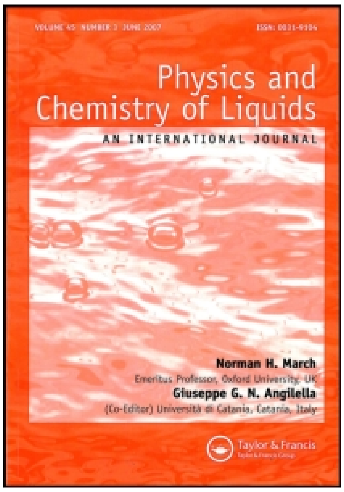

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Structure of acetone and dimethyl sulfoxide from Monte Carlo simulations and MM2 calculations

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Structure of acetone and dimethyl sulfoxide from Monte Carlo simulations and MM2 calculations

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The structure of acetone and dimethyl sulfoxide in the liquid phase is investigated using Monte Carlo simulations and MM2 calculations. The principal site–site correlations and degree of structure in both liquids have been investigated. The results showed that dimethyl sulfoxide is more structured than acetone. At short distances the dipoles of neighboring molecules are found to be in antiparallel configurations, but further apart the molecules tend to be aligned predominantly as head to tail. In both liquids there is evidence of strong methyl–oxygen interaction, important to the structure of the liquids. The contacts suggest weak hydrogen bonds between methyl hydrogen and oxygen.

Keywords: Acetone; Dimethyl sulfoxide; Monte Carlo simulations; MM2 calculations; Liquid structure

1. Introduction

Intermolecular interactions in the liquid state is a challenging subject to be investigated, since understanding those interactions is essential to understand medium effects on the structure and reactivity of molecules [1–3]. Keeping that in mind, we have recently undertaken theoretical investigations of pure polar aprotic organic liquids and binary mixtures emphasizing relationships among intermolecular interaction, structure and thermodynamic properties [4–8]. Acetone and DMSO are two of the mentioned type of liquids, widely used as organic solvents. Both have high dielectric constants and dipole moments (listed in table 1) in the gas phase [9].

Despite the similarity in the molecular formula of the molecules, they adopt different geometries, which are, a pyramidal shape for DMSO (C_s geometry) with

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an S=O polar group on one edge of the pyramid, and a triangular planar shape for acetone (C_{2v} geometry) with the central carbon on the geometric center of the triangle. In both cases there is a possibility of hydrogen bond formation with the neighbors and the two CH_3 groups can originate hydrophobic effects when in an aqueous medium. The polarity of the DMSO S=O bond has been investigated [11–13], which permits the conclusion that an S^+–O^- formulation is a best representation for the S/O bond rather than a formal double bond as aforementioned. On the other hand, the C=O bond in the acetone is a formal double bond. This might be in the root of the difference of the dielectric constant and dipole moment between the two liquids.

Both DMSO and acetone have received a great deal of attention by diffraction [14–19] as well as simulation [6,16,17,20–30], although the structure of pure acetone has not been as widely reported as that of DMSO. DMSO has been the subject of special attention because of its numerous applications in many branches of chemical and biochemical sciences [31,32]. In previous works, we have reported studies of the acetone–water mixture and pure liquid DMSO, both using Monte Carlo simulations [6,8]. Computational simulations are very useful techniques to study the structure of molecular liquids, since they permit to obtain detailed radial distribution functions (rdf) of the liquids. The insights given by site–site correlation functions calculated by computer simulations can be very useful in the interpretation of the liquid structure, since, because the presence of many scattering centers in polyatomic molecules as well as in the neighborhood of molecules in condensed phase, diffraction experiments for molecular liquids present strong interference of scattered waves [33], making difficult the experimental study of the liquid structure. Very recently McLain *et al.* [34] published an article reporting a comparative study between the acetone and DMSO structure using neutron diffraction and computer simulation by empirical potential structure refinement. The article is very elucidative and the authors discussed the similitude and differences between the molecules raised from their results. The liquids are similar in several aspects, the differences being over all a consequence of the molecular geometries. DMSO is more structured than acetone [34]. In the present article, we analyzed results obtained by Monte Carlo simulations for both the liquids. The results seem to be worth publishing since they complement some aspects presented in the mentioned article [34]. Moreover, they are useful because, as they were obtained through another technique and so help to corroborate the previous results [34], as well as presenting a new point of view for the finds.

