



**Computer simulation studies of the liquid mixtures water-  
dimethylsulfoxide using different effective potential models:  
Thermodynamic and transport properties**

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**ABSTRACT**

This work demonstrates the first part of the results obtained in the framework of our extensive molecular dynamics simulations (MDS) of binary mixtures of water with dimethylsulfoxide (H<sub>2</sub>O-DMSO). The present treatment has been devoted to the estimation of the ability of previously proposed potentials for pure liquid water and DMSO in predicting certain properties of the water-DMSO mixtures at ambient conditions. Three widespread effective potential models for water (**SPC**, **SPCE**, **TIPS2**), in combination with the **P2** model of DMSO, were employed to simulate the mixtures at state points for which experimental data are available. The present simulations have revealed that the results obtained differ from model to model. Specifically, we found that among the three models used, the **SPC/P2** model, and **TIPS2/P2** to a lower extent, yields the most reasonable descriptions of the mixture. However, these models yield results of somewhat restricted accuracy compared to the experimental data. Therefore, a further modification of the potential parameters used seems to be needed to improve agreement between the simulated and experimental properties of the system over the entire range of compositions.

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## 1. INTRODUCTION

During recent years, the properties of pure liquid dimethyl sulfoxide (DMSO) and DMSO binary mixtures have been extensively studied by using a variety of experimental and theoretical techniques. As far as we know, among the most experimentally investigated DMSO mixtures are certainly the DMSO aqueous solutions. Note that the water-DMSO system is of particular importance due to its extensive use as a mixed solvent.

The fact that the properties of water-DMSO mixtures exhibit some exceptional behavior compared to the properties of the pure components is of particular interest. Needless to say, that even for the pure components, they are far from being simple. For instance, water is a strongly associated (H-bonded) liquid, while the high freezing (18.5 °C) and boiling (189°C) points of pure DMSO indicate the existence of some kind of short-range molecular ordering among the nearest species in the system. Previous studies have shown that the methyl groups of DMSO molecule do not participate in the hydrogen bonding of the system [1]. On the other hand, in water-DMSO mixtures the first component seems to be capable to associate with the second one. In addition, the associative character among the molecules is displayed in the behaviour of some macroscopical properties of the mixture such as density [2,3], viscosity [4-6], compressibility [2], dielectric permittivity [2,7] and surface tension [2,7], as well as in the behaviour of the freezing point-composition curve [8]. Note also that all the aforementioned properties go through minima or maxima in the mole fraction 0.3-0.4 of DMSO. We mention, for instance, that the viscosity isotherms of water-DMSO mixtures go through maxima [2,4-6]. Such a behaviour of the mixture may be a sign of the formation of molecular aggregates due to the existence of strong hydrogen bonds among the water hydrogen and DMSO oxygen atoms. So, it is understandable why there is so much interest in exploring the underlying molecular mechanisms, which are responsible for the overall behaviour of the mixture.

To the best of our knowledge, several thermodynamical and spectroscopical studies [9,10] are available in the literature concerning the properties of the mixture under study. Information regarding the microstructure of the hydrated DMSO, the hydrogen bonding network, as well as the hydrogen bond dynamics, has been obtained from previous computer simulation (CS) studies and X-ray or neutron diffraction (ND) experiments. Vaisman and Berkowitz (VB) [11] have carried out an earlier CS study of the mixture. According to the technical details given by VB in that paper, their simulations were carried out at very low DMSO concentrations ( $x_{\text{DMSO}} = 0.005, 0.04, 0.2$ ). In a subsequent MD treatment, Luzar and Chandler (LC) reported additional information concerning the hydrogen bonding network and H-bond dynamics of the mixture, at the same thermodynamic conditions ( $x_{\text{DMSO}} = 0.21, 0.35$ ) with those of the ND experiments [12,13]. Apart from the work of VB and LC, Borin and Skaff (BS) have also carried out recently a series of MD simulations of water-DMSO, spanning the whole composition range of the mixture [14,15]. In that study the concentration dependence of the molecular association between the water and DMSO molecules in the solution, at normal conditions, were reinvestigated.

