

information of the water structure and distribution in the hydration shells of phenol. Fig. 2 shows site-site RDFs, $g(r)$, for the molecular pairs (C_pO_w and C_pH_w) in the aqueous solution with one phenol molecule at the different temperatures. C_pO_w and C_pH_w denote the intermolecular site-site pairs between the phenol site and the oxygen and hydrogen atoms of water. The phenol site C_p is located at the geometric center of the benzene ring of the phenol molecule.

Fig. 2 Radial distribution functions of the center of the benzene ring in phenol and the water oxygen and hydrogen atoms at the different temperatures.

The RDFs depicted in Fig. 2 characterize the distributions of water molecules around phenol for the systems at the different temperatures. Fig. 2(a) shows the C_pO_w RDFs with the evident peak and trough at 4.5 and 6.0 Å, respectively. It is noted that there exists non-monotonous change of the derivative of the C_pO_w and C_pH_w RDFs within the range of 2 ~ 4 Å. In particular, the C_pO_w RDF for 273 K presents a rise of low amplitude at about 3.4 Å. As the temperature increases, the peak becomes inconspicuous instead of a gentle slope. This is consistent with the C_pO_w RDF for 298 K reported previously^[16]. The C_pH_w RDFs shown in Fig. 2(b) exhibit the first and second peaks at about 2.45 and 4.7 Å with the minima at 2.8 and 6.4 Å. As the temperature increases, the first peak also gradually fades away.

Thus, knowledge is got from Fig. 2 that temperature has little effect on the positions of the peaks and the troughs, but has effect on the amplitudes of the peaks and troughs. The increasing temperature supplies the energy for water self-diffusivity, resulting in the disruption of the local structure in the vicinity of phenol. For example,

as shown in Fig. 2, the peak declines as the temperature increases, and the peak has the opposite trend with temperature. Especially, the first peak gradually fades away with increasing the temperature for both C_pO_w and C_pH_w RDFs. The effect of temperature on the phenol-water RDFs is agreement with the previous MD simulation^[15].

The range from 0 to 3.4 Å in the C_pO_w RDF, where there appears the rise with small amplitude, is defined as the first hydration shell. Besides, the range from 3.4 to 6.0 Å for the whole peak is defined as the second hydration shell. For the case of the C_pO_w and C_pH_w RDFs at 273K, the first distribution maxima of the oxygen and hydrogen atoms of water around the benzene ring of phenol are shown at the positions of 3.4 and 2.45 Å, respectively. It implies that the water in the first hydration shell tends to point toward the phenol molecule with the either O-H bond, forming π -type complexes with the center of the benzene ring. This is consistent with the findings reported previously^[15]. Moreover, in order to elucidate the non-monotonous change of the derivative of the RDFs of Fig. 2, it is necessary to observe the spatial structure of the water molecules in the first and second hydration shells of phenol molecule.

3.1.2. Orientational ordering

The abovementioned RDFs characterize the whole direction-averaged interaction between phenol and water molecules in the first and second hydration shells of the phenol molecule, and they cannot fully reflect the information such as the details of the water distribution in all direction around the phenol molecule. In this section, according to the relative position of water to phenol, we compute the local distributions of the water molecules in the first and second hydration shells of phenol, respectively. The relative position is defined by the angle ϕ , which denotes the angle between the vector from the center of the benzene ring to the oxygen atom of water and the normal vector of the benzene plane, as depicted in Fig. 3.

Fig. 3 Definition of the angle ϕ for describing the relative position of water around the phenol molecule.

Based on the definition of angle ϕ , we computed the distributions of the water molecules in the first and the second hydration shells of phenol. Fig. 4 presents the water distributions in the first and second hydration shells as a function of the defined angle ϕ . As shown in Fig. 4(a), the water distributions at the different temperatures present the single peak at the angle $\phi=12^\circ$, and there is no water distribution in the region beyond 40° . In the first hydration shell of phenol, water molecules all appear in the area above and below the benzene ring. This is primarily contributed by π bonding interaction^[15]. Fig. 4(b) shows that the water distribution in the second hydration shell of phenol increases as the angle ϕ increases, and the temperature has little effect on the water distribution. In the second hydration shell of phenol, water molecules mostly appear in the vicinity of the edge of the benzene ring.

Fig. 4 Distributions of the water molecules in the first (a) and second (b) hydration shells as a function of angle ϕ at the different temperatures.

