Molecular Dynamics Simulations of the liquid mixtures

N, N -dimethylformamide - water using available potential

models

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ABSTRACT

This work reports the first computational study of N, N-dimethylformamide (DMF)-water mixtures performed by the molecular dynamics simulation (MDS) technique over the entire concentration range. The MDS results obtained have been used to assess the effectiveness of previously proposed potential models for pure liquid water (SPC, SPCE ,TIPS2) and DMF (CS2) in predicting certain properties of the DMF-water mixtures at ambient conditions. Thus, the sensitivity of the bulk thermodynamic and transport properties of the mixture to the details of the combined intermolecular potentials (CS2/SPC, CS2/SPCE, CS2/TIPS2) used has been obtained and discussed. Specifically, hydrogen bonds among the DMF and water molecules in the mixture are revealed in the behaviour of the concentration dependent appropriate (O_{DMF}–H_{water}, O_{DMF}–O_{water}) site-site pair distribution functions.

Finally, the bulk thermodynamic results obtained have shown that among the three aforementioned potentials for water used, the SPC model, and TIPS2 to a lower extent, in combination with our CS2 model for pure liquid DMF provides the most accurate descriptions of the DMF-water mixtures.

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I. INTRODUCTION

Aqueous solutions of organic compounds (protic or aprotic) are particularly interesting molecular liquids due to their extensive use in many fields of solution chemistry. To our knowledge, considerable effort has been made to clarify the behavior of the physicochemical properties of such systems over the last two decades. In particular, the problem of the microstructure and molecular dynamics in aqueous solutions has attracted much experimental and theoretical attention [1-4]. This scientific interest is due to the fact that many questions regarding the properties of such hydrogen-bonded systems have not yet been definitively answered. Notice that hydrogen bonding is known to be one of the most important weak interactions between the molecules in aqueous solutions leading to the formation of well-defined molecular aggregates.

N, N -Dimethylformamide (DMF) is one of the most simple amide compounds with very interesting properties. Previous studies have shown that the molecular nature of DMF is not capable of forming H-bonds in its pure liquid phase [5]. Note however that DMF is an aprotic dipolar fluid and its intermolecular structure is determined by some kind of strong dipolar association between the molecules. On the other hand, DMF is miscible with water in all proportions. Moreover, due to the negatively charged oxygen of the amide group, it is expected that DMF in aqueous solutions is capable of forming H-bonds with water molecules. This associative character of DMF with water is reflected in the most physicochemical properties of the DMF-water mixture such as density [6, 11], viscosity [6, 10], compressibility [9], heat of mixing [6-10, 11], partial molar enthalpies [6-10], as well as in the behavior of the excess thermodynamic functions [7]. All these properties go through minima or maxima in the mole fraction 0.3–0.4 of DMF. We mention, for instance, that the viscosity-concentration isotherms of the mixture pass through maxima at about 0.30 mole fraction of DMF and temperatures from 5 to 40°C. This result has led several researchers to suggest the formation of some strong hydrogen bonded complexes among the DMF and water molecules at the expense of water-water H-bonds. Similar conclusions have been drawn from the negative heat of mixing [8]. Generally, the aforementioned observations have been attributed to the formation of $DMF.nH_2O$ (n= 2, 3) H-bonded molecular aggregates. Nevertheless, the existence of well-defined DMF-water complexes in these mixtures has not been definitively established in the literature so far. Note that the above considerations represent the pure thermodynamic point of view. It is obvious that the interpretation of those thermodynamic data in terms of the microstructure among the molecules in the mixture tends to be qualitative. On the other hand, in order to investigate the connection between the microscopic structure and the bulk thermodynamic properties of the system, one needs information about the molecular details underlying the average structure of the first solvation shell around the given molecules. However, following the literature we can notice that all the experimental methods employed to study the DMF-water mixtures so far, are not well suited in principle to provide information regarding the microstructure, the H-bonding network and H-bond dynamics over the entire concentration range of the mixture. No further experimental and computational studies of the mixture, e.g. by the most appropriate {X-ray diffraction (XD), neutron diffraction with several isotopic substitutions (ND) and NMR} experimental methods and computer simulation techniques, were found in the literature. As far as we know, only a limited number of theoretical treatments via computer simulation on the molecular system under investigation have been reported. It is of particular interest to mention here the Monte Carlo (MC) simulation study of J. Gao [11] devoted to the estimation of the potential of the mean force for the isomerization of DMF in aqueous solutions. In that study, the MC simulations were carried out with the combined QM/MM approach to calculate the free energy of solvation for the system of 1 DMF molecule dissolved in 216 water molecules. Note also that we are unaware of any other previous simulation study or discussion of the