Despite the substantial research effort on the water-DMSO mixture, one may assert that a deeper understanding of the behavior of the properties of this molecular system has not yet been achieved. We mainly refer to the fact that none of the aforementioned ND and CS studies provide information concerning the temperature and/or density dependence of the structure, dynamics and transport properties of the mixture under consideration. For example, the H<sub>2</sub>O-H<sub>2</sub>O and H<sub>2</sub>O-DMSO H-bonding network of the system, as a function of different

thermodynamic variables and specifically at state points close to the composition-freezing curve, has not yet been explored. As mentioned in ref. [16], a detailed investigation of the orientational correlation of the nearest molecules in the system is still needed. As it becomes finally apparent from the earlier CS studies of the mixture, there is no systematic investigation concerning the level of accuracy of the potential models used to model the DMSO aqueous mixture up to present time.

From the above considerations, the need for a further experimental and computational work on the water-DMSO mixture, in order to probe certain properties of interest, can be clearly seen. At this stage, we decided to extend the previous CS studies on the mixture over a wide range of state points for which the corresponding system properties are still far from being understood. Thus, we have carried out an extensive MD investigation on the composition and temperature dependent properties of the system. Some preliminary results obtained from our MD simulations have been presented and discussed previously [17].

In this report we demonstrate the first part of our systematic CS studies of the mixture. This work has been devoted to the investigation of the bulk and transport properties of the system using different effective potential models and the MD technique. The present simulation is thus of interest as a power tool in the study of the accuracy of various effective potentials employed to simulate the mixture under investigation. Finally, the computational details and results are presented and discussed in the following Sections.

## 2. DETAILS OF THE MOLECULAR DYNAMICS SIMULATION

### 2.1 Potential Models

As mentioned in the Introduction, this work aims to investigate the properties of various potential models used to describe the water-DMSO mixture. Thus, in order to fulfill our purpose better, we checked to what extent popular effective potential models for liquid water and DMSO, when employed for the water-DMSO mixture, can provide CS results for the bulk properties and specifically for the transport coefficients of the mixture in quantitative agreement with experiment.

Before proceeding further, it is interesting to present and discuss the available potential models which have been used in the framework of this study. To start with, we mention that in the case of pure liquid water a considerable number of different effective potentials have been developed by several groups so far to model the molecular interactions in the fluid. Among all the selected water models, only the following three effective potentials have been used in this work. These are: the widespread three-site simple model, **SPC** [18], the extended **SPC** model, **SPCE** [19], and the four point intermolecular potential, **TIPS2** [20]. We have based our choice essentially on the following reasons:

- a. The three aforementioned water models are computationally very simple.
- b. Previous CS studies of bulk water [21,22] have revealed 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 water effective potentials. Specifically, as it was pointed out by Berendsen et al. [22] and Zhu et al. [23], the **SPCE** model was found to be superior to the **SPC** and other models regarding the properties of the bulk water.

On the other hand, following the literature we can notice that two-body effective water models are most often used in CS studies of various organic and bioorganic compounds dissolved in water. Concretely, CS studies of such solutions [22] have shown that the models **SPC**, **TIP4P**, and model **TIP3P** to lower extent, yield the most successful results compared to the **SPCE** one.

Although the possibilities of the aforementioned water models have been explored in the case of very diluted aqueous solutions via CS studies, however, with regards to the behavior of aqueous binary solutions of very common organic compounds (protic or aprotic), and over the entire range of solute compositions, the properties of these models have not been examined in detail up to date.

Let us now present the most popular intermolecular potentials for pure liquid DMSO. Since we are concerned with the influence of two-body effective potential models upon the properties of the mixture under investigation, so models of that type for DMSO are of great interest in the present study. Thus, we mention the model proposed by Rao and Singh (**RS**) [24], the **P1** and **P2** models of Luzar and Chandler [12,25], the model of van Gunsteren et al. (**VG**) [26], as well as the OPLS model optimized by Jørgensen (**JM**) [27]. All the aforementioned models are rigid and nonpolarizable. They have a similar functional form including short range Lennard-Jones and long-range electrostatic terms. Most properties of these models, including their structural, thermodynamical, transport, as well as single dynamical properties, have been studied and reported by LC and VG et al. in their corresponding CS studies of pure liquid DMSO. Furthermore, Skaff has investigated the static dielectric properties of these models in a subsequent MD treatment [15]. By inspecting the results obtained from the studies mentioned above, we may conclude that the **P2**, **JM** and **VG** models are superior to the **RS** and **P1** ones. Consequently, it is of particular interest to reassess the properties of the water-DMSO mixture for the three most accurate DMSO models (**P2**, **JM** and **VG**) in combination with the three water models presented above. This is what has been done in the framework of our exploratory MD studies of the properties of the aforementioned water/DMSO mixture models. Note that in this article we report only the simulations of the mixture on the basis of **SPC**, **SPCE** and **TIPS2** water models in combination with the **P2** model for DMSO. Moreover, concluding remarks concerning the suitability of the rest water/DMSO models used in our studies are also given below.

