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Rapid communication

Apparent molar volume anomaly in water-dimethyl sulfoxide liquid mixtures. Molecular dynamics computer simulations

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We have studied the composition dependence of density of liquid water-DMSO mixtures at different temperatures by using the isobaric-isothermal (NPT) molecular dynamics computer simulations. The non-polarizable semi-flexible, P1 and P2 models for the DMSO molecule combined with the TIP4P-2005 water model are considered. The excess mixing volume and the apparent molar volumes of the species are reported. We have established that the P1-TIP4P-2005 model for the mixture provides a very good description of the location of the minimum of apparent molar volume for DMSO species indicating the anomaly. Most important is that the temperature interval where the hydrophobic effect exists, is correctly captured with this modelling, in contrast to the P2-TIP4P-2005 model.

Key words: *molecular dynamics, water-dimethylsolfoxide mixtures, apparent molar volume*

Liquid mixtures of dimethyl sulfoxide (DMSO) and water are widely used in organic chemistry, chemical engineering, and biomedical applications. In this rapid communication we refer to the static light scattering experiment performed on aqueous solutions of dimethyl sulfoxide (DMSO) at various compositions and at two temperatures, 20°C and 50°C [1]. In the concentration range around 10 mol percent of DMSO, an abnormal maximum of scattered light was detected, the intensity of which decreases with an increase of temperature. This maximum has been attributed to the hydrophobic effect and has been interpreted in terms of the minimum of apparent molar volume of DMSO upon concentration. Inspired by this report, we have undertaken the study of the composition dependence of density of water-DMSO liquid mixtures at 298.15 K, 318.15 K and 338.15 K by using molecular dynamics computer simulations complementing our recent study performed at 298.15 K [2]. Our focus is on the capability of simple non-polarizable models for DMSO and water to reproduce the experimental observations by capturing peculiar composition interval in the restricted temperature range.

Previously, binary mixtures of water with DMSO, in particular at a low DMSO concentration, were the subject of study in different laboratories [2–7]. Specifically, in [3, 4] the focus is on the composition trends of certain properties at a single temperature 300 K. The NPT setup was used. On the other hand, the NVT simulations at 298.15 K, 318.15 K and 338.15 K and at a fixed DMSO molar fraction ($X_{\text{dmso}} = 0.055$) were performed. The experimental density values were assumed. In this study, we have chosen quite popular, nonpolarizable, P1 and P2 models for DMSO species [8], from a huge set of force fields for DMSO [9, 10], and well tested TIP4P-2005 water model [11]. Technical details of our isobaric-isothermal molecular dynamics computer simulations were described very recently in the previous publication on the topic [2].

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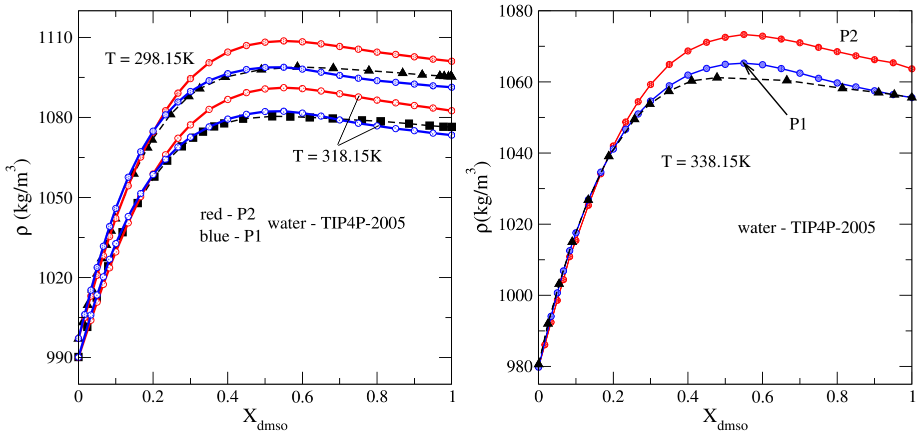

Figure 1. (Colour online) Panel a: Composition dependence of the density of water-DMSO mixtures from the NPT MD simulations of P2-TIP4P-2005 model (solid red lines), P1-TIP4P-2005 model (solid blue lines) in comparison with the experimental data (dashed lines with triangles) at 298.15 K [12] and at 318.15 K (dashed line with squares) [13]. Panel b: Similar to the panel a, but at 338.15 K. Experimental data (dashed line with triangles) are from [14].