intermolecular potentials for aqueous mixtures containing DMF.

As it becomes apparent from the above considerations, the research effort on the DMF-water mixtures is inadequate in order to probe certain properties of the system. It is therefore logical to extend these previous experimental and computational studies of the mixture in order to fill this gap. Theoretically, among several well-established statistical mechanical computational methods, the molecular dynamics simulation (MDS) technique is particularly advantageous due to its ability to provide insight into the molecular details underlying not only the thermodynamics and structure but also the time dependent physicochemical properties of the liquid state.

In the present study we consider various aspects of the DMF-water mixtures with our interest on the thermodynamic and structural properties as well as the self-diffusion coefficients as computed from extensive molecular dynamics simulations of the system. In particular, we first attempt to quantitatively assign the influence of various previously proposed effective potentials for the pure liquid components, when used with simple combining rules to simulate the mixture, on the properties of aqueous solutions of DMF. Thus, the calculated quantities can further verify the accuracy of the checked potential models in predicting certain properties of the mixture in the entire concentration range and at ambient conditions.

II. DETAILS OF THE MOLECULAR DYNAMICS SIMULATION
A. MOLECULAR MODELS

As mentioned in the Introduction, the first task in the present MD treatment has been to estimate the effectiveness of some previously proposed effective potential models for pure liquid DMF and water to describe the properties of the DMF-water mixtures. Specifically, we are concerned with the influence of two-body additive OPLS potential models upon the physicochemical properties of the fluid under study. It is therefore very useful to present in this paragraph some details concerning the DMF-DMF and water-water potentials employed to simulate the DMF-water mixture.

To start with, we mention that the force fields considered in this study are rigid and non-polarizable. They consist of site-site pairwise additive potentials which contain coulombic plus short-range Lennard-Jones (L J) terms. The LJ interaction parameters between sites of different types are set by the usual Lorenz-Berthelot combining rules. Note also that the long-range part of the electrostatic interactions has been treated by the Ewald method.

For the DMF-DMF interactions in the mixture we employed the six-interaction-site OPLS computational model (CS2) developed by Chalaris and Samios in a very recent MD treatment [17] of the pure liquid DMF. We have based our choice essentially on the fact that the performance of the pair potential CS2 is sufficiently more satisfactory compared to other three available models for liquid DMF from the literature [18]. Concretely, we find that the CS2 model can predict not only the thermodynamic and structural properties but also the dynamic (single and Debye relaxation) and the transport coefficients of the liquid with good accuracy in the entire temperature range and at normal pressure.

In what follows we will present the potentials used in the present study to model the water-water interactions in the mixture. As far as we know, due to the great interest in pure water and aqueous solutions, numerous computational treatments have been devoted by several groups to the development of intermolecular potential models for the water dimmer that can be used for the calculation of the liquid properties by computer simulations or by analytical statistical mechanical techniques. Thus, a large number of simple potential models have been developed to model water as a liquid. Note also that several comparisons of the results obtained by different water models for the properties of liquid water can be found in the literature [13, 14, 16]. On the other hand, another point of particular importance is the

influence of the water models on the properties of aqueous solutions. It should be mentioned, however, that with regards to the behaviour of aqueous binary solutions the properties of these models have not been systematically studied.

