

Computer simulation study of the intermolecular structure of phosphoric acid–*N,N*-dimethylformamide mixtures

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Abstract The structures and energies of the complexes (H_3PO_4)₂, H_3PO_4 –DMF, and (H_3PO_4)₂–DMF were analyzed at the B3LYP level of approximation. It was found that H-bonds form between H_3PO_4 and DMF molecules, but the strength of the H-bond depends strongly on its molecular environment. Effects of the solvent were taken into account via the CPCM approach. According to the B3LYP–CPCM calculations, the O···O distance in (H_3PO_4)₂–DMF is shorter and its H-bonds are stronger than in the other complexes studied. In order to study the effects of concentration on the intermolecular structure, molecular dynamics simulations of H_3PO_4 –DMF mixtures with mole fractions of acid of <0.1 were performed. The calculations indicated that the largest fraction of the acid protons are involved in hydrogen bonding with oxygen atoms of the DMF molecules. An increased probability of acid–acid hydrogen-bond formation at phosphoric acid mole fractions >0.06 was also noted.

Keywords Hydrogen bonds · Phosphoric acid · DMF-rich mixtures · Ab initio computations · Molecular dynamics simulations

Introduction

This work continues our earlier studies of the structural characteristics of and hydrogen-bond formation in binary H_3PO_4 –DMF systems [1–6]. Phosphoric acid (H_3PO_4) solutions in

N,N-dimethylformamide (DMF) are of fundamental interest when studying the nature of acid–base interactions and proton-transfer processes, where the formation of H-bonds plays a key role. It is well known that proton-conducting gels can be obtained by doping polymers with phosphoric acid [7–9]. Furthermore, the structure of neat H_3PO_4 is well described as an extended intermolecular H-bond network that permits high proton conductivity, making it of interest in fuel cell design [10]. Since proton transfer occurs mostly in solution, the effects of the molecular environment play an important role [11].

In a previous paper [1], we examined various conformations of dimers of phosphoric acid in the gas phase. As expected, the most stable dimeric acid structure is a cyclic form with the molecules bound together by a pair of hydrogen bonds. In these acid dimers, the geometric parameters of both H-bonds are equal ($r(\text{O}\cdots\text{O}) = 2.579 \text{ \AA}$ and $\angle(\text{O}–\text{H}\cdots\text{O}) = 174.3^\circ$). The binding energy is $-96.66 \text{ kJ mol}^{-1}$.

Using molecular dynamics (MD) simulations [4], we examined the structures of H_3PO_4 –DMF mixtures as a function of composition in detail. It was shown that H-bonds can form between the H_3PO_4 molecules and between H_3PO_4 and DMF. The distribution of molecules according to the number of H-bonds formed between OH groups/O(=P) atoms of H_3PO_4 and O(=C) atoms of DMF was calculated for H_3PO_4 –DMF mixtures with $x_{\text{H}_3\text{PO}_4}$ (i.e., the acid mole fraction) > 0.1 [6]. The existence of more than one H-bond per proton acceptor site O(=P) on H_3PO_4 across the entire concentration range was demonstrated. Snapshots of the configurations at $x_{\text{H}_3\text{PO}_4} = 0.1$ showed that the phosphoric acid exists in monomeric as well as dimeric forms that are solvated by DMF. It is interesting to note that, even at low acid concentrations, dimeric phosphoric acid units can form. We found that the formation of acid polymeric chains along with dimers is possible at acid concentrations >0.3. A similar assumption about cyclic dimer formation was made on the basis of experimental data

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obtained via physicochemical and spectral methods [12]. It should be noted that acid–acid H-bonds also exist in aqueous solutions with $x_{\text{H}_3\text{PO}_4}=0.51$ [13]. When $x_{\text{H}_3\text{PO}_4}>0.8$, proton-accepting acid molecules form more than two H-bonds, implying significant polymerization of H_3PO_4 . These data are comparable with the results of X-ray studies of crystalline H_3PO_4 [14–17], which showed that acid molecules tend to form two-dimensional layers connected by H-bonds.

