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A MOLECULAR DYNAMICS SIMULATION STUDY OF Li^+ - Cl^- ION PAIR DISSOLVED IN DMF (-d7).

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Abstract

The molecular dynamics simulation of Li^+- Cl^- ion pair dissolved in liquid N-N dimethylformamide (DMF-d7) has been performed in order to study the mobility and the solvation structure of these ions in the solution at room temperature. The calculations were based upon an optimized 6-site effective potential model employed in the simulation to describe the DMF-DMF and ion-DMF interactions. All relevant site-site pair correlation functions between each ion and the interaction sites of the DMF solvent , as well as the velocity autocorrelation functions of the ions and the DMF-d7 solvent have been obtained. The self-diffusion coefficients of the ions in the solution were calculated and the obtained values are found to be realistic. In the case of DMF-d7 as solvent, the diffusion coefficient of the solute Cl^- ion has been found to be smaller than that of the solvent. This result has been discussed in terms of the cage connectivity around the ion. The number of DMF molecules in the first coordination shell around each ion was estimated. Also, by inspecting the short range behavior of the predicted PCFs, it was possible to propose the most likely arrangement of the DMF solvent and the Cl^- and the Li^+ ion. Finally, the results are compared with those from a previous neutron diffraction study with chlorine isotopes substitution on LiCl in fully deuterated DMF solution.

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1. INTRODUCTION

N,N-Dimethylformamide (DMF, $HCON(CH_3)_2$) is a small and relatively simple molecule containing the biologically important amide group. The liquid is a widely used organic solvent and provides very interesting physicochemical properties. Among the amides, liquid DMF is of particular interest due to the lack of hydrogen bonding and therefore, it is a suitable system for investigation dipolar interactions. Moreover, the molecule in the gas phase has a relatively large dipole moment of about 3.8 D [1]. It is also expected that in the liquid state the dipole-dipole interactions will dominate the intermolecular forces and should form well ordered intermolecular structure [2].

In view of the importance of this molecular system, the pure liquid and its mixtures have been the subject of numerous experimental studies. These studies include thermodynamic, transport and spectroscopic measurements. Thus, the densities and viscosities, as well as the diffusion coefficients of the liquid were obtained and discussed in a wide temperature range[3]. The anisotropic rotation motion of the molecules in the liquid has been also studied by different spectroscopic techniques [4-8].

Recent ab initio quantum mechanical studies [9] at HF, MP2 level of theory and density functional calculations have shown that the equilibrium structure of DMF molecule has C_S symmetry with a planar nitrogen bond configuration. Moreover, the intermolecular structure of the liquid has been studied by X-ray diffraction (XD) experiments [10,11] and also by computer simulation (CS) studies [12-16].

To our knowledge, due to the great technological and academic interest, the investigation of the ion solvation processes in aqueous and in nonaqueous solutions has proliferated in recent years. Among the nonaqueous electrolyte solutions, several metal ions in DMF solutions were recently studied by means of X-ray diffraction, neutron scattering and EXAFS (extended X-ray absorption fine structure) measurements [17-20]. More recently, structural results obtained from a neutron diffraction study with chlorine isotopes substitution on LiCl in fully deuterated DMF(-d7) solution have been reported [21]. On the basis of these results the number of DMF molecules around the chlorine ion was estimated. Also, the most likely arrangement of the DMF solvent and the chlorine ion was proposed and discussed in terms of the solvent properties. However, apart from the intrinsic information about the solvation structure that this neutron diffraction study can give us, a large number of questions concerning the properties of this solution remain to be answered. For example, the previous experimental study provided very useful results about the Cl^- related total radial distribution function, $G_{Cl}(r)$, which is the sum of the weighted partial pair distribution functions $g_{xy}(r)$ (x=Cl, y=O, D, C, N, Li, Cl). Consequently, this function includes information about all of these partial pair distributions and the exact determination each of them is a crucial experimental problem. On the other hand, the knowledge of the behaviour of these functions at short and intermediate distances offers the possibility to determine precisely (at a microscopic level) the most probable solvation structure of the electrolyte solution.

In the present work we start to study the properties of the Li^+- Cl^- ion pair diluted in DMF-d7 using molecular dynamics (MD) simulation techniques. As far as we know, this is the first CS treatment on this electrolyte solution. We mention however that electrolyte solutions of several ions in other organic solvents have been already investigated by means of MC and MD techniques [22,25]. The present study is mainly motivated by the predictions of the previous diffraction experiment on this molecular system. Therefore, our objective here is to study the structural and some dynamical properties of the Li^+ and Cl^- ions in this highly dipolar liquid. Attention will be also paid to the interactions between the various species in the solution.

Finally, the computational procedure and the obtained results are presented and discussed herein.

2. MOLECULAR DYNAMICS SIMULATION

Potential models

It is well-known that the success of the computer simulation (CS) studies depends thoroughly on the potential models used to describe the interactions of the molecules in the simulated fluids. In fact, potential interaction models between molecules may either be determined empirically or obtained from quantum mechanical calculations for two isolated molecules. In the second case the derived potentials are usually satisfactory in reproducing properties of dimers and small aggregates [26]. However, it is widely accepted that these potential models have a limited utility in CS studies of molecular liquid systems. On the other hand, previous extensive CS studies on various dense fluids have established that empirical potentials can be devised in order to overcome this difficulty. It should be emphasized furthermore that, in the most of these studies the molecules in the system interact in a pair-wise additive fashion. In some cases the well-known polarization effects on molecules has been implicitly (in an average sense) incorporated in the effective potential parameters [27]. This can also be done by taking the polarization effects explicitly into account. Of course, the use of polarizable potentials in CS studies requires an significant increase in CPU time and computer dynamical memory. However, this procedure has already been used successfully in CS studies of a limited number of molecular liquids [28].

Following the literature, we can see that CS studies on pure liquid DMF have been performed in the past. Thus, before proceeding further it is interesting to mention these studies in brief. As far as we know, the first CS treatment on this system was a MC study reported by Jorgensen and Swenton [12]. This treatment was carried out in the NPT ensemble at 298 K and was based on an optimized 5-site pair-wise additive potential model (hereafter refereed as model A). We mention here that the predicted densities and heats of vaporization are found to be in good agreement with experimental results. However, this study was limited to the calculation of thermodynamic and structural properties of liquid DMF. In a subsequent MC study [29] of this system, the authors pointed out that the thermodynamic and structural properties are unaffected by the inclusion of long-range electrostatic interactions in the form of the reaction field [30]. However, they found that the calculated cross dipole-dipole correlation function, at various dipole-dipole distances r, is very sensitive to these forces and to the simulation conditions.

To the best of our knowledge, only a limited number of MD simulation studies on this liquid have been reported. The first MD simulation of DMF was reported by Yashonath and Rao [13]. This treatment was carried out in NVE ensemble based on a very small number of molecules (N=64) in the central simulation box. The potential model used was that of the above mentioned as model A. Only one thermodynamic point of the liquid, corresponding to the room temperature and normal pressure, has been investigated. Moreover, according to the presented technical details in this paper, the simulation was extended to a time interval of about 20ps, which is relatively very small in order to calculate accurately time correlation functions of various dynamical properties. More recently, Schoester et al. [15] published a MD study of the intermolecular structure of the liquid amides FA, NMA and DMF at 289 K. In the frame work of this study, the intermolecular interactions were reinvestigated and a new generalized optimized potential model for these molecular systems has been proposed. In this case, the DMF-DMF optimized potential was a 6-site pair-wise additive model (hereafter refereed as model B). It is interesting to note here that the distinct structure functions kH(k) obtained from X-ray diffraction [10,11] measurements and from this MD study are found to be in agreement. Small discrepancies, however, between them at small k values have been obtained. Note also that the obtained MD results about the energetic and dynamical properties of the system have not been reported in this or in another subsequent paper. In order to check to what extent the bulk properties of DMF depend on the details of this potential model, we have performed trial MD calculations with 256 and 500 DMF molecules at 298 and 373 K using the parameters and the molecular geometry employed in the previous treatment. The obtained results have shown that the 6-site model B overestimates the mean potential energy of liquid DMF by about 7% and predicts too high pressure (1.2 Kbar) at these thermodynamic points. Also, we found that this model underestimates the diffusion coefficients by a factor of 2.6 compared to the experimental values. Therefore, while model B gives relatively good structural results in comparison with experimental data, it is unreliable in reproducing successfully the bulk properties of this liquid.

Finally, J. Gao et. al. [16] reported recently a MC study of liquid amides FA, NMA, NMF and DMF. In the framework of this study the authors developed a polarizable potential model (hereafter refereed as model C). It is interesting to note that, the obtained heats of vaporization and densities for these liquids are found to be within 2% and 3% of experimental results, respectively. Also, in the case of liquid DMF they found that the polarization effects are about 6% of the total liquid energy, which corresponds approximately to about 4% of the system potential energy. In addition, they found that the van der Waals contribution to the energy of this liquid is greater than the electrostatic terms.

In the following, we describe some details of the potential model employed in the present MD study. Our potential model is constructed in the following way. The intermolecular DMF-DMF, DMF-ion and ion-ion potentials are taken as the site-site pairwise additive Lennard-Jones (LJ) and Coulombic terms. Specifically, the site-site potential is given by

$$U_{\alpha\beta}(r) = 4\,\varepsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^{6}] + q_{\alpha}q_{b}/4\pi\varepsilon_{o}r \quad , \qquad (1)$$

where α and β are interactions sites on different molecules, r is the site-site distance, q_α and q_β are the partial charges which coincide with LJ interaction sites. Note that the cross LJ interaction sites are obtained by using the Lorenz-Berthelot combing rules. Also, the long-range electrostatic interactions were handled by using the direct Ewald method. We have chosen this type of potential model for the following reasons. As mentioned above, the previous extensive MC study of Gao et al. has shown that, in the case of liquid DMF, the polarization effects contribute only a few percent to the mean potential energy of the system. Also, the obtained structural properties for DMF with polarizable intermolecular potential function (PIPF) are found to be in good agreement with previous MC results obtained with OPLS [12] potential models. Consequently, although an obvious advantage of the PIPF potential against OPLS models is its ability to provide useful information about the importance of polarization effects taken place on molecular processes involving significant changes in environment, concerning however the bulk properties of DMF both potential model approaches seem to be reliable. It should, however, be borne in mind that the PIPF formalism is more computationally intensive compared to the OPLS approach. Thus, taking into account the above considerations, we decided to employ the OPLS potential model given by Eq. 1.

According to this model, for the solvent-solvent (DMF-DMF) interactions we have employed a 6-site LJ (12-6) pair-wise additive potential plus charge-charge electrostatic terms. Each CH_3-group (cis , trans) is approximated as a united interaction site located at the position of the methyl carbon. Therefore, the main conceptual difference between our model and the two previous OPLS models (A,B) is the actual number of the interaction sites used per DMF molecule and the values of the parameters assigned to them. In addition, the employed molecular geometry of DMF was kept planar, while the polarization effects have been incorporated implicitly in the potential parameters. In order to refine the potential parameters, an extensive parametrization procedure was applied based on numerous MD simulations of the pure liquid. The initial LJ potential parameter values used in our iterative MD procedure are taken from the 5-site OPLS model A. The final potential parameter values were found to deviate slightly from those of the prior MC (A) study. However, we found that our parameter values differ significantly from those of model B [15]. Also, the local charge distribution used in our simulation is very similar to that employed in model A. We mention that the local charge on the formyl D [D (C=O)] atom was taken equal zero. This local charge distribution produces an effective dipole moment somewhat greater (4.42D) than the gas-phase experimental value (3.8 D). The energetic, structural and dynamical properties obtained by means of our MD simulation of pure DMF will be presented in a subsequent paper. At this point it is interesting to note that the calculated mean potential energy (44.2 KJ mol^{-1}) and pressure (0.1 Kbar) on the basis of our 6-site potential model show the best agreement with experimental results (44.4 KJ mol^{-1},0.001 Kbar) [31].

As mentioned above, for the ion-ion and ion-DMF interactions we have used potential models similar to the DMF-DMF model. Concretely, the ion-ion (Li^+-Li^+, Cl^--Cl^-) LJ parameter values were taken from a previous CS study of the Li^+- Cl^- ions in water [32]. The ion-DMF potential parameters are obtained by using the Lorenz-Berthelot combining rules. Finally, the model details and parameters are summarized in table 1.

Table 1: Intermolecular potential parameters and the local charge distributions of DMF, Li^+, and Cl^- ions used in the present MD study. The geometrical parameters of DMF molecule are taken from Ref. [10].

OPTIMIZED 6-SITE MODEL

	H	C	O	N	Me1(cis)	Me2(trans)	Li^+	Cl^-
σ (nm)	0.220	0.370	0.296	0.320	0.380	0.380	0.1518	0.4414
ε (K)	8.00	52.00	104.00	82.00	84.00	84.00	100.0	60.56
Q (e)	0.00	0.500	-0.500	-0.570	0.285	0.285	+1.0	- 1.0

Geometrical parameters of DMF molecule:

$r_{N\text{-}Me1}$= $r_{N\text{-}Me2}$=1.449 Å, $r_{C\text{-}O}$=1.229 Å, $r_{C\text{-}N}$=1.335 Å, $r_{C\text{-}H}$=1.090 Å

Bond angle, deg

< C-N-Me1	121.9	**< O-C-N**	122.9
< C-N-Me2	119.8	**< N-C-H**	114.5

Computational details

We have performed MD simulations of a system consisting of 254 DMF-d7 solvent molecules and a Li^+ (a) - Cl^- (b) pair ion. The simulations were carried out with periodic boundary conditions in NVE statistical mechanical ensemble. The electrolyte solution was studied by placing the ion pair in the equilibrated system at a suitable initial separation r_{ab} between 6 and 8 Å. The prepared new system was then equilibrated for a few picoseconds (30ps). The thermodynamic state considered for the simulated solution was chosen to make possible comparisons with experimental data. Thus, the system was simulated at temperature of 298 K and corresponding density. The molecular characteristics of DMF in the ground state, used in the present study, are given in table 1. As mentioned above, the interactions between the species in the system were site-site pair-wise additive . A spherical cutoff with half box length as the cutoff distance was used to truncate the short-range interactions. The long-range interactions were treated by using the Ewald method [33].

The orientation of the solvent molecules have been formulated using a quaternion interpretation. The translational and rotational equations of motion are solved using lepfrog algorithms. The employed integration time step was 3.10^{-15}s in all MD runs. We found that this time step insures stability of the calculated macroscopical properties. The number of the equilibration time steps was 170.000. Each production run was extended approximately to 250.000 time steps (750ps) and some of them longer. All MD computations were carried out on the system Convex C3820 and on the cluster of 8 HP-735 machines of the super-computing center of the university of Athens.

3. RESULTS AND DISCUSSION

Solvation structure

The solvation structure of this electrolyte solution has been studied by means of the most interesting pair correlation functions (PCFs). Due to the dilution of the two ions in DMF-d7 these functions are:

i) the two PCFs between each ion and the center of mass (COM) of the DMF solvents, namely $G_{Cl\text{-}DMF}(r)$, $G_{Li\text{-}DMF}(r)$, and

ii) the twelve site-site PCFs (six for each ion x: $G_{x\text{-}D}(r)$, $G_{x\text{-}o}(r)$, $G_{x\text{-}C}(r)$, $G_{x\text{-}N}(r)$, $G_{x\text{-}Me1}(r)$, $G_{xMe2}(r)$) between the ions and the interaction sites of the solvent.

All these correlations have been calculated and their characteristic extrema, as well as the estimated coordination numbers, are given in table 2. These PCFs are also shown in figures 1,2,4.

The ion-solvent and the solvent-solvent COM PCFs are presented in figure 1. As we can see from this figure, the DMF-DMF function is in excellent agreement with the corresponding results obtained in previous MC simulations of the pure liquid DMF [12,29]. Integration of the first peak up to the minimum of this function yields 12 or 13 DMF molecules. On the other hand, both the Li^+- DMF and Cl^- - DMF correlations are sharper peaked than the solvent-solvent correlation. Also, the first peak of these functions is located at shorter distance than the first peak of the DMF-DMF function. The appearance of these sharper peaks in these functions is a clear evidence that each ion in the solution is strongly solvated by a well-defined first solvation shell constructed by the most nearest solvent molecules. The DMF solvent first

Table 2: Peak positions and heights of the first maximum in the calculated PCFs(r($\overset{\circ}{A}$):$G_{a-b}(r)$). The second lines denotes the coordination numbers of the ions up to first minimum of the PCFs.

$G_{com-com}(r)$	DMF-DMF		Cl^--DMF		Li^+-DMF	
	5.5 :1.8		5.2:2.9		3.8:8.6	
	12.9		9.9		5.3	
$G_{Li-xsite}(r)$	Li^+-O	Li^+-N	Li^+-C	Li^+-Me1(-cis)	Li^+-Me2(-tr.)	Li^+-D
	2.0:46.8	4.1 :6.8	3.2:15.4	4.3:3.6	5.5:4.8	3.9:6.7
	5.3	5.6	5.3	6.1	8.4	6.1
$G_{Cl-xsite}(r)$	Cl^--O	Cl^--N	Cl^--C	Cl^--Me1(-cis)	Cl^--Me2(-tr.)	Cl^--D
	6.6:1.7	5.0:3.2	4.4:0.9	3.9:2.4	3.9:5.1	3.4:1.2
	17.8	10.4	2.0	4.3	8.1	2.3

shell around the chlorine ion is composed by about 10 and for the Lithium ion by about 5.3 molecules. This result is a consequence of the different distribution of the DMF molecules

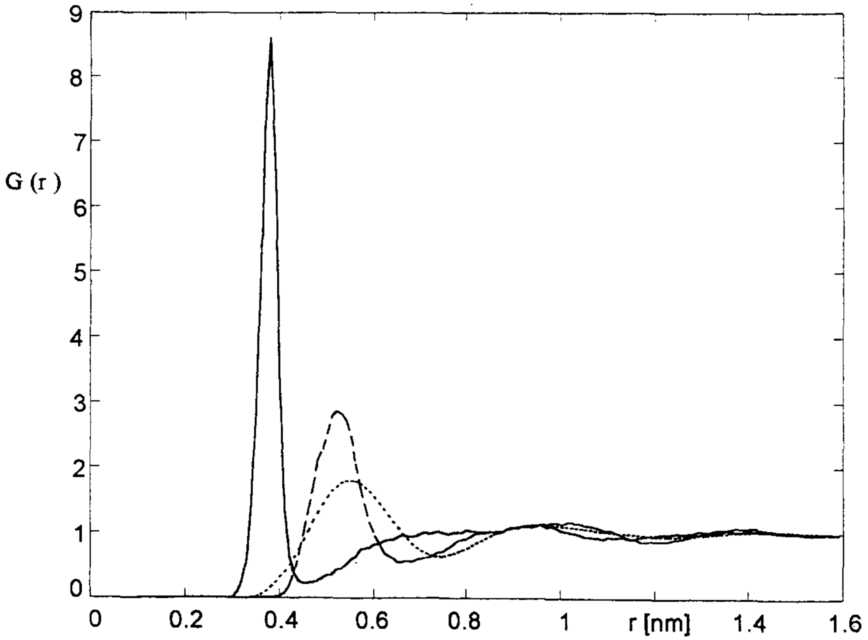


Figure 1: The simulated center of mass pair correlation functions DMF - DMF (- - -), Li^+- DMF(——) and Cl^- - DMF (— — —).

around the two ions due to the different interactions and to the fact that the radius of the first solvation shell of Cl^- ion is somewhat larger than that of Li^+ ion. We mention also that the solvation number of DMF around the Li$^+$ ion can not be tested against experiment since experimental results concerning this property are not available in the literature. It should be noticed that the occupation number in the first shell around the Cl$^-$ ion tends to be somewhat higher from the present CS study (≅10) than that obtained in the previous diffraction study (≅ 7) [21]. Several causes can explain this difference. We believe however that it is due to the higher solute concentration (≅1.75M) in the experimental sample compared to the corresponding one employed in the present simulation. In order to illustrate this point, we mention the results obtained in a previous diffraction study of aqua ions, where the solute concentration dependence of the ion solvation numbers has been studied [34]. From these results we may easily conclude that by increasing the solute concentration in the solution the solvation numbers around the ions decrease. Thus, in the case of LiCl in H_2O, and for a solute molality of 27.77, the hydration number of Li$^+$ ion was found to be about 2.3, while for a solute molality of 3.57 and 1.0 the corresponding numbers were found to be 5.5 and 10, respectively. This tendency has been also observed for the Cl$^-$ hydration numbers at these solute concentrations.

Comparable information about the coordination numbers of Li$^+$ and Cl$^-$ ions in various solvents is now available in the literature. A summary of these data obtained in previous experimental and computer simulation studies is given in table 3.

Table 3: Coordination numbers for the first shell of Li$^+$ and Cl$^-$ in various solvents from the present and previous experimental(EXP) and computer simulation(CS) studies.

SOLVENT/SOLUTE	Li$^+$	CL$^-$
H_2O	$(2.3\text{-}5.5,10)^{\text{EXP[34]}}$, $4.1^{\text{CS[32]}}$	$(4.4\text{-}5.9)^{\text{EXP[34]}}$, $7.4^{\text{CS[32]}}$
MeOH	$4.0^{\text{CS[35]}}$	$4.0^{\text{EXP[ ]}}$, $5.0^{\text{CS[35]}}$
NH_3	$(4.0\text{-}7.0)^{\text{EXP[36]}}$, $4.0^{\text{CS[35]}}$	$12.0^{\text{CS[35]}}$
CH_3NH_2	$4.0^{\text{CS,EXP[35]}}$	$(6.0\text{-}8.0)^{\text{CS[35]}}$
CH_3CN	$3.0^{\text{EXP[37a]}}$, $4.0^{\text{EXP[37b,c,d]}}$	$3.2^{\text{EXP[38]}}$
DMF(-d7)	$5.3^{\text{CS[this work]}}$	$6.8^{\text{EXP[21]}}$, $9.9^{\text{CS[this work]}}$
DMSO	$5.0^{\text{EXP[39]}}$, $5.8^{\text{CS[40]}}$	$7.6^{\text{CS[40]}}$

In order to study the local structure around the ions in detail, it is necessary to inspect the site-site PCFs between each ion and the interaction sites of the DMF molecules. As mentioned above, the corresponding to the Cl$^-$ ion six PCFs are presented in figures 2 a,b. From the behavior of these PCFs we can see that the first peak in the Cl$^-$ - D (formyl D) correlation is located at the most shorter distance than the first peak in the other functions. This result is in accordance with that pointed out in the previous experimental study [21]. According to some argumentation, the authors concluded that the first peak at 2.85 Å in the experimental normalized total radial distribution functions should be ascribed to the Cl$^-$-D interactions. Also, they concluded that the second peak at 3.7 Å in this function should be ascribed to the Cl$^-$ - C

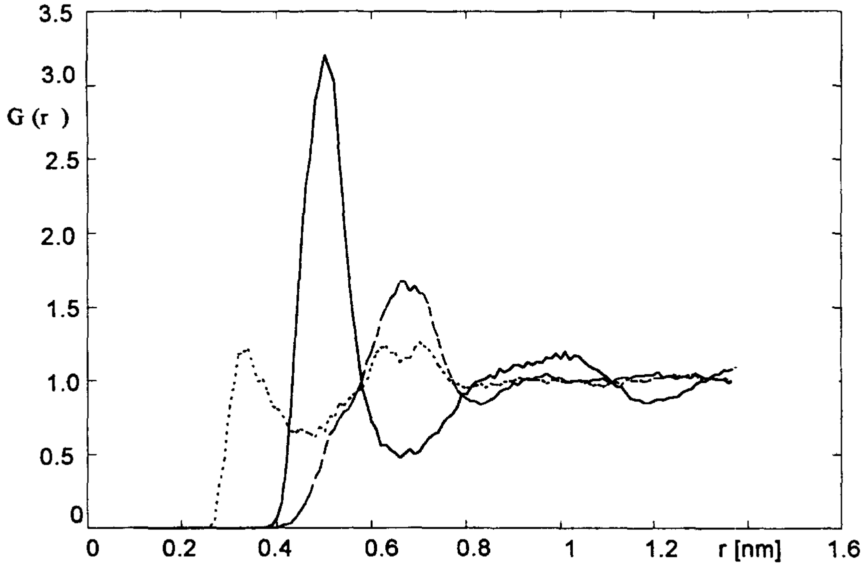


Figure 2a: The simulated site-site pair correlation functions Cl^- - D (- - -), Cl^- - N (——) and Cl^- - O (— — — —).

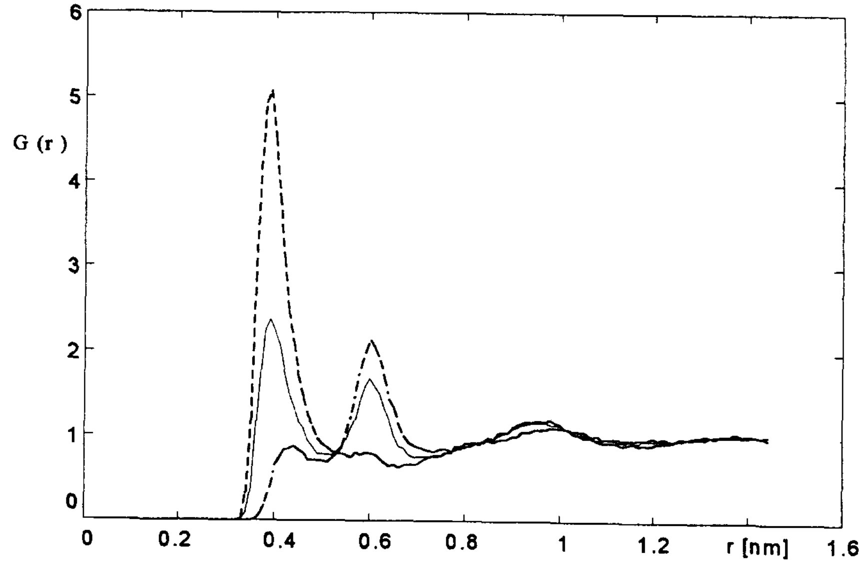
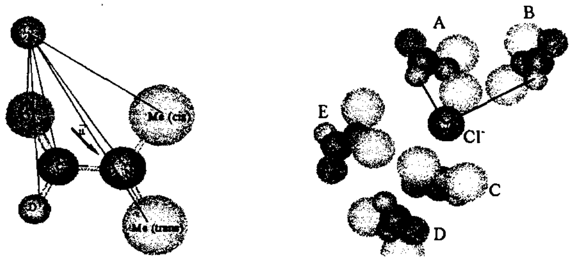


Figure 2b: The simulated site-site pair correlation functions Cl^- - C (- - -), Cl^- - Me1(cis) (———) and Cl^- - Me2(tr) (— — —)

(-C=O) interactions. By inspecting our Cl⁻-C PCF in figure 2b, we observe two well constructed peaks. The first one is centered at $\cong 4.2\,\mathrm{\mathring{A}}$ and the second at $\cong 6\,\mathrm{\mathring{A}}$. This behavior indicates some specific orientation of the solvent molecules around the Cl^- ion. From the position of the first maximum in the other PCFs we easily conclude that the most likely arrangement of the DMF solvent and the Cl^- ion differs somewhat from that postulated experimentally. In figure 3b, a snapshot of the most nearest DMF molecules around the Cl^- ion from the present simulation is shown. From this figure, we may observe two DMF molecules (A, B) to be very closed separated to the Cl^- ion. The bond lines indicate the distances between the ion and the D formyl atom on each molecule. This DMF-ion arrangement differs from that proposed in the previous diffraction study of this solution (fig. 3c in Ref. [21]). The main reason should be the high concentration of LiCl in the experimental sample compared to that in our simulated system. However, this assumption remains to be checked experimentally by investigating a relatively small concentrated LiCl/DMF electrolyte solution. Moreover, it is interesting to note that the neighboring molecules A and B are found to be not in an antiparallel arrangement. It is evident that this situation arises due the strong interactions between these molecules and the neighboring ion at relatively short distances up to about $5.5\,\mathrm{\mathring{A}}$, which seems to be destructive for the preferential antiparallel arrangement of these neighboring DMF molecules. On the other hand, from the same figure we observe two other neighboring molecules (C,D) at somewhat large distances from the ion with an antiparallel orientation. According to this arrangement, the CH_3 (trans) group of the C molecule prefers to associate with the O atom compared to the CH_3 (cis) group of the neighboring D molecule. This preferential orientation of the molecules has been proposed on the basis of the NMR [6] and previous CS results [13].

The PCFs involving the Li^+ and the interactions sites of the DMF molecules are shown in figure 4a,b. From the ordering of the first maxima of these functions, we may conclude that the DMF molecules in the Li^+ first shell prefer to orient with their O atoms pointing toward the ion. In other words, the Li^+ ion in liquid DMF has a well defined dipole ordered first solvation shell constructed by about 5 solvent molecules (see table 3). Figure 3a shows the most probable relative orientation of the DMF molecule and the Li^+ ion. As expected, the most probable Li^+/DMF arrangement differs significantly from that obtained for the Cl^-/DMF in this solution. Moreover, by inspecting these PCFs at somewhat large distances, we observe a weakly only defined secondary solvent shell. Therefore, there is no evidence that the influence of the Li^+ ion extends quite far into this solvent.



(a) (b)

Figure 3 : The most probable orientations of DMF molecules in the first shell around the ions in the solution. (a) Li^+ -DMF, (b) Cl^--DMF.

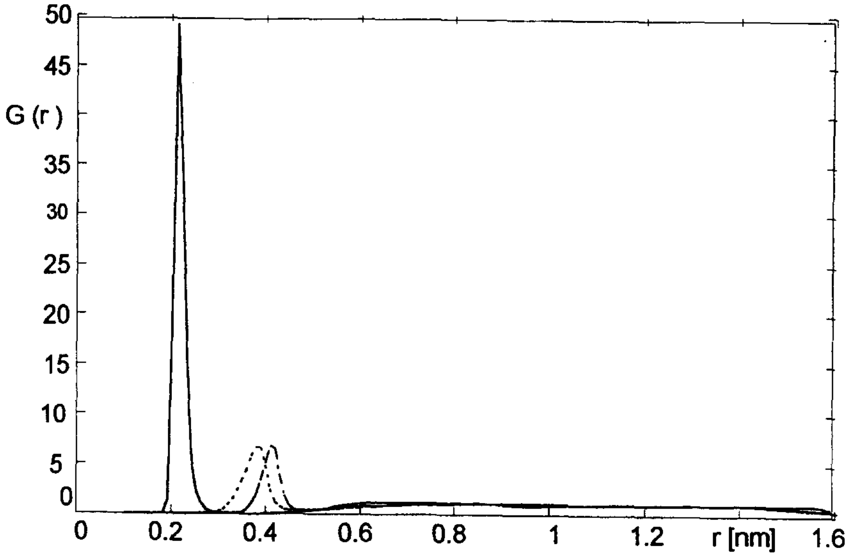


Figure 4a: The simulated site-site pair correlation functions Li$^+$ - N(-- —— - -), Li$^+$ - O (——) and Li$^+$ - D(- - -)

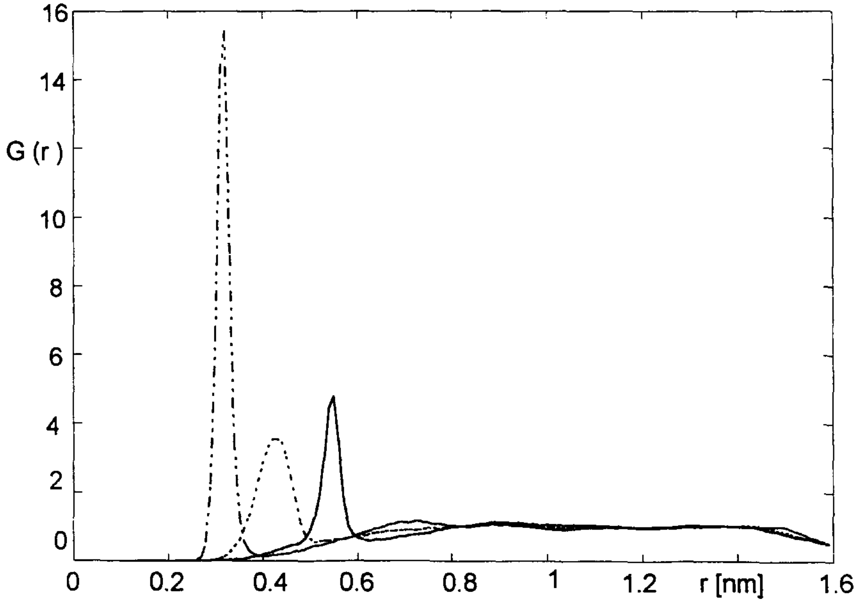


Figure 4b: The simulated site-site pair correlation functions Li$^+$ - C (- - —— - -), Li$^+$ - Me1(cis) (- - -) and Li$^+$ - Me2(tr) (——)

In figure 5 we show the center of mass (COM) linear velocity autocorrelation functions (VACFs) of the two ions and of the DMF solvents. The curves show the following qualitative behavior. The VACF of the DMF molecules first goes through a shallow negative minimum (in less than 0.21ps) and then converges slowly to zero after approximately 1.5ps. This COM translation motion of DMF molecules can be assigned to be the same as for the species in the most molecular liquids. On the other hand, the VACFs of the ions show a characteristic damped oscillated behavior with negative minima and positive maxima, which in the case of the Li^+ ion are most pronounced. This denotes the greatness of the perturbation of the ion translation motion due to strong connectivity of the ion-cage solvent molecules. We note that this behavior has been also obtained in CS studies of other electrolyte solutions [25].

Finally, it should be noted that the diffusion coefficients(D_S) have been evaluated from the VCFs of the ions and of the COM of the DMF solvents by integrating the functions up to 3.6ps. The diffusion coefficient values for Li^+, Cl^- and DMF are found to be 3.1, 1.25, 1.45 10^{-9} m^2s^{-1}, respectively. By comparing the Li^+ and Cl^- diffusion values we see a realistic differentiation between them. However, the D_s^{Cl} appears to lie below the D_s^{DMF} though the molar mass of the DMf-d7 is greater than that of Cl^-. This constructing behavior of these diffusion coefficients may be explained in terms of the microscopic dynamics of the Cl^- ion and the cage molecules

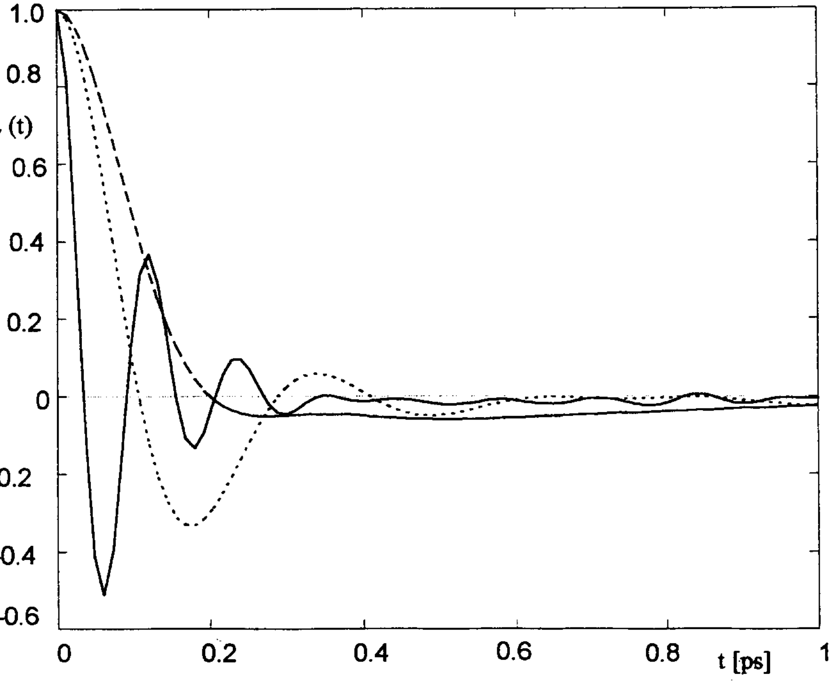


Figure 5: Normalized linear velocity autocorrelation functions of the Li^+(——) ion, Cl