In the present study, we have used the three popular effective potentials of water, namely the three-site simple model, SPC [12], the extended SPC, SPC/E [15], and the four point intermolecular potential, TIPS2 [13], as published. The three aforementioned water models have been used here because they are computationally very simple and previous CS studies of bulk water [14, 16] have shown that these models, to a higher or lower degree, yield the most realistic results for many important properties of the system in comparison to other widespread water models. The accuracy of the above three water models has been explored by Chalaris and Samios [22] in the framework of a very recent MD treatment of DMSO-water mixtures.

B. SIMULATION DETAILS

In order to test the applicability of the DMF/water models used, we mention that all the MD simulations and the estimation of the mixture's properties were performed in exactly the same way described herein. Thus, we carried out MD simulations of the mixture with DMF mole fractions X_D= 0.07, 0.30, 0.49, 0.70 at average temperature of 298K and densities corresponding to the normal pressure [6, 10]. The simulations were performed in the NVE statistical mechanical ensemble with 256 molecules in cubic boxes with periodical boundary conditions. In all cases, the Lennard-Jones forces were cut off at half the box length (r_c=L_{BOX}/2). Ewald sums with conducting boundaries were applied to the long-ranged portions of the electrostatic forces. The equations of motion were integrated using the leapfrog algorithm with a time step of 1.0 fs. The orientation of the molecules has been formulated using quaternion formalism. Each mixture was simulated for a relatively long time period of about 200ps, starting from a FCC lattice over which the molecules of the system were randomly distributed. Note also that each production run was done during the last 100ps of the total simulation period from which statistics have been obtained.

Finally, the self-diffusion coefficients of both species in the mixtures, D_x (x= water, DMF), have being calculated by using the well-known Einstein relation for the molecule mean-square displacement (MSD).

III. RESULTS AND DISCUSSION
Thermodynamic Properties. As mentioned above, our first aim in the present MD study is to quantify the dependence of the DMF-water mixture properties upon the potential models used for both components to describe the molecular forces in the system. Thus, in our first paper devoted to this issue, the most important thermodynamical properties of the mean potential energy per mole, U^{sim}, and pressure, P, for each mixture model studied were calculated and compared with corresponding available experimental data. Note that the experimental potential energy of each mixture, U^{exp}, has been estimated from the experimental vaporization heats of the pure mixture components ($\Delta H_{vap}^{mix}, \Delta H_{vap}^{mix}$) and the excess heat of mixing [9], ΔH_{mix}, according to the following relations:

$$U_{mix}^{exp} \cong \Delta H_{vap}^{mix} - RT \quad (1)$$

$$\Delta H_{vap}^{mix} \cong X_{DMSO} \cdot \Delta H_{vap}^{DMF} + X_{Water} \cdot \Delta H_{vap}^{Water} \pm \Delta H_{mix} \quad (2)$$

The bulk thermodynamical data obtained from the simulations of these model mixtures are depicted with available experimental data [9] in Table 1. As we can see from Table 1, the potential energy results from the model SPC or TIPS2 for water with CS2 force field of DMF are considerably better than those obtained using the CS2/SPCE model of the mixture. We

mention here that a similar conclusion has been drawn about the reliability of the aforementioned water models from our recent MD treatment of DMSO-water mixtures [22]. Specifically, the mixture with CS2/SPCE combined models overestimates the potential energy by about 1.8-5.0KJmol⁻¹, while the CS2/TIP2S mixture model underestimates this property by about 0.13-2.89KJmol⁻¹. The best results for the potential energy have been obtained in the case of the CS2/SPC mixture model. Note that the aforementioned model underestimates this property by about 0.13-1.16 KJmol⁻¹ over the entire range of concentration. It is also clearly seen that the best results for the pressure have been obtained in the case of the CS2/SPCE and CS2/SPC to a somewhat lower extent. On the other hand, the CS2/TIPS2 mixture provides unrealistic values for the pressure of the system.