The aim of the study reported in the present paper was to investigate the structural characteristics of acid–acid and acid–DMF configurations and H-bond formation between these molecules at the B3LYP level of calculations and using MD simulations. The effect of the solvent on the geometry of the H-bond was taken into account using the conductor polarized continuum model (CPCM) approximation. MD simulations were performed for H_3PO_4 –DMF mixtures with acid mole fractions of <0.1 (for convenience, these are called “DMF-rich mixtures” hereafter). Such mixtures had not been considered before this study, so the question of the concentrations at which the H_3PO_4 molecules can form acid–acid hydrogen bonds was unanswered.

The results of our investigation should therefore contribute to a greater understanding of the interaction mechanisms associated with binary Brønsted acid–organic solvent systems.

Simulation details

Geometric parameters and partial charges (determined according to the CHELPG procedure) for the H_3PO_4 and DMF atoms were estimated at the B3LYP/6–31++G(d,p) level of theory and used as parameters in pair-interaction potentials. B3LYP is the most popular DFT functional [18], and it gives reasonable results for H-bonded complexes [19]. All ab initio calculations were performed with the GAUSSIAN 09 software package [20]. We tested the accuracy of quantum chemical calculations on single phosphoric acid and DMF molecules for which experimental geometries were available (see the “Electronic supplementary material,” Tables AS1 and S2). The structural parameters of the initial molecules agree very well with gas-phase electron diffraction data [21] for DMF and X-ray diffraction data [22] for phosphoric acid.

The optimized structures of the $(\text{H}_3\text{PO}_4)_2$, H_3PO_4 –DMF, and $(\text{H}_3\text{PO}_4)_2$ –DMF complexes [1] were taken as initial configurations for the B3LYP–CPCM computations. Effects of the solvent were taken into account via the CPCM approach [23]. The minimum energy states of the complexes were confirmed by calculating the harmonic frequencies. The binding energies for the H-bonded complexes, ΔE , were calculated from the energy differences between the complex and the individual monomers.

MD simulations were performed using the GROMACS simulation software package [24]. The H_3PO_4 – H_3PO_4 ,

H_3PO_4 –DMF, and DMF–DMF interactions were described by the optimized potentials for liquid simulations force field (OPLS). The simulations were performed in the NVT ensemble at $T=298.15$ K. A cubic simulation box containing in total 512 mol^{-1} , including both H_3PO_4 and DMF, was used, with periodic boundary conditions. The size of the box was chosen in accord with the experimental density of H_3PO_4 solutions in DMF [25]. The time step was 2 fs and the leapfrog algorithm [26] was used as an integrator for the equation of motion. The MD simulation was equilibrated for 20 ns, and a 1-ns production run was then performed for data collection. All bond lengths of the DMF and H_3PO_4 molecules were constrained by the Shake algorithm [27]. Intermolecular interactions were calculated as the sum of atom–atom interactions, and a cutoff of half the size of the box was used. The shifted force method was used for non-Coulomb interactions and the reaction field method for Coulomb interactions.

Because of the low magnitudes of the first and second dissociation constants of H_3PO_4 and DMF ($\text{p}K_1=8.2$ – 8.8 , $\text{p}K_2=10.4$ – 10.8 [28]), the starting configurations for MD simulations contained only their molecular forms.

The intermolecular structures of the H_3PO_4 –DMF mixtures were studied by means of radial pair distribution functions (RDFs), $g(r)(x\cdots y)$, which represent the probability of finding an atom of type y at a distance r from an atom of type x .

The preferential orientations of the acid protons nearest to the $\text{O}(=\text{P})$ or $\text{O}(=\text{C})$ atoms in the DMF-rich mixtures were obtained using the ranked radial distribution functions (ranked RDFs) technique [29]. The ranked RDFs were the local densities of the nearest, second-nearest, etc. neighbors with respect to the phosphoryl or carboxyl oxygen (in our case). The sum of the ranked RDFs provided the complete pair correlation function $\text{O}(=\text{P})\cdots\text{H}$ or $\text{O}(=\text{C})\cdots\text{H}$.

The geometric criteria used to identify H-bonds during H-bond analysis in the MD simulations were $r(\text{O}\cdots\text{H}) \leq 2.5 \text{ \AA}$ and an angle between the $\text{O}–\text{H}$ and the $\text{P}=\text{O}$ of H_3PO_4 (or $\text{C}=\text{O}$ of DMF) bond vectors in the range 50 – 70° ($0.34 \leq \cos(\varphi) \leq 0.64$).