Table 1. Values of some properties [9] for acetone and dimethyl sulfoxide at 25°C.

Property	Acetone	DMSO
Boiling point (°C)	56.2	189.0
Melting point (°C)	−95.35	18.54
Density ($g\,cm^{-3}$)	0.790	1.095
Dielectric constant	20.7	47.2
Dipole moment (D)	2.88	3.96
Heat of vaporization ($kcal\,mol^{-1}$)	7.41	12.64 [10]
Heat capacity (C_p) ($cal\,mol\,K^{-1}$)	30.21	36.60

2. Computational details

2.1. *The intermolecular potential function*

Following usual procedures in force field calculations, the molecules were modeled by collections of interacting sites, and the energy E_{ab} between molecules *a* and *b* represented by a sum of Coulomb and Lennard Jones potentials centered on the sites:

$$E_{\mathrm{ab}} = \sum_{ij} \left[\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{r_{ij}} \right] \tag{1}$$

where r_{ij} is the distance between site *i* in a and site *j* in b and q_i and q_j are fractional point charges located on the *i* and *j* molecular sites (it has been supposed that the electrostatic contribution to the intermolecular potential is suitably represented by fractional charges located on the molecular sites). For each site *k*, the parameters A_{kk} and B_{kk} were given by $A_{kk} = 4\varepsilon_k \sigma_k^{12}$ and $B_{kk} = 4\varepsilon_k \sigma_k^{6}$, where ε_k and σ_k are the Lennard–Jones parameters for the *k*th site. Parameters A_{ij} and B_{ij} for a non-diagonal interaction $[i, j]$ were obtained using the geometric combining rules $A_{ij} = (A_{ii}A_{jj})^{1/2}$ and $A_{ij} = (B_{ii}B_{jj})^{1/2}$ [35]. There are other types of combining rules that have been used to take into account these interactions [35].

2.2. *Molecular models*

A four-site potential optimized previously in this laboratory was used for DMSO [6] while for acetone the OPLS potential was used [36]. Both are rigid models, therefore, contributions from intramolecular relaxation effects were not considered, an approximation which have been successfully used in liquid simulations [8]. McLain *et al.* have used the *P*1 and *P*2 potentials of Luzar and Chandler [21] for DMSO and for acetone the potentials developed by Ferrario *et al.* [37] as well as a potential developed by Wheller and Rowley [38]. Other potentials have been published [20,22,23], all of them rigid models. In table 2, the Lennard–Jones potential parameters used for both liquids in this work are shown.

2.3. *Monte Carlo simulations*

The simulations were carried out in the NPT *ensemble* at 298 K and 1 atm with Metropolis importance sampling and periodic boundary conditions on systems

Table 2. Values of the potential parameters for DMSO (the three first parameters) and acetone (the last three) used in the simulation.

Site	σ (Å)	ε (kcal mol^{-1})	q (au)
O	2.94	0.066	−0.53
S	3.56	0.202	0.17
CH_3	3.80	0.190	0.18
O	2.96	0.210	−0.424
C	3.75	0.105	0.300
CH_3	3.91	0.160	0.062

consisting of 400 molecules placed in a cubic box [39]. In the calculation of the total configurational energy using equation (1), a full intermolecular interaction was considered whenever any of the site-to-site distance r_{ij} fell bellow a cutoff radius of 11 Å. The contributions of Lennard–Jones interactions beyond the cutoff radius were considered using the formalism presented by Allen and Tildesley [35]. Several methods are used to take into account long-range Coulombic interactions. In the present calculations these interactions are not be considered beyond the cutoff radius. Reasons for using this methodology have been discussed previously [8]. Site–site pair correlations, thermodynamic properties, and single particle dynamics of polar liquids appear to be quite insensitive to the long-range forces in the system [5]. Starting from the initial distribution of molecules in the central box, new configurations were generated by randomly translating and rotating a randomly chosen molecule along Cartesian coordinates. As the calculations were carried out in the NPT ensemble, new configurations were also generated through volume changes. A volume movement was tried on every 500th attempted molecular move. After volume changes, the center of mass coordinates of all molecules in the reference box were scaled in the usual way [35]. Ranges for translating and rotating the molecules and for volume moves were adjusted to yield an acceptance/trial ratio between 0.40 and 0.45 for new configurations. Each calculation started with an equilibration phase with 1.2×10^7 configurations, and the averages were then obtained after a new segment with other 1.2×10^7 configurations. Statistical uncertainties were calculated from separate averages over blocks of 2×10^5 configurations.