Table 1. Bulk thermodynamical properties from the NVE-MD simulations of DMF-H_2O mixtures using different effective potential models at ambient conditions. Depicted are the experimental densities [g/cm^3] and the following equilibrium properties: Temperature, T [K], Pressure, P [Kbar], Potential Energy, U_p [KJ/mol] and the self-diffusion coefficients of the two components D_x [10^{-9} m^{2}s^{-1}].

	SPC	SPC/E	TIPS2	EXP
	X_D= 0.07, ρ=0.99647			
T	298.5	297.1	297.1	298.0
P	0.340	-0.170	2.162	0.001
-U_P	43.36	47.98	39.60	42.49
D_D	1.09	0.82	1.33	-
D_W	2.41	1.45	3.57	-
	X_D= 0.30, ρ=0.9924			
T	297.5	297.6	291.9	298.0
P	0.612	0.225	1.47	0.001
-U_P	44.83	48.20	42.77	44.49
D_D	0.62	0.40	0.63	-
D_W	1.15	0.69	1.30	-
	X_D= 0.49, ρ=0.9783			
T	299.5	292.7	294.0	298.0
P	0.416	0.123	0.925	0.001
-U_P	45.82	47.91	43.99	44.66
D_D	0.65	0.50	0.57	-
D_W	0.72	0.51	0.91	-
	X_D= 0.70, ρ=0.9625			
T	299.1	297.1	293.1	298.0
P	0.167	0.185	0.523	0.001
-U_P	45.28	46.51	44.51	44.64
D_D	0.73	0.60	0.77	-
D_W	0.72	0.48	0.93	-

The estimated errors were maximal: ±3K for T, ± 0.4 % for U_p, and ± (0.3-0.4) Kbar for P. X_D denotes mole fraction of DMF.

Self-diffusion coefficients. As mentioned above, the transport properties for the aforementioned three DMF/water mixture models are also of great interest in the present study. Generally, diffusion coefficients are very important properties because they allow a careful estimation of the ability of a constructed force field to describe successfully the

properties of a fluid. It is logical therefore to investigate the influence of the potential models used in the present simulations on the self-diffusion coefficients of the species in the mixture.

The calculated self-diffusion coefficients for water, D_w, and DMF, D_D, in the mixtures are depicted in Table 1. Also, the behavior of D_w and D_D with composition is shown in Figs 1, 2, respectively.
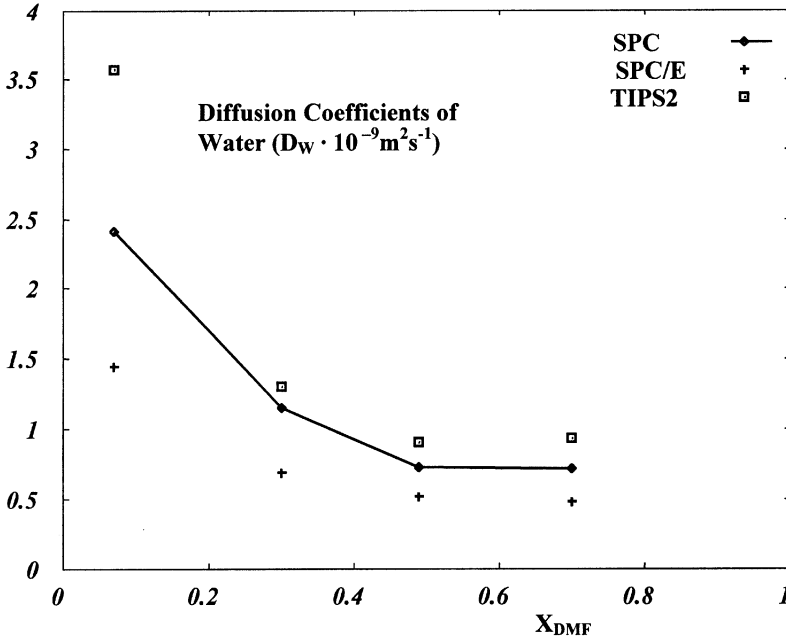

Figure 1. The composition dependence of the simulated self-diffusion coefficients for water molecules, D_w, from CS2/SPC, CS2/SPCE and CS2/TIPS2 mixture models at ambient conditions.