The angle distribution function $g(\cos(\varphi))$ was calculated via

$$\cos(\varphi) = d_1 \cdot d_2, \quad (1)$$

where d_1 is the vector that is codirectional with the $\text{P}=\text{O}$ (H_3PO_4) or $\text{C}=\text{O}$ (DMF) bond and d_2 is the vector that is codirectional with the $\text{O}–\text{H}$ (H_3PO_4) bond.

Results

We start with the results obtained from quantum-chemical calculations based on the B3LYP/6–31++G(d,p) approximation. For comparison purposes, the calculated values of the

geometric and energetic parameters of the hydrogen bonds in the complexes $(\text{H}_3\text{PO}_4)_2$, H_3PO_4 -DMF and $(\text{H}_3\text{PO}_4)_2$ -DMF in the gas phase [1] and DMF are listed in Table 1.

From the data in Table 1, it is evident that the strength of the H-bond depends on its environment. According to the B3LYP-CPCM computations, a gradual lengthening of the O-H distance and shortening of the O...O distance is observed for all complexes. The H-bond angles do not significantly deviate from 180° .

In DMF, the O...H distance for the initial acid dimer is quite short. H-bond formation in H_3PO_4 -DMF and $(\text{H}_3\text{PO}_4)_2$ -DMF causes a more pronounced elongation of the O-H bond of the acid in the DMF than found for these complexes in the gas phase. The distance between the O(=C) atom of the DMF and the hydrogen atom of the H_3PO_4 in $(\text{H}_3\text{PO}_4)_2$ -DMF is shorter than that for H_3PO_4 -DMF. In the presence of the DMF molecule, the characteristics of the hydrogen bonds in the acid dimer change in the gas phase as well as in DMF.

The B3LYP-CPCM computations predict smaller binding energies for the H-bonded complexes than for the complexes in the gas phase. The total binding energy for $(\text{H}_3\text{PO}_4)_2$ -DMF is higher than those for the other complexes.

Since the strengths of the acid-acid and the acid-DMF interactions depend on environmental effects, we carried out MD simulations of the DMF-rich mixtures. The structures of H_3PO_4 -DMF mixtures with acid mole fractions >0.1 have already been investigated [4].

In this study, we only considered the strong H-bonds that form between a hydroxyl group or the O(=P) atom of H_3PO_4 and the O(=C) atom of DMF. The nitrogen atom of DMF is a weak H-bond acceptor, despite its significant negative charge [31].

Figure 1 shows the RDFs between the oxygen atoms in the P=O or C=O groups and the hydrogen atoms, as well as the

P...P RDFs. The RDFs exhibit a pronounced increase in the first peak upon increasing the acid concentration.

The RDFs in Fig. 1 indicate that it is the composition of the solvent that mainly affects the intermolecular acid-acid correlations, rather than the acid-DMF RDFs. The peaks in the O(=C)...H distributions at 1.61–1.63 Å are well defined over the entire range of concentrations. These results suggest that there is a short H-bond between the H_3PO_4 and DMF molecules. The computed O(=C)...H RDFs for the DMF-rich mixtures are similar to those obtained in earlier studies for mixtures with $x_{\text{H}_3\text{PO}_4} > 0.1$ [4].