To observe the water distribution in the space around the phenol molecule, Fig. 5 presents two-dimensional contour density plot of water as functions of the angle ϕ and the distance L at the temperature of 363 K. The distance L is defined as the distance of the oxygen atom of water to the benzene center of phenol. Herein, the water molecules with the distance L in the range less than 6.0 Å are taken into account in the computation. Water molecules show the highest distribution in the area around the position of $\phi=90^\circ$ and $r=4.6$ Å. The water distribution decreases along the ϕ and L axes from the maximum point.

Fig. 5 Two-dimensional contour density plot of the water molecules with different angles ϕ and the distances L from the center of the benzene ring in phenol for the temperature 363 K.

The dipole angle of the water in the vicinity of the phenol molecule gives an indication of their short-range interaction. For the sake of convenience to present the dipole distribution of water in different directions around the phenol, we defined the angle θ between the dipole vector of water molecule and the interfacial normal vector of the benzene plane. Fig. 6 depicts two-dimensional contour density plots for water with different angles θ in the direction of angle ϕ around the phenol at the temperature of 323 K. The water molecules in the first and second hydration shells are analyzed respectively. It is observed in Fig. 6(a) that a majority of the water molecules in the first hydration shell present the angle θ in the range from 20° to 90° . The highest probability of water distribution is located in the region around $(\theta = 60^\circ, \phi = 13^\circ)$. As illustrated in Fig. 3, the distribution further confirms that the water in the first hydration points toward the center of the benzene ring, resulted from π bonding^[15]. As shown in Fig. 6(b), the density distribution of the water in the second hydration shell diminishes from the region of about $(\theta=90^\circ, \phi=90^\circ)$ to all around. It should be noted that the color bar of Fig. 6(a) is numerically high than that of Fig. 6(b), and the water distribution of Fig. 6(b) is more disperse than that of Fig. 6(a). It demonstrates that the water in the first hydration shell has more ordered structure than the water in the second hydration shell around phenol. The short-range interaction between water and phenol has a contribution to the non-monotonous change of the derivative of the C_pO_w and C_pH_w RDFs within the range of $2 \sim 4 \text{ \AA}$, as shown in Fig. 2(a).

Fig. 6 Two-dimensional contour density plots of the water molecules with different angles θ in the direction of angle ϕ in the first (a) and second (b) hydration shells of phenol for the temperature 323 K.

3.2. Hydrogen bonding analysis

3.2.1. Definition of hydrogen bond

In this section, we turn to focus on studying the structural properties of water around the hydroxyl group of phenol. As reported previously^[15, 16], the hydroxyl group of phenol molecule has the hydrophilic property. It is necessary to investigate the hydrogen bonding interaction between water and phenol hydroxyl. Thus hydrogen bond criterion should be defined to determine hydrogen bond between water and phenol hydroxyl. Geometric criterion is widely used due to its effectiveness and convenience. In order to determine one hydrogen bond $O\cdots H-O$, geometric criterion may involve the geometric parameters including the intermolecular distance $O\cdots O$, hydrogen bond length $O\cdots H$, and the angles $O\cdots O-H$, $O\cdots H-O$ and $H\cdots O\cdots O$. The commonly used geometric criterion is defined with three or two of the geometric parameters. The adopted geometric criterion in this work is stated as follows:

(1) The distance R_{OO} between hydrogen bond donor and acceptor should be less than the corresponding threshold distance R_{OO}^C ;

(2) Hydrogen bond length R_{OH} should be less than R_{OH}^C ;

(3) The $O\cdots O-H$ angle α does not exceed the angle threshold α^C .

The threshold values for (1) and (2) can be determined with the aid of the site-site RDFs of the corresponding atom pair. There are two types of hydrogen bonds between water and phenol hydroxyl, in which the hydrogen atom could be donated by either water or phenol hydroxyl. Thus it is needed to compute the RDFs of $g_{OpOw}(r)$, $g_{OwHp}(r)$ and $g_{OpHw}(r)$, in which the subscripts 'Op' and 'Hp' denote the oxygen and hydrogen atoms of the hydroxyl group in phenol, and 'Ow' and 'Hw' denote the oxygen and hydrogen atoms of water. Fig. 7 plots the RDFs of $g_{OpOw}(r)$, $g_{OwHp}(r)$ and $g_{OpHw}(r)$ at the different temperatures. As expected, all the RDFs for various temperatures exhibit a substantial degree of order, reflecting the hydrophilic nature of the water-hydroxyl interaction. The first peaks of the RDFs indicate the presence of hydrogen bonding

249 interaction between water and the hydroxyl group of phenol.