As can be observed from the aforementioned diffusion results, the coefficients D_W and D_D show a non-linear dependence with composition. Also, the diffusion data for both components show that the molecular mobility of one species is slowed down with addition of the other and vice-versa. As we can see from Figure 1, the D_w values for CS2/SPC follow a similar course with DMF concentration in the mixture, X_D, compared to the D_w values for the other two investigated mixture models. Concretely, the coefficients D_w decrease sharply and non-linearly with addition of DMF in water and up to the equimolar composition. Overall, we find that model CS2/TIPS2 exhibits sufficiently faster translational dynamics for the water molecules than CS2/SPC and CS2/SPCE. It can be clearly seen from Fig. 2 that the variation in the DMF self-diffusion coefficients with composition exhibits similar futures compared to the D_w data from CS2/SPC, CS2/SPCE and CS2/TIPS2 mixture models. A numerical inspection of the D_D data obtained shows the existence of a shallow minimum located in the range $X_D = 0.3 - 0.4$ for all the models used. It is also interesting to notice here that the aforementioned self-diffusion behaviour parallels that of the experimental viscosity and other thermodynamical properties [6-10] of the mixture. Overall, we find that the water molecules diffuse faster than the DMF molecules in the mixture models, as expected. Finally, due to the lack of the self-diffusion experimental results for DMF/water, a direct comparison between

our simulated self-diffusion coefficients for the mixture with experiment is not possible at the present time. Note however that the diffusion results from the present simulation exhibit the expected behaviour as in the case of similar aqueous solutions [19-23].
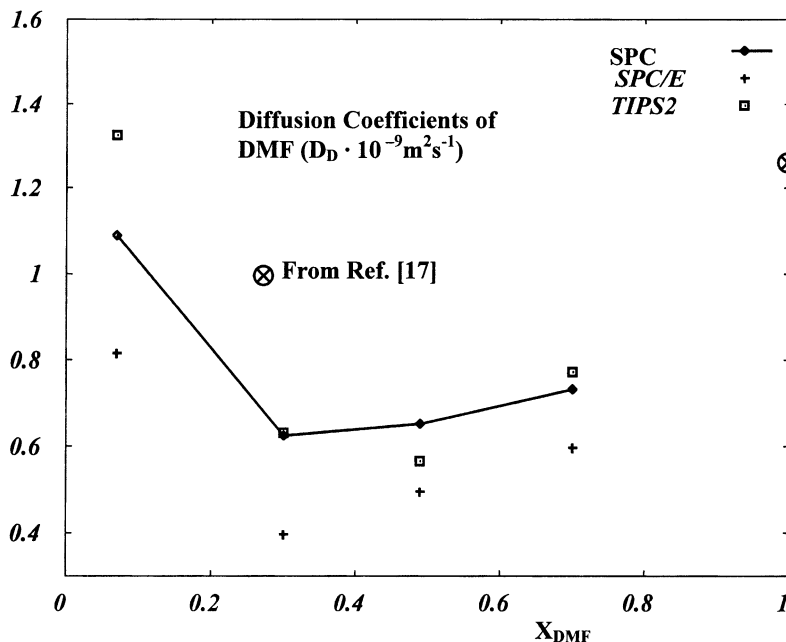

Figure 2. The composition dependence of the simulated self-diffusion coefficients for DMF molecules, D_D, from CS2/SPC, CS2/SPCE and CS2/TIPS2 DMF-water mixture models at ambient conditions.