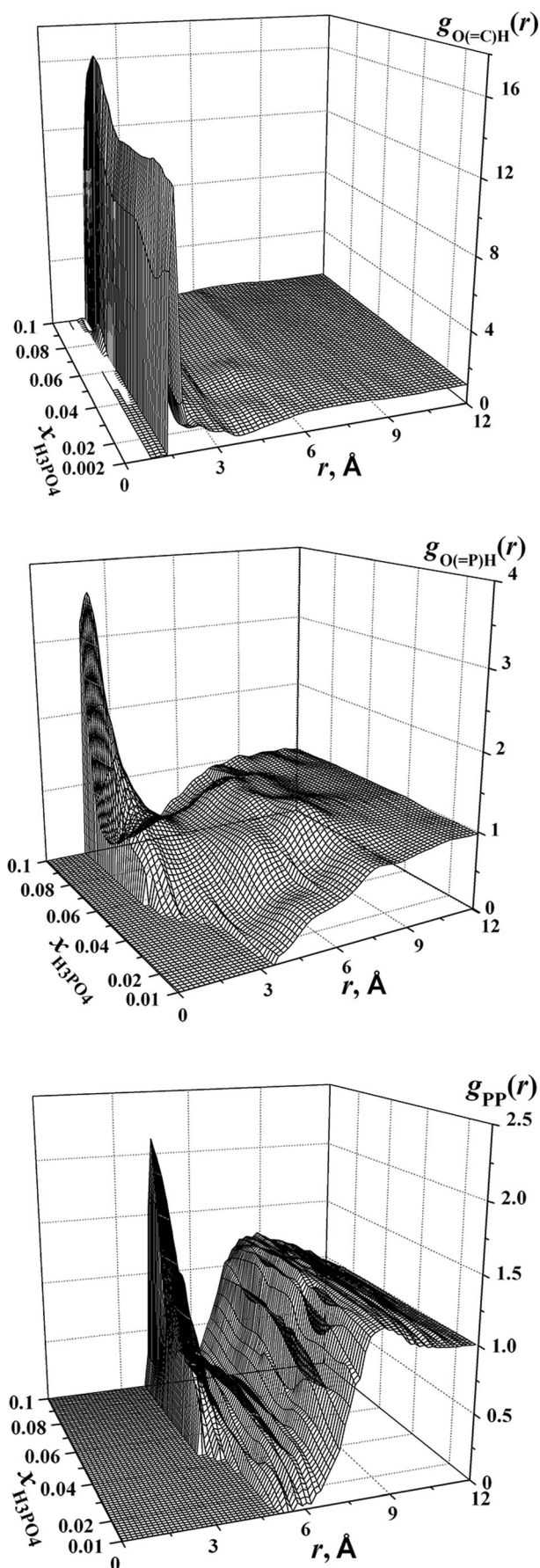
The O(=P)...H RDFs for H_3PO_4 -DMF mixtures with $x_{\text{H}_3\text{PO}_4} < 0.06$ do not show peaks at distances < 2.5 Å, so no acid-acid H-bonds are formed in these systems. The peak in $g_{\text{O(=P)H}}(r)$ first appears at $x_{\text{H}_3\text{PO}_4} \sim 0.06$ and rapidly increases with increasing acid concentration. The O(=P)...H distance decreases from 1.90 to 1.75 Å.

A peak in $g_{\text{PP}}(r)$ also appears at acid mole fractions > 0.06 . The P...P distance is nearly independent of the acid concentration. The value of the nearest-neighbor P...P distance in this complex, 4.40 Å, is ca. 0.4 Å longer than that observed in the pure H_3PO_4 crystal, in which each acid molecule is connected by two H-bonds [32].

In the liquid state, the DMF and H_3PO_4 compete as proton acceptors [6]. Since H_3PO_4 can form different numbers of H-bonds with DMF and other acid molecules, it is important to consider the distance between the phosphoryl (or carboxyl) oxygen and the nearest (ranked) protons as well as the angle between the O-H and P=O vectors of H_3PO_4 (or C=O of DMF) (Eq. 1). As an example, Fig. 2 shows the ranked O(=P)...H RDFs for mixtures with acid mole fractions of 0.06 and 0.09. The distributions of the angles between the O-H and P=O vectors at those acid concentrations are presented in Fig. 3.

Table 1 Bond lengths, angles, and the binding energies determined using B3LYP/6-31++G(d,p) for the hydrogen-bonded complexes (data for the gas phase taken from [1])