As common, the strategy of exploration is to describe a desired property on composition and to capture its deviation from ideality as well. We do that for the mixture density at each fixed temperature. A set of results is shown in figure 1. The panel a of this figure refers to $T = 298.15$ K and $T = 318.15$ K, whereas the panel b illustrates the results at $T = 338.15$ K. This temperature was also chosen in [5] due to the availability of experimental data. From the inspection of the results, we observe that the P1-TIP4P-2005 and P2-TIP4P-2005 are quite accurate in the interval of composition from pure water, $X_{\text{dmso}} = 0$, up to $X_{\text{dmso}} \approx 0.2$. At a higher DMSO content in the mixture, the simulation data begin to deviate from the experimental results. The maximum density at a certain composition, $X_{\text{dmso}} \approx 0.58$, is captured by both models in question. Nevertheless, it can be seen that the P1-TIP4P-2005 model performs much better than its P2-TIP4P-2005 counterpart. This latter model overestimates the density in the interval above $X_{\text{dmso}} > 0.2$. Moreover, the deviation from the experimental points does not decrease while the temperature grows from 298.15 K up to 338.15 K. The P1-TIP4P-2005 model exhibits a small inaccuracy for density at “intermediate” compositions, but performs much better than P2-TIP4P-2005. It is difficult to judge the precision of computer simulations data at low X_{dmso} values at the scale in the figure 1. Better insights follow from the excess properties.

We describe geometric aspects of mixing of the species in terms of the excess mixing volume defined as common, $\Delta V_{\text{mix}} = V_{\text{mix}} - X_d V_d - (1 - X_d)V_w$, where V_{mix}, V_d and V_w refer to the molar volume of the mixture and of the individual components, DMSO and water, respectively. Apparently, this property is not strongly dependent on temperature in the interval we deal with. This follows from the experimental results shown in figure 2. The mixing volume slightly decreases in magnitude upon increasing temperature, as expected. In general terms, computer simulation results show that the excess mixing volume is overestimated in the framework of models assumed. Thus, the mixture of water and DMSO species from simulations is predicted to be more non-ideal than its laboratory counterpart in almost entire composition range at $T = 298.15$ K. The ΔV_{mix} values from simulations decrease in magnitude in agreement with experimental trends. However, the location of the minimum along X_{dmso} axis from simulations and experiments is slightly different. Finally, one can observe that the performance of the P1-TIP4P-2005 model is slightly better compared to the P2-TIP4P-2005 model.

In order to discern the contribution of each species of the mixture into the mixing volume, it is common to resort to the excess partial molar volumes as we have done recently [2]. However, similar insights into the geometric aspects of mixing on composition, both from experiments and simulations, can be obtained by resorting to the notion of the apparent molar volume of species, rather than to the partial molar volumes.

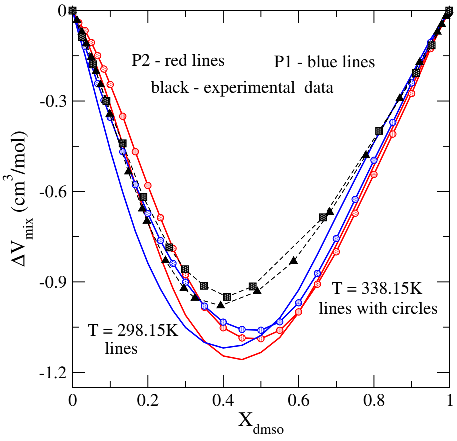

Figure 2. (Colour online) A comparison of the composition dependence of the excess mixing volume of water-DMSO mixtures for two DMSO models, P1 and P2, combined with TIP4P-2005 water model, with the experimental data at 298.15 K ([12]—black triangles) and at 338.15K ([14]—black squares).