A complete description of the parameters for each available model for pure water and DMSO used in the present study of the water-DMSO mixture is given in Table 1 and 2, respectively. Note that in all cases the Lennard-Jones parameters between interaction sites of different types are set by the usual Lorenz-Berthelot (LB) combination rules. However, the fundamental question “ what kind of effect the application of the LB or another combination rules might have on the CS results obtained” has not been answered in the present or previous studies. The resulting assessment of the strength or weakness of these water/DMSO models for the simulation of the mixture is based on the MD results obtained for the mean potential energy and pressure, as well as for the most important transport properties of the system, namely, the self-diffusion coefficients of the molecules in the mixtures.

**Table 1.** Parameter values for the available potential models for pure liquid water employed in the present MD study of the water-DMSO solutions.

<b>Water-Water</b>	<b>SPC [18]</b>	<b>SPCE [19]</b>	<b>TIPS2 [20]</b>
$r_{OH}$ (nm)	0.10	0.10	0.0957
$\angle HOH$ (deg)	109.47	109.47	104.52
$\sigma_{oo}$ (Å)	3.156	3.156	3.241
$\epsilon_{oo}/k_B$ (K)	78.23	78.23	78.08
$q_o$ (e)	-0.82	-0.8476	0.0
$q_H$ (e)	0.41	0.4238	0.535
$q_M$ (e)	0.0	0.0	-1.07
$r_{OM}$ (Å)	0.0	0.0	0.15
$\mu$ (Debye)	2.27	2.35	2.17

**Table 2.** Parameter values for the available potential models for pure liquid DMSO employed in the present MD study of the water-DMSO solutions.

<b>DMSO-DMSO</b>	<b>P2 [12,25]</b>	<b>JM [27]</b>	<b>VG [26]</b>
$\epsilon_{OO}/K_\beta$ (K)	36.0	140.86	206.32
$\sigma_{OO}$ (nm)	0.280	0.293	0.263
$q_o$ (e)	-0.459	-0.459	-0.459
$\epsilon_{SS}/K_\beta$ (K)	119.96	198.71	156.0
$\sigma_{SS}$ (Å)	0.340	0.356	0.356
$q_s$ (e)	0.139	0.139	0.139
$\epsilon_{CC}/K_\beta$ (K)	147.94	80.49	113.23
$\sigma_{CC}$ (Å)	0.380	0.381	0.366
$q_C$ (e)	0.160	0.160	0.160
$r_{SC}$ (Å)	1.80	1.80	1.95
$r_{OS}$ (Å)	1.53	1.53	1.53
$\angle OSC$ (deg)	106.75 <sup>0</sup>	106.75 <sup>0</sup>	106.75 <sup>0</sup>
$\angle CSC$ (deg)	97.4 <sup>0</sup>	97.4 <sup>0</sup>	97.4 <sup>0</sup>
$\mu$ (Debye)	4.48	4.48	4.59

## 2.2. MD Simulation details

To test the water/DMSO models used, we have simulated water-DMSO mixtures with DMSO mole fractions  $X_D = 0.055, 0.19, 0.30, 0.35, 0.67$  at average temperature of 298 K and densities corresponding to the normal pressure. With regards to the simulation methodology employed in the present studies of the mixture, we mention that all the MD runs and the evaluation of the relevant mixture's properties were carried out in exactly the same way

described herein. Thus, we were able to investigate the impact of the potential models used on the simulated properties of the mixture.

All the MD simulations presented here were performed in the NVE statistical mechanical ensemble and some of them in NVT with 500 molecules placed in cubic boxes with periodical boundary conditions. In all cases, a full spherical cutoff radius ( $r_c=L_{\text{BOX}}/2$ ) as the cutoff distance was applied to truncate the short-range interactions among the interactions sites of the molecules in the system. Also, the long-range electrostatic forces were treated using the well-known Ewald sums with conducting boundaries. The equations of motion were integrated using the leapfrog algorithm [28] with a time step of 1.5 fs. The orientation of the molecules has been formulated using quaternion formalism. Each model mixture was simulated for a relatively long time period of about 1.2 ns, starting from a FCC lattice over which the molecules of the system were randomly distributed. Note furthermore that the molecules with the smaller concentration in the mixture were uniformly distributed among the rest molecules in the system. Finally, each model mixture was equilibrated during the first 200ps of the total simulation period.