Complexes	Phase	Lengthening of O-H (Å)	H-bond length, Å		H-bond angles ($^\circ$)	$-\Delta E$ (kJ mol $^{-1}$)
			[O...H]	[O...O]		
H_3PO_4 dimer	Gas	0.047	1.567	2.579	174.3	96.66
	DMF	0.048	1.547	2.566	178.4	67.99
H_3PO_4 -DMF	Gas	0.034	1.558	2.632	175.6	62.46
	DMF	0.071	1.472	2.513	177.9	55.40
$(\text{H}_3\text{PO}_4)_2$ -DMF	Gas	0.046	1.575	2.587	176.2	166.26
	DMF	0.040; 0.063	1.606; 1.498	2.612; 2.527	175.3; 175.1	
Acid dimer		0.074	1.457	2.500	175.3	
Acid dimer		0.039; 0.059	1.594; 1.501	2.603; 2.531	178.1; 179.7	125.56
H-bond strength [30]	Strong	0.08–0.25	1.2–1.5	2.2–2.5	170–180	60–160
	Moderate	0.02–0.08	1.5–2.2	–3.2	>130	20–60
	Weak	<0.02	>2.2	>3.2	>90	<20



◀ **Fig. 1** O(=C)⋯H, O(=P)⋯H, and P⋯P radial distribution functions for H₃PO₄-DMF mixtures with $x_{\text{H}_3\text{PO}_4} < 0.1$ (data for $x_{\text{H}_3\text{PO}_4} = 0.002$ taken from [5] and $x_{\text{H}_3\text{PO}_4} = 0.1$ from [4])

Fig. 2a shows that the two nearest protons contribute to the formation of the first peak in $g_{\text{O(=P)H}}(r)$ when $x_{\text{H}_3\text{PO}_4} = 0.06$. The O(=P)⋯H distances are 1.85 and 2.15 Å for the nearest and second-nearest neighbors, respectively. The maximum in $g_{\text{O(=P)H}}(r)$ for the third-nearest proton is obtained only at an acid mole fraction of 0.09; its position corresponds to 2.30 Å (Fig. 2b). Upon increasing the concentration, the peak heights increase and the O(=P)⋯H distances in the ranked RDFs decrease. According to our data [4], the maximum in the ranked $g_{\text{O(=P)H}}(r)$ is found at $x_{\text{H}_3\text{PO}_4} = 0.3$.

Two maxima are observed in the distributions of the angles between the O-H and P=O vectors (Fig. 3). The average angles are found to be 56.1° and 54.3°. These angles are in agreement with the geometric criteria for H-bond formation, as discussed above. These results suggest that, at $x_{\text{H}_3\text{PO}_4} > 0.06$, the O(=P) atom of the acid should be able to form more than one H-bond with acidic protons. The strength of the acid-acid interaction increases with increasing H₃PO₄ content.

As an example, the ranked O(=C)⋯H RDFs and the distributions of the angles between the O-H and C=O vectors at $x_{\text{H}_3\text{PO}_4} = 0.01$ are presented in Fig. 4. A qualitatively similar dependence was also observed for all other studied compositions.

The three nearest protons contribute to the formation of the first peak in $g_{\text{O(=C)H}}(r)$, and the O(=C)⋯H RDFs show sharp, pronounced peaks at 1.564 and 1.753 Å for the nearest and the second-nearest neighbors, indicating the formation of a strong H-bond. The O⋯H distance between the O(=C) atom and the third-nearest neighbor is approximately 3 Å, which is larger than the range of accepted hydrogen-bond lengths ($r(\text{O}⋯\text{H}) \leq 2.5$ Å). The H-bond in acid-DMF is considerably shorter than that in acid-acid configurations. According to our calculations, the O(=C)⋯H distances increase slightly and the peak heights decrease as the acid mole fraction increases from 0.002 [5] to 0.3 [4]. The average angles are 52.7 and 53.9°. According to the geometric criteria for H-bond formation (namely, the O⋯H distance and the H-bond angle), we believe that both O(DMF) and O(H₃PO₄) should be able to form H-bonds with their two nearest neighbors.

Discussion

The formation of hydrogen bonds between H₃PO₄ molecules and between H₃PO₄ and DMF molecules is possible in the system under investigation. The results from the B3LYP-CPCM calculations are in accord with the MD