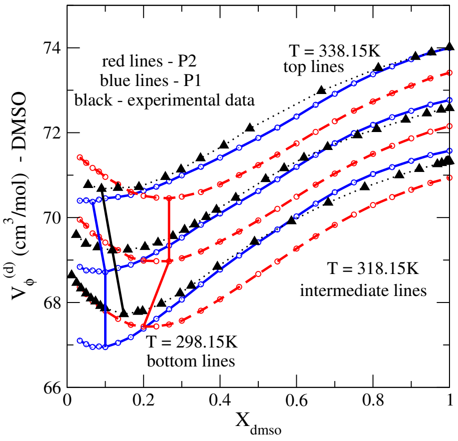

Figure 3. (Colour online) A comparison of the composition dependence of the apparent molar volume of DMSO from simulations with the experimental data marked as triangles from [12] at 298.15 K, from [13] at 318.15 K and from [14] at 338.15 K.

The apparent molar volume for each species, according to the definition [15], is: $V_{\phi}^{(w)} = V_w + \Delta V_{\text{mix}}/(1 - X_d)$ and $V_{\phi}^{(d)} = V_d + \Delta V_{\text{mix}}/X_d$. We elaborated the experimental density data from [12, 13] and the results from our simulations to construct the plots shown in figures 3 and 4. The most important and illuminating results for the apparent molar volume for DMSO species, $V_{\phi}^{(d)}$, are shown in figure 3. Namely, we observe that both models in question predict the existence of miminum at certain composition X_{dmso}. The points describing the location of the minimum at different temperatures from simulations and experiments are joined by respective lines. Evolution of the minimum with temperature is appropriately captured by the P1-TIP4P-2005 model in contrast to the P2-TIP4P-2005 model. Moreover, the P1-TIP4P-2005 model correctly predicts that the hydrophobic trends diminish with increasing temperature. Performance of the P2-TIP4P-2005 model in this aspect contradicts the experimental trends and is not satisfactory. We have obtained the minimum for $V_{\phi}^{(d)}$ for this model, even at a higher temperature equal to 358.15 K (the respective plot is not shown for economy of space).

Concerning the behaviour of the apparent molar volume of water species, $V_{\phi}^{(w)}$, upon composition (figure 4), it is worth to mention a rather satisfatory performance of the P1-TIP4P-2005 model in the entire composition range, especially for higher temperatures. The respective figure at 298.15 K is given in [2] (figure 3d). It is necessary to mention, however, that the experimental results for DMSO-rich (more specifically, extremely rich) mixtures are difficult to obtain precisely, because high-purity DMSO is an exceedingly hygroscopic solvent, the discussion of this issue is given in [12].

To conclude, we have established that the P1 and P2 models for DMSO combined with the TIP4P-2005 water model yield a minimum of the apparent molar volume for DMSO species at low values for X_{dmso}. This behavior is the manifestation of hydrophobic effects in these mixtures at a specific composition interval. However, it appears that the predictions from P1-TIP4P-2005 model agree better with the experimental trends than the ones from P2-TIP4P-2005 model. Moreover, the P1-TIP4P-2005 model predicts the existence of a minimum of $V_{\phi}^{(d)}$ for DMSO within the correct temperature interval from 298.15 K up to 338.15 K. At this highest temperature, the minimum almost disappears, as deduced from experimental data. By contrast, P2-TIP4P-2005 model does not provide an accurate estimate for a peculiar composition interval and does not yield a decay for the hydrophobicity trends on temperature. In various publications this model is claimed to be the best, see for example [18]. Here, we show that this conclusion is valid in certain aspects at a room temperature only. In addition, it is important to mention that the combination of the OPLS model for DMSO with TIP4P-2005 model for water does not provide a correct composition dependence of density at room temperature, cf. figure 2 of [2] and at temperatures of this study. In consequence, the anomaly of the apparent molar volume is not captured by this type of model at all. These results are available upon request.