As discussed before, the transport properties for the aforementioned water/DMSO mixture models are of particular interest here. Note that the diffusion coefficients, for instance, belong to the most important class of properties of a fluid that allow a careful estimation of the ability of a model to describe successfully the system. Specifically, in the present study the self-diffusion coefficients of the molecules in the mixture,  $D_x$  ( $x=$  water, DMSO), have been obtained from their mean-square displacements (MSD), using the usual Einstein relation:

$$6D_x = \lim_{t \rightarrow \infty} \frac{1}{t} \langle [\Delta r_x(t)]^2 \rangle \quad x = \text{water, DMSO} \quad (1)$$

Note also that in the calculation of the MSD of each molecule, the molecule positions are not subjected to periodical boundary condition shifts. Also, our results were obtained on the basis of relatively long MSD plots of about 450 ps, from which only the last 200 ps were used to estimate the self-diffusion coefficients.

### 3. RESULTS AND CONCLUDING REMARKS

As mentioned above, in order to estimate the accuracy of these models a series of trial but very long NVE MD simulations of different water/DMSO mixture models was carried out at ambient conditions and over the entire range of compositions. In the framework of these trial simulations, the most important thermodynamical properties of the mean potential energy per mole,  $U^{\text{sim}}$ , and pressure,  $P$ , for each mixture model were calculated and compared with corresponding experimental data. Note that the experimental potential energy,  $U^{\text{exp}}$ , of each mixture has been estimated from the available experimental vaporization heats of the pure liquid water and DMSO ( $\Delta H_{\text{vap}}^{\text{Water}}$ ,  $\Delta H_{\text{vap}}^{\text{DMSO}}$ ) and the excess heat of mixing [3,29,30],  $\Delta H_{\text{mix}}$ , according to the following relations:

$$U_{\text{mix}}^{\text{exp}} \cong \Delta H_{\text{vap}}^{\text{mix}} - RT \quad (2)$$

$$\Delta H_{\text{vap}}^{\text{mix}} \cong X_{\text{DMSO}} \cdot \Delta H_{\text{vap}}^{\text{DMSO}} + X_{\text{Water}} \cdot \Delta H_{\text{vap}}^{\text{Water}} - \Delta H_{\text{mix}} \quad (3)$$

By inspecting carefully our preliminary computational results for the mixture, we were able to draw some very useful conclusions concerning the accuracy of various potentials used to model this molecular system. With regards to the quality of the predicted bulk properties for the investigated mixture models, we found that these potentials may be arranged in the following categories: SPC/P2 with SPC/JM, TIPS2/P2 with TIPS2/JM and SPCE/P2 with SPCE/JM belong to the first, second and third group, respectively, with the results for the first and second group significantly better than those of the third one. The rest three investigated water/DMSO models (SPC/VG, TIPS2/VG and SPCE/VG), on the other hand, do not seem to provide a better description of the mixture's bulk properties than the first three model groups. In other words, the present MD have shown that the VG model of DMSO is of little use when combined with these water models to simulate the mixture.

In the following we present and discuss the CS results obtained for **SPC/P2**, **SPCE/P2** and **TIPS2/P2** mixture models. The results obtained for the rest potential models used in our MD calculations of the mixture will be presented and discussed in a subsequent paper. The bulk thermodynamical results from the NVE MD simulations of the aforementioned three model mixtures are compared with experimental and previous simulation data [14, 25] in Table 3. A close inspection of these data reveals clearly the strength or the weakness of each tested model in describing the properties of the solution under investigation. As we can see, the computed potential energies show systematic differences among the three mixture models. The results for the potential energies show that the SPC/P2 model and TIPS2/P2 to a lower extent provide the best agreement between calculated and experimental data compared to the SPCE/P2 model. It is also clearly seen that the SPC/P2 model predicts the best results for the pressure of the mixture in comparison to the rest of the models.

Generally, in terms of the calculated bulk thermodynamical properties of the mixture, the SPC/P2, and TIPS2/P2 to a lower extent, seem to yield the best descriptions of the mixture. On the other hand, the SPCE/P2 model seems to be of little use for the reliable description of the thermodynamics of the water-DMSO solutions.