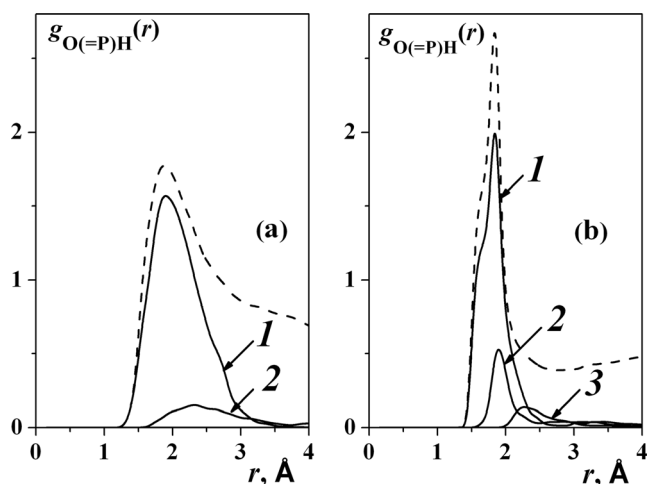


Fig. 2a–b Ranked O(=P)⋯H radial distribution functions in H₃PO₄–DMF solutions with $x_{\text{H}_3\text{PO}_4}=0.06$ (a) and $x_{\text{H}_3\text{PO}_4}=0.09$ (b). Dashed line is the radial pair distribution function. Rank of proton: 1 nearest neighbor, 2 second-nearest neighbor, 3 third-nearest neighbor

simulation findings. The differences in the geometric parameters of the H-bonds are comparable.

According to the data from the B3LYP calculations, the phosphoric acid molecules can form dimers with two symmetric H-bonds. An ability of the –POOH group to participate in strong intermolecular interactions leading to the formation of cyclic dimers was also shown [32–35]. The distance between the phosphoryl (or carboxyl) oxygen and the acid proton was introduced as an indicator of the H-bond strength [30]. The three types of H-bonds that are most frequently mentioned in the literature are weak (>2.2 Å), moderate (1.5–2.2 Å), and strong (1.2–1.5 Å) (see Table 1). Our results suggest that the H-bond strength is different in the acid–acid and acid–DMF complexes. In the gas phase, the H-bond is stronger in the acid dimer, whereas the H-bond becomes slightly weaker and the binding energy decreases slightly with

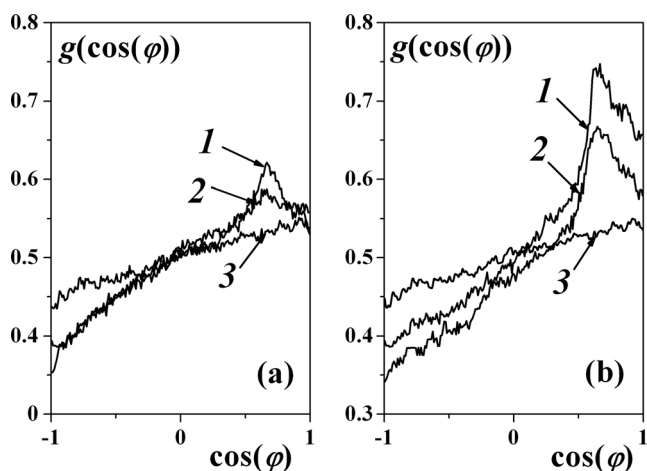


Fig. 3a–b Distributions of the angles between the O–H and P=O vectors in H₃PO₄–DMF solutions with $x_{\text{H}_3\text{PO}_4}=0.06$ (a) and $x_{\text{H}_3\text{PO}_4}=0.09$ (b). Rank of proton: 1 nearest neighbor, 2 second-nearest neighbor, 3 third-nearest neighbor

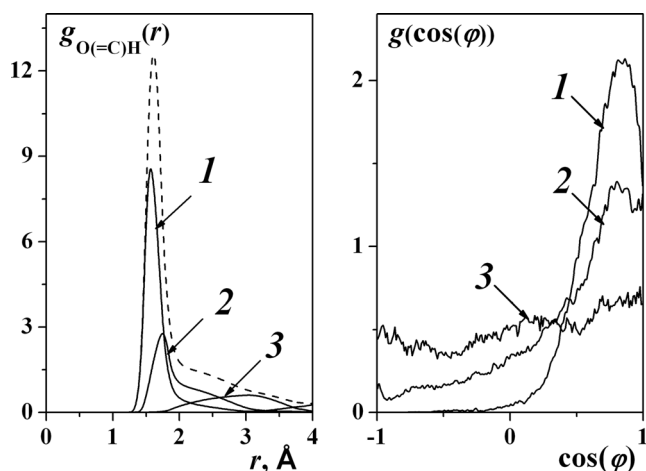


Fig. 4 Ranked O(=C)⋯H RDFs and distributions of the angles between the O–H and C=O vectors in H₃PO₄–DMF solution with $x_{\text{H}_3\text{PO}_4}=0.01$. Rank of proton: 1 nearest neighbor, 2 second-nearest neighbor, 3 third-nearest neighbor