3. Results and discussion

3.1. *Radial distribution function*

Radial distribution function (rdf) plots for both liquids are shown in figure 1.

Our results for DMSO show general agreement with other theoretical ones published earlier [20,21] and, more recently, with the results of McLain *et al.* [34]. Despite the great difference verified in the Lennard–Jones ε parameter of the oxygen atom of the

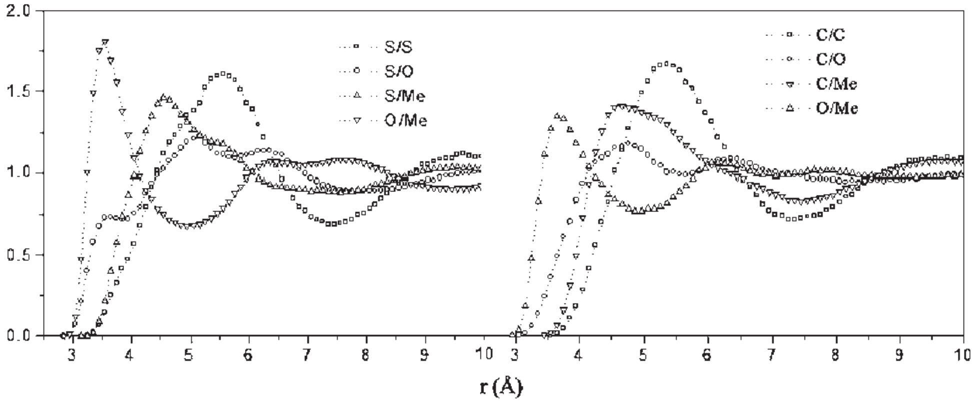

Figure 1. Plots of radial distribution function for DMSO (left) and acetone (right).

DMSO model used in this work and the model developed by Luzar and Chandler [21], used for McLain *et al.* [34], the rdf are quite similar between both the models. All correlation distances agree with intermolecular correlation reported previously [34,40]. The site–site rdf's showed for both liquids are characteristics of liquids with little inner structure (large band and intermolecular mean distance about 5.5 Å). Integrating the S–S rdf from DMSO and C–C rdf from acetone up to the first minimum distance a coordination number of 12 was obtained for both cases. This value agrees with those found by Luzar and coworkers from dynamics molecular simulation and neutron diffraction for DMSO [16] and by Bertagnolli and coworkers for acetone [15], and is the characteristics of a non-associated packed liquid [41]. The shortest pair–pair intermolecular correlation is the O–Me in both the liquids, more intense in DMSO. Previous works on DMSO have based on this peak to suggest the presence of weak O–Me hydrogen bond in the liquid [16,21], however, as pointed out by McLain *et al.*, this datum for itself is a weaker evidence of the existence of hydrogen bonds in DMSO as well as in the acetone [34]. Previously, Luzar and Chandler have shown that a substantial part of this peak correlation can be attributed to packing effects in the DMSO liquid, and not solely to the molecular association effects (simulations made with null charge on methyl group produce a O–Me rdf peak with practically the same height) [21]. Although nothing about that has been found in the literature concerning acetone, the great similarity between the rdf graphics of both liquids permits to infer that these considerations could be applied to acetone too. Studies based on dielectric data discard the possibility of a defined alignment between DMSO molecules in the liquid, and emphasized that any form of molecular array existent in the liquid must be related with dipole–dipole interaction between the molecules [42]. Since that the rdf's of both liquids are quite similar, this must be equally true for acetone. Anyway, the O–Me interaction must play an important role in the intermolecular arrangement of these liquids.

3.2. *MM2 calculations*

As it has been published in previous reports [43], it has been intended to obtain the dimer configuration that reproduces the rdf for both liquids by using molecular mechanics at MM2 level [44]. The calculations have been performed using the PCModel program [45]. Such calculations have arisen two stable dimers for both liquids that are shown in figure 2; acetone dimers a and b at left and DMSO dimers c and d at right. Let us start with the analysis for acetone.