250

251

252 Fig. 7 Radial distribution functions of the O_pO_w (a), O_wH_p (b) and O_pH_w (c) pairs in
253 the phenol/water binary mixtures at the different temperatures.

254 It is shown in Fig. 7 that increasing the temperature brings down the first and
255 second peaks, and raises the first valley in the plots of the RDFs. This indicates that
256 enhancing the thermal motion of molecules leads to disruption of the ordered local
257 structure. Besides, temperature has little effect on the positions of the peaks and valley.
258 Fig. 7(a) shows that the $g_{OpOw}(r)$ RDF present the first peak centered at 2.75 Å
259 followed by the first minimum at 3.3 Å and a second pronounced peak at around 4.55
260 Å. As shown in Figs. 7(b) and 7(c), the $g_{OwHp}(r)$ and $g_{OpHw}(r)$ RDFs at the different
261 temperatures show two distinct peaks at 1.8 and 3.4 Å with the first minimum located
262 at 2.45 Å. This is consistent with the experimental and MD simulation results of
263 Sidhu et al.^[22] The first peaks of $g_{OwHp}(r)$ and $g_{OpHw}(r)$ RDFs reflect the presences of
264 the water-phenol (W-P) and phenol-water (P-W) hydrogen bonds, where the former
265 and latter molecules are hydrogen bond donors and acceptors, respectively. It is noted

that the first peak of $g_{\text{OWHp}}(r)$ is about twice as much as that of $g_{\text{OpHw}}(r)$, and the first peak widths are much the same for $g_{\text{OWHp}}(r)$ and $g_{\text{OpHw}}(r)$. This suggests that hydrated phenol prefers to act as hydrogen bond donor. As previously reported^[23], the global potential energy minimum corresponds to the case when phenol acts as a hydrogen bond donor, and a second global potential energy minimum occurs when hydroxyl group of phenol acts as a hydrogen bond acceptor.

Fig. 8 Distributions of the angle α denoted by the colored snapshots for the water-phenol (a) and phenol-water (b) pairs.

According to the plots of $g_{\text{OpOw}}(r)$, $g_{\text{OWHp}}(r)$ and $g_{\text{OpHw}}(r)$ RDFs, it is reasonable to adopt the unified distance thresholds for the W-P and P-W hydrogen bonds. Then the values of the distance threshold R_{OO}^{C} and R_{OH}^{C} are determined as 3.3 and 2.45 Å, respectively. As for the angle thresholds α^{C} , Fig. 8 presents the angle distribution for the molecular pairs with the probable formation of the W-P or P-W hydrogen bonds. The molecular pairs satisfying the geometric criterion (2) are taken into account in the computation of the angle distribution. It is shown that only a negligible proportion of molecular pairs form the angle α larger than 40°. In view of the angle distribution, we adopted a less strict definition for the angle threshold as $\alpha^{\text{C}} = 40^\circ$. The method for defining the less strict angle threshold was also used in previous study^[2].

3.2.2. Hydrogen bond statistics

Based on the geometric criterion defined above, we performed the analysis of the

W-P and P-W hydrogen bonds at the different temperatures. The hydrogen bond statistics provides the information of the local structure in the vicinity of the phenol molecule in terms of the distribution of the hydrogen bonds between phenol and water. Fig. 9 depicts the average numbers of the W-P and P-W hydrogen bonds at the different temperatures. It is observed that temperature has effect on the two types of hydrogen bonds. As the temperature increases, the results of n_{pw} and n_{wp} show a small decrease. The dependences of n_{pw} and n_{wp} on temperature are consistent with the previous study^[15]. As expected, phenol molecule in aqueous solution is a better hydrogen bond donor than acceptor. On average, phenol forms one hydrogen bond as donor and less than one hydrogen bond as acceptor. The total number of hydrogen bonds formed by the hydroxyl group of phenol was estimated to be approximately 1.69 at ambient conditions. Fig. 9 only presents the average hydrogen bonding state of phenol rather than the state that phenol may form hydrogen bonds more than or less than the average number. Thus, it is necessary to study the hydrogen bonding states of phenol in aqueous solution.