The calculated self-diffusion coefficients for water,  $D_w$ , and DMSO,  $D_D$ , in the mixtures are selected in Table 3 together with the corresponding experimental data from Packer and Tomlinson (PT) [31]. The concentration dependence of the simulated  $D_w$  and  $D_D$  coefficients for the three mixture models is also indicated in Figures 1, 2, respectively. Also shown are the experimental results for each molecular species in the mixture.

As can be observed from the diffusion data in these Figures, the calculated coefficients  $D_w$  and  $D_D$  changes with composition. Also, they show a non-linear behavior with composition. It is worthwhile to note here that this result is in agreement with experiment. Further, the simulated results show that the water molecules are more mobile than the DMSO molecules over the entire range of compositions. This MD result is also in accordance with experimental findings. In addition, the simulated diffusion coefficients for SPCE/P2 and SPC/P2 models present extrema in the range of 30-40% composition of DMSO. The experimental data show a minimum at about 33% DMSO. Around the equimolar composition the calculated coefficients  $D_w$  and  $D_D$  for the SPCE/P2 model are considerably smaller than the experimental results. Note that our SPCE/P2 MD result for  $D_D$  is in contrast to that obtained previously by Skaff [14].

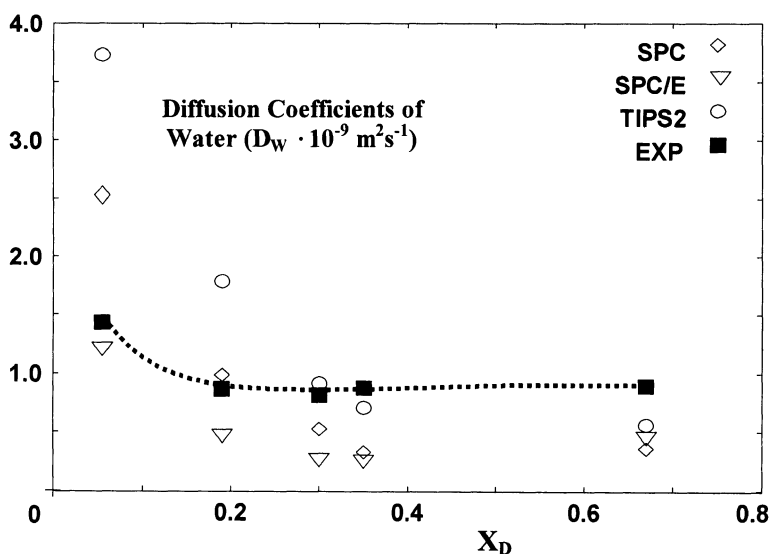
Finally, the simulated self-diffusion coefficients  $D_w$  and  $D_D$  show clearly that among the three investigated mixture models, the SPC/P2 one exhibits the most reliable description of the mobility of each molecular species in the mixture.

**Table 3.** Thermodynamic results from the NVE-MD simulations of H<sub>2</sub>O-DMSO solutions using different effective potential models at ambient conditions. Depicted are the experimental densities [g/ml] and the equilibrium properties: Molar volume,  $V_m$  [cm<sup>3</sup>], temperature,  $T$  [K], potential energy,  $U_p$  [KJ/mol], pressure,  $P$  [Kbar], and the self diffusion coefficients of both species [ $10^{-9}$  m<sup>2</sup>s<sup>-1</sup>]. The number in parentheses are results from previous MD studies of the mixture.  $X_D$  denotes mole fraction of DMSO