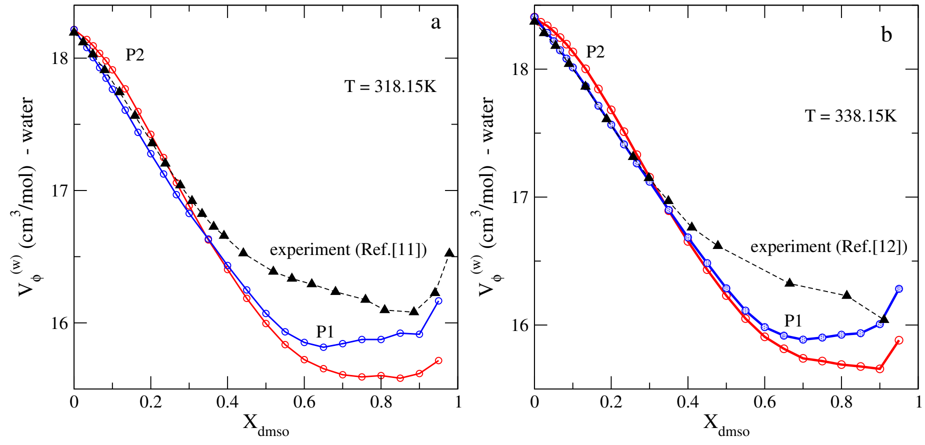

Figure 4. (Colour online) Panels a and b: A comparison of the composition dependence of the apparent molar volume of water from simulations with the experimental data (triangles [13]) at 318.15 K and [14] at 338.15 K. Similar plot at 298.15 K is shown as figure 3d of [2].

Previously, we explored the minimum of the methanol apparent molar volume on composition for water-methanol mixtures [16] at 298.15 K, see also [17] for the interpretation of the observed phenomena. This kind of system is the mixture of two hydrogen bonded liquids. By contrast, in the systems of the present study there is no bonding between the DMSO solutes in water. Apparently, the temperature trends should be slightly different for these two classes of systems.

In addition, it seems intriguing to investigate the evolution of trends of hydrophobicity in water-DMSO mixtures upon changing the external pressure as well. One can be guided by important experimental observations, see e.g., [19, 20]. More generally, from the simulations perspective it is challenging to construct a more complete map of anomalies, in pressure, temperature and composition variables, that would involve, for example, the temperature of maximum density and the minimum of isothermal compressibility, even by using the non-polarizable models. These data would serve as a useful benchmark for the following development of polarizable models. In the case of water-DMSO mixtures, certain progress has been reached at this level of modelling in [21, 22]. However, the BK3 polarizable water model seems to be a more convenient starting point, because the principal anomalies of pure water are quite well captured in this framework [23, 24]. Some of these issues are under study in our laboratory.

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Аномалія видимого молярного об’єму рідких сумішей вода-диметилсульфоксид. Комп’ютерне моделювання методом молекулярної динаміки

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Досліджено концентраційну залежність густини рідких сумішей вода-диметилсульфоксид (ДМСО) при різних температурах з використанням комп’ютерного моделювання методом ізобарично-ізотермічної молекулярної динаміки. Розглядаються неполяризовні напівгнучкі моделі P1 і P2 для молекули ДМСО у поєднанні з моделлю TIP4P-2005 для води. Наведено результати обчислень для надлишкового об’єму змішування та видимих молярних об’ємів компонент суміші. Встановлено, що модель P1-TIP4P-2005 для цієї суміші забезпечує дуже добрий опис положення мінімуму видимого молярного об’єму компоненти ДМСО, який вказує на аномалію. Найбільш важливим є те, що вибрана модель, на відміну від її відповідника P2-TIP4P-2005, правильно передбачає наявність температурного інтервалу, в якому існує гідрофобний ефект.

Ключові слова: *молекулярна динаміка, суміші вода-диметилсульфоксид (ДМСО), видимий молярний об’єм*