increasing dielectric constant. The B3LYP–CPCM computations predict smaller H-bond lengths for all complexes. The H-bonds in the acid–DMF complexes are very short. The highest binding energy is observed for the (H₃PO₄)₂–DMF complex. It should be noted that the binding energies for the complexes formed between the acid dimer and an acetone [36], urea [37], or betaine [38, 39] molecule are higher than those for complexes with other compositions.

The MD results show that the hydrogen bonds are a little shorter for acid–DMF than for acid–acid configurations in DMF-rich mixtures. The H-bond between H₃PO₄ and DMF molecules may be classified as quite strong, with O⋯H distances close to 1.5 Å. Although the H-bond configuration depends very much on the acid concentration in the mixture, the variations in the ranked RDFs and the distributions of the angles between the O–H and C=O vectors are not large. The shapes and positions of the peaks in the ranked RDFs agree very well with our earlier calculations for an infinitely dilute solution [5] and mixtures with high acid concentrations [4].

An important aspect of the results is that, at $x_{\text{H}_3\text{PO}_4}<0.06$, the probability of forming acid–acid H-bonds is low; the largest fraction of the acid protons are involved in hydrogen bonding with the oxygen atoms of the DMF molecules. At acid concentrations >0.06 , the formation of H-bonds between two phosphoric acid molecules is possible. Some of the acid molecules form cyclic dimers. Even at this acid concentration, O(=P) should be able to form more than one H-bond with other molecules. The hydrogen bonding between the phosphoric acid molecules in the cyclic dimers is very important, since the formation of acid polymeric chains along with dimers has been observed at elevated acid concentrations [4]. Upon increasing the acid mole fraction to 0.3, the probability of H-bond formation in the acid–acid pairs is increased, whereas it is reduced in acid–DMF pairs, where the H-bonds

are slightly weaker. The strengths of the H-bonds between the phosphoryl oxygen (or carboxyl oxygen) and the nearest protons are not identical. This may indicate that the H-bond to the nearest neighbor is the strongest.

Conclusions

We have performed ab initio computations and MD simulations of the H_3PO_4 -DMF system to study its structural characteristics and the formation of the hydrogen bond within it. We calculated the effects of the solvent at the B3LYP level using the 6-31++G(d,p) basis set with the CPCM model. The changes in the geometries of the $(\text{H}_3\text{PO}_4)_2$, H_3PO_4 -DMF, and $(\text{H}_3\text{PO}_4)_2$ -DMF complexes were found to be comparable. The B3LYP-CPCM computations gave shorter O...H distances. The O...H distance in $(\text{H}_3\text{PO}_4)_2$ -DMF was calculated to be the shortest, so the hydrogen bond in this complex is thought to be stronger than those in the other complexes. In DMF, the binding energy of the initial acid dimer is reduced and its H-bond strength weakens.

Based on the molecular dynamics simulations of the H_3PO_4 -DMF system with $x_{\text{H}_3\text{PO}_4} < 0.1$, it was shown that the strengths of the acid-acid and acid-DMF interactions are not identical. The acid-DMF H-bonds are very short and strong, and the $\text{O}(\text{=C})\cdots\text{H}$ distance remains constant across the entire concentration range. When $x_{\text{H}_3\text{PO}_4} < 0.06$, the probability of forming acid-acid H-bonds is low; most of the hydroxyl groups on the acid molecules are involved in H-bonds with oxygen atoms of DMF molecules. Hydrogen bonds between acid molecules appear more frequently with increasing H_3PO_4 content. At $x_{\text{H}_3\text{PO}_4} \sim 0.1$, acid monomers and dimers are present, surrounded by DMF. $\text{O}(\text{=P})$ in H_3PO_4 and $\text{O}(\text{=C})$ in DMF can form up to two H-bonds by acting as proton acceptors.

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