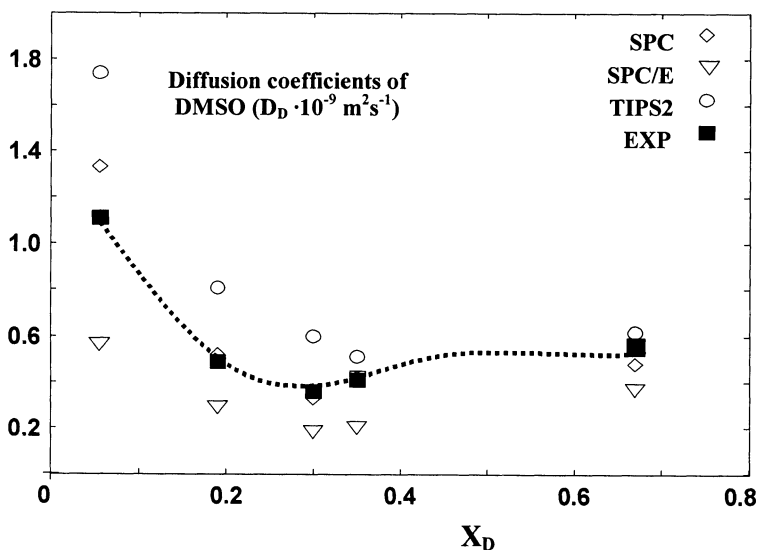
	SPC	SPC/E	TIPS2	EXP
<b><math>X_D=0.055, \rho=1.0238</math> g/ml</b>				
$V_m$	20.871	20.871	20.871	20.871
$T$	298.9	299.5	297.9	298
$P$	0.014	-0.458	1.910	0.001
$-U_p$	44.31	48.99	40.47	42.9
$D_D$	1.33	0.57	1.74	1.11
$D_W$	2.55	1.22	3.73	1.433
<b><math>X_D=0.19, \rho=1.0683</math> g/ml</b>				
$V_m$	27.406	27.406	27.406	27.406
$T$	298.3	297.9	296.5	298
$P$	-0.217 (0.41) <sup>a</sup>	-0.550	1.298	0.001
$-U_p$	47.46 (47.90) <sup>a</sup>	51.53	44.60	45.39
$D_D$	0.526	0.2961	0.8079	0.49
$D_W$	0.887	0.4847	1.7478	0.87
<b><math>X_D=0.30, \rho=1.0881</math> g/ml</b>				
$V_m$	33.125	33.125	33.125	33.125
$T$	299.7	298.0	297.6	298
$P$	-0.386	-0.640	0.695	0.001
$-U_p$	49.33	52.58	47.15	46.7
$D_D$	0.33	0.19	0.60	0.36
$D_W$	0.526	0.28	0.92	0.82
<b><math>X_D=0.35, \rho=1.0927</math> g/ml</b>				
$V_m$	35.734	35.734	35.734	35.734
$T$	298.3	299.9	296.1	298
$P$	-0.543 (0.41) <sup>a</sup>	-0.781 (-0.15) <sup>b</sup>	0.398	0.001
$-U_p$	50.20 (49.90) <sup>a</sup>	52.99 (49.6) <sup>b</sup>	47.95	47.2
$D_D$	0.42	0.21	0.51	0.41
$D_W$	0.33	0.27	0.71	0.88
<b><math>X_D=0.67, \rho=1.0990</math> g/ml</b>				
$V_m$	52.819	52.819	52.819	52.819
$T$	298.3	298.6	297.9	298
$P$	-0.590	-0.648 (0.07) <sup>b</sup>	-0.400	0.001
$-U_p$	50.52	51.88 (50.6) <sup>b</sup>	50.30	49.30
$D_D$	0.48	0.377	0.618	0.55
$D_W$	0.36	0.47	0.563	0.896

<sup>a, b</sup> from Refs.[25] and [14], respectively. The estimated errors were maximal :  $\pm 3$  K for  $T$ ,  $\pm 0.4\%$  for  $U_p$ , and  $\pm(0.3 - 0.4)$  Kbar for  $P$ .





**Figure 1.** The composition dependence of the simulated self-diffusion coefficients for water molecules in water-DMSO mixtures compared with available experiment data [31] at ambient conditions.



**Figure 2.** The composition dependence of the simulated self-diffusion coefficients for DMSO molecules in water-DMSO mixtures compared with available experimental data [31] at ambient conditions.

#### 4. SUMMARY

In this paper we have presented molecular dynamics simulations of the liquid mixture water-DMSO over the entire composition range and at ambient conditions. The focus of this work was to investigate systematically the molecular interactions in this binary solution. Thus, the accuracy of previously proposed effective two-body potential models for pure liquid water and DMSO in predicting the properties of the water-DMSO mixtures was explored. This was achieved by performing long simulations of the mixtures using exactly the same simulation methodology.

The present MD results have shown that, among the different water/DMSO mixture models, which were used to simulate the bulk thermodynamical and transport properties of this solution, the SPC/P2 mixture model provides the best agreement with experiment. However, the comparison with experiment has also shown that a further modification of the potential parameters used is needed in order to improve agreement with experimental data over the entire range of compositions. Further CS studies on the properties of water-DMSO mixtures at lower temperatures are planned.

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