The dimer a is the same reported by Frurip *et al.* and labeled *A* in their article [46]. The structure has formation energy of $-4.53\,\mathrm{kcal\,mol^{-1}}$, in good agreement with that estimated by Frurip and coworkers ($-4.92 < \Delta E_{\mathrm{el}} < -4.71\,\mathrm{kcal\,mol^{-1}}$). It was not possible to obtain the structure labeled b by Frurip *et al.* [46], because it collapses to structure a. The dimer b has formation energy of $-2.43\,\mathrm{kcal\,mol^{-1}}$, and it is less stable than the dimer a. The rdf plots shown do not agree with the structure reported for liquid acetone by Bertagnolli and coworkers, mainly because the O–O pair correlation, that show coordination of oxygen by two oxygen atoms at a distance of 3.0 Å [15], are not verified in the simulations reported here. According to the results published by McLain *et al.* [34], both liquids are organized in such a way that at short distances the neighboring molecules are found to be in antiparallel configurations respecting their

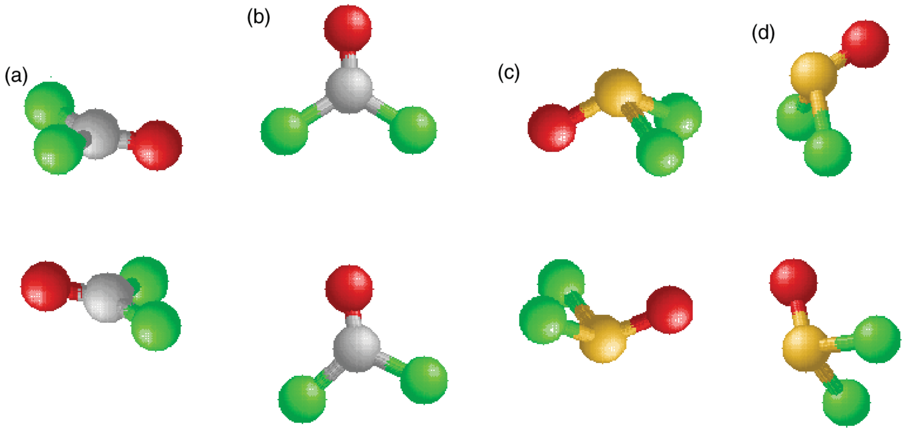

Figure 2. (a) The most stable dimer of acetone in gas phase, (b) the dimer that reproduce the $g(r)$ plots as found with the PCModel program. d(C–C) = 5.2 Å, d(C–Me) = 4.6 Å, d(O–Me) = 3.4 Å, d(O–C) = 4.0 Å (the listed distance are between the closest sites), (c) the most stable dimer of DMSO in gas phase, (d) the dimer of DMSO that reproduce the $g(r)$ plots as found with the PCModel program. d(S–S) = 5.4 Å, d(S–Me) = 4.7 Å, d(O–Me) = 3.3 Å, d(O–S) = 5.6 Å.

dipoles, whilst further out the molecules tend to be aligned as head-to-tail, resembling dipolar ordering. It is interesting to notice that the dimers a and b, obtained by MM2 calculations are exactly these two types of dimers, and that the results of McLain *et al.* [34] shown that the dimer a (the most stable), is the dimer that populates predominantly the short distances. On the other hand, the dimer b is the dimer that better agrees with the $g(r)$ plots (some site–site distances are listed on the figure caption). This finding permits to infer that dimer b contributes more to the $g(r)$ than dimer a. It is interesting to notice also that the dimer a has a dipole moment roughly zero, while dimer b has dipole moment of 5.6 D. This indicates that in the liquid phase the dimer that has a higher dipole moment predominates on the more stable one. This seems to be an indication that a dimer with dipole moment zero is an individual species, and does not contribute for the arrangement that raises the liquid structure. This analysis is valid for acetone as well as for DMSO. In the dimer b each methyl group has two hydrogen atoms located at 3.0 Å from oxygen and one at 4.0 Å. These values agree with the ones reported by Frurip and coworkers [46], that showed by *ab initio* STO-3G calculations there is a small charge transference between the molecules and an increased polarization of the electronic charge in both the molecules. Both these effects are observed in hydrogen-bonded molecules in a stronger degree. So, the O–Me site–site interactions seems to present in some extension a kind of weak hydrogen bond interaction. It is interesting to observe a little unalignment between the dipoles of the dimer b, which agrees with the Kirkwood factor obtained for acetone of 1.11 [15].