Fig. 9 The average numbers of the water-phenol and phenol-water hydrogen bonds as a function of temperature.

A quantity $f(m, n)$ was defined to detailedly describe the hydrogen bonding states of phenol, where m and n denote the numbers of the hydrogen bonds donated by phenol and water, respectively. In other words, phenol in the hydrogen bonding state $f(m, n)$ has m P-W hydrogen bonds and n W-P hydrogen bonds. Within the studied

temperature range, the upper limits of m and n were found to be 2 and 3. Table 2 provides the percentages of $f(m, n)$ in the phenol/water mixture at 323 K. It is shown that the probability of phenol acting as hydrogen bond donor is much higher than that for acceptor. The probabilities of phenol acting as donor and acceptor are 97.34 and 40.85 %, respectively. Obviously, phenol prefers to produce two hydrogen bonds in both forms of P-W and W-P. The probability of more than 97 % is that phenol stays in the hydrogen bonding states with one P-W hydrogen bond. This further proves that phenol is a good hydrogen bond donor in the aqueous solution. A handful of aggregations formed by phenol are observed in the hydrogen bonding states such as $f(0, 1)$, $f(0, 2)$, $f(1, 2)$, $f(1, 3)$, $f(2, 0)$ and $f(2, 1)$. It should be noted that there is about 1.16 % of the hydrogen bonding states in $f(0, 0)$, which means that the hydroxyl group of phenol is not hydrogen bonded to any water molecule. Besides, temperature has slight effect on the hydrogen bonding states of phenol within the studied temperature range. For the sake of brevity, the percentages of the phenol molecule in different hydrogen bonding states for the other four temperatures are shown in the Supplemental information (Table S1). As temperature increases, the proportions of the hydrogen bonding states of $f(0, 0)$, $f(0, 1)$, $f(0, 2)$, $f(1, 0)$, and $f(1, 3)$ increase and $f(1, 1)$ and $f(1, 2)$ decrease.

Table 2 Percentages ($P(f(m, n))$ %) of the phenol molecule in different hydrogen bonding states $f(m, n)$ in the phenol/water mixture at 323 K

$m \backslash n$	0	1	2	3
0	1.16	1.34	0.16	0.00
1	39.39	47.29	9.94	0.11
2	0.30	0.27	0.04	0.00

4. Conclusions

In present paper we have employed classical MD simulations to study phenol in aqueous solution with infinite dilution at the temperatures ranging from 273 to 263 K. The structure and hydrogen bonding properties of the hydrated phenol were mainly

investigated in order to characterize the short-range interaction between phenol and water molecules. RDF could directly reflect the local distribution of the water in the vicinity of the phenol molecule. There is structured local distribution of water around phenol in the range of 0 ~ 8 Å. The local structure is gradually disrupted by the increasing temperature. According to the characteristics of the RDFs, two hydration shells were defined to further investigate the short-range interaction between phenol and water. In the first hydration shell, water prefers to locate in the direction with the angle ϕ around 12° , and there is little water distribution beyond the angle $\phi=40^\circ$. The water molecules in the second hydration shell tend to appear in the region near the edge of the benzene ring of phenol. Besides, the water molecules in different hydration shells show different orientation distributions. According to the analysis of the orientation of water molecules in the two hydration shells, it is found that the water in the first hydration shell shows more ordered structure than that in the second one.

In order to study the hydrogen bonding interaction between water and phenol hydroxyl, hydrogen bond criterion was first identified with the geometric thresholds. It is shown from hydrogen bond statistics that phenol hydroxyl is a better hydrogen bond donor than acceptor. This finding is consistent with the previous studies^[15, 23]. To further investigate the hydrogen bonding behavior of phenol in aqueous solution, we defined the hydrogen bonding states for phenol according to its different numbers of P-W and W-P hydrogen bonds. It was found that the probability of phenol acting as donor is about twice more than that as acceptor. Furthermore, the hydrogen bonding states of phenol forming one P-W hydrogen bond take the dominate role. The results further prove that phenol hydroxyl is a good hydrogen bond donor. Temperature in the studied range has slight effect on the hydrogen bonding states of phenol hydroxyl. The present paper contributes to further describing and understanding the structure and hydrogen bonding behavior of phenol in the aqueous solution.

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