Structural Properties. It is well known that detailed information about the intermolecular structure of liquids can be gained by means of computer simulations and neutron scattering or X-ray diffraction experiments. Concretely, the various site-site pair distribution functions (pdfs), $g_{xy}(r)$, obtained from the aforementioned experimental and theoretical techniques provide a convenient and powerful method to discuss the structure of liquids. In the present MD study, each simulated mixture has a relatively large number of distinct pdfs involving DMF-DMF, water-water as well DMF-water site pairs. It is, of course, impractical to present and analyze all the pdfs calculated in the framework of the present study. We begin here by looking at the DMF-water pdfs involving the O_D-H_w and O_D-O_w pairs of sites belonging to DMF and water molecules. The computed O_D-H_w and O_D-O_w site-site pdfs are presented in Figs. 3 and 4. Concretelly, Figure 3A shows how the shape of the O_D-H_w pdf , obtained at X_D=0.07 and ambient conditions, varies with the mixture potential models. As in Figure 3A, Figure 3B shows the behavior of the simulated O_D-O_w site-site pdfs. The results obtained from the DMF-water solution at X_D= 0.30, corresponding close to minima and maxima in several thermodynamic properties of the mixture, are depicted in Figs. 4A, B.
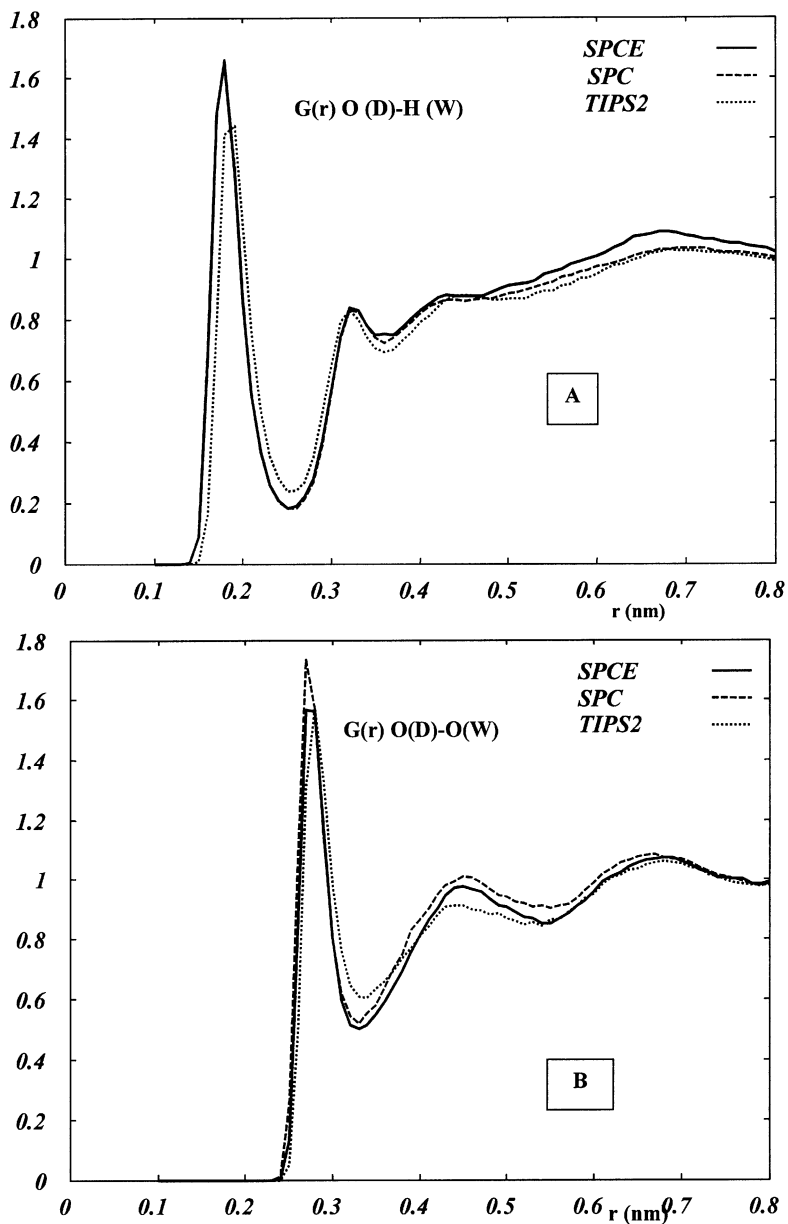
Figure 3. O(DMF) - H(water) (A) and O(DMF)-O(water) (B) site-site pair distribution functions for CS2/SPC, CS2/SPCE and CS2/TIP2 DMF-water mixture models at $X_{DMF} = 0.07$ and ambient conditions from this MD study.
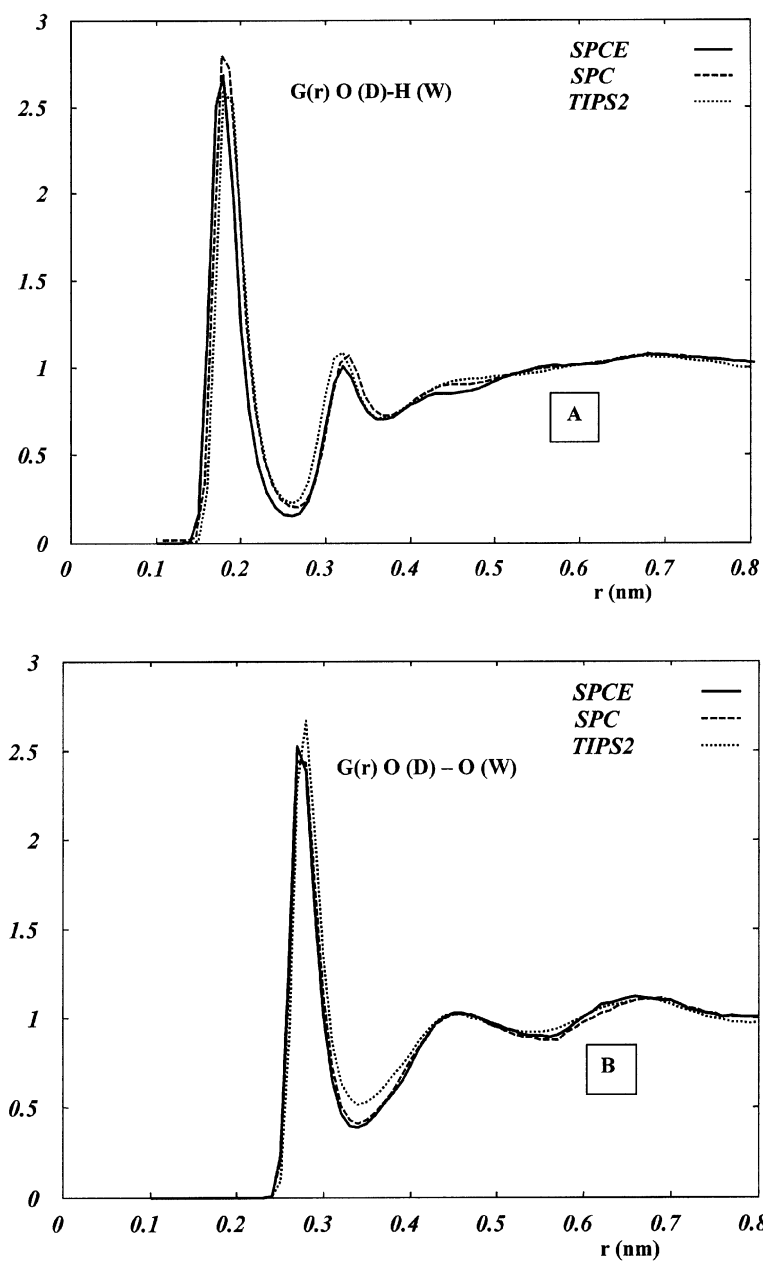
Figure 4. O(DMF) - H(water) (A) and O(DMF)-O(water) (B) site-site pair distribution functions for CS2/SPC, CS2/SPCE and CS2/TIP2 DMF-water mixture models at X_{DMF} =0.30 and ambient conditions from this MD study.

The inspection of the curves which appear in Figs. 3A, B, confirms that in all cases the qualitative trends observed in the pdfs for CS2/SPC mixture model are also observed in the functions obtained using the other two models, CS2/ SPCE and CS2/TIPS2. However, some differences can be observed between the above mentioned functions produced by these models at the lowest mole fraction of the mixture (X_D=0.07) studied here. In particular, the CS2/TIPS2 mixture model shows a systematic lower first peak of the O_D-H_w pdf, which is located at somewhat longer correlation distance, compared to the other two models. Note also that, as it can be seen from the Figs. 4A and 4B, the overall behaviour of each of the three pdfs (O_D-H_w or O_D-O_w) is found to be quite similar in all models used in the present MD study. This is apparent from the positions and heights of the extrema of the presented correlation functions. This result indicates strong similarities in the constructed local structure arround the DMF molecules produced by these models at an approximatelly intermediate mole fraction of the mixture.

The above structural results provide additional very interesting insights regarding the microscopic structure arround the DMF molecules in th emixture. The presence, for instance, of a very sharp first peak in O_D-H_w correlation function at correlation distance 0.17 nm, as well as in O_D-O_w at 0.26 nm, shows clearly that O_D is hydrogen bonded by water molecules. The integration of the O_D-H_w function up to the correlation distance r=0.25nm gives a coordination number of about 1.29 for X_D=0.30. This result is still present even at the lowest concentration of DMF in the mixture. It means that even at X_D=0.07 the molecules remain highly structured in this diluted solution. The reliability however of all the structural results obtained with these models should be judged from their comparison with suitable real experimental data. Neutron diffraction experiments with hydrogen/deuterium isotope substitution are suitable in principle to predict structural data on molecular liquids. Since, however, ND studies have not been performed in DMF aqueous solutions, a definitive solution to the problem of the microscopical intermolecular structure in the solutions cannot be given at the present time. Finally, a complete discussion of the structural properties of these mixture potential models obtained from the present MD simulations will be reported in a subsequent paper.

IV. SUMMARY

In this paper, the molecular dynamics technique was employed to study the liquid mixture DMF-water using two-body optimized molecular potential models. The mixture was simulated in the micro-canonical (NVE) statistical mechanical ensemble over a wide range of mole fractions at 298 K and densities corresponding to the normal pressure. The main purpose of this work was to investigate the intermolecular interactions of the system. This was achieved by exploring the effectiveness of previously proposed potential models for pure liquid water (SPC, SPCE, TIPS2) and DMF (CS2) in predicting certain properties of the mixture at ambient conditions. To realize this, we have performed very long simulations of the system using exactly the same simulation methodology. Several properties of the solutions, including their bulk thermodynamical, local structure and transport properties, have been calculated and discussed. The sensitivity of the aforementioned properties to the details of the combined DMF/water potentials (CS2/SPC, CS2/SPCE, CS2/TIPS2) has been discussed. Specifically, hydrogen bonds among the DMF and water molecules are revealed in the behavior of the O_{DMF}-H_{water} and O_{DMF}-O_{water} site-site pair distribution functions.

Finally, among the three DMF/water mixture models used in the present study, the CS2/SPC one was found to yield the most successful results in comparison to the other two ones. Further MD studies with CS2/SPC potential model are planned including investigations of the single and collective dyanamical properties of the mixture under study.

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