Let us now to analyze the results for DMSO, dimers c and d at the right on the figure 2. The most stable dimer is the anti parallel dimer c that has a formation energy of $-5.24\,\mathrm{kcal\,mol^{-1}}$ and a dipole moment roughly zero, whilst the dimer d presents a formation energy of $-3.74\,\mathrm{kcal\,mol^{-1}}$ and a dipole moment of 6.4 D. Both dimers agree with the results related for McLain *et al.* [34] Such for acetone, at short distances neighboring molecules are predominantly found as dimer c, while further out the molecules tend to align as dimer d. Also, as such for acetone, dimer c does not

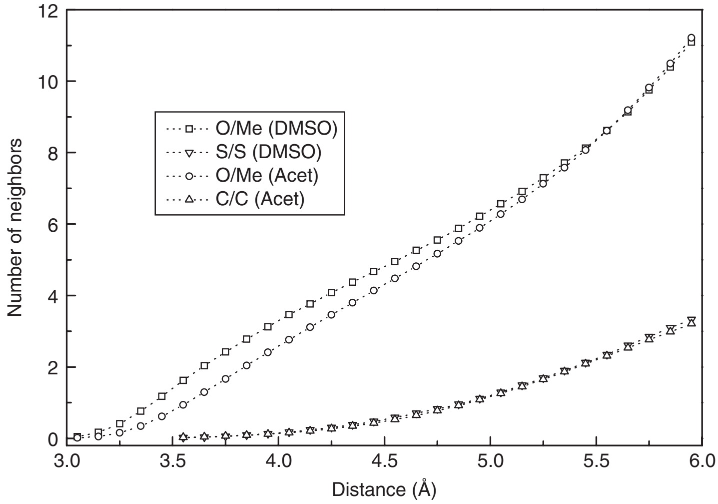

Figure 3. Number of neighbors as a function of distance obtained from the integration of $g(r)$ curves for both liquids.

contribute too much for the $g(r)$ plots, which are predominantly described for dimer d. Such as for acetone in the liquid phase predominates the dimer that has a higher dipole moment instead of the more stable one. It could be proposed that the behavior found for acetone and DMSO in this work and also by McLain *et al.* must be characteristic of these type of liquids. Such in dimer b as in d the shortest intermolecular correlation is between oxygen and hydrogen of methyl groups, and the distances between them are roughly the same of the acetone. Of course, it is difficult to ensure the existence of hydrogen bonds between these atoms, even the weak hydrogen bonds, based only in the discussed distances.

3.3. *Coordination numbers*

From the integration of the $g(r)$ plots, it is possible to obtain the plots of coordination numbers as a function of the intermolecular distance shown in figure 3. The curves of site–site "center of mass" correlations (C–C in acetone and S–S in DMSO), show a behavior typical of non-organized liquids. The number of neighbor molecules increase in a smooth way as the site–site distance increase. So, from this point of view both liquids have the same degree of disorder. However, the analysis of O–Me site–site correlation, the most important correlation accordingly the site–site $g(r)$, permits to infer that DMSO is a little more organized than acetone, since the $g(r)$ curve presents a incipient plateau, less visible in acetone. The flatter the plateau the more organized the solvation shell.

4. Conclusions

Through a detailed study of the liquid structure by Monte Carlo simulations and MM2 calculations it was found that DMSO and acetone show similarities but also stressed differences between their nearest-neighbor dipole alignments in the liquid. The structure of the liquids are strongly influenced by the shape of the molecule, with a predominance of close contacts around the oxygen atom of both molecules. The stronger correlations are between oxygen and methyl groups. A general behavior for both molecules is that outside of the antiparallel alignment prevailing at short distances, the molecules adopt more a head-to-tail configuration, reminiscent of the dipole ordering over long-distance scales. In both liquids, there is evidence for weak intermolecular Me–H $\cdots$ O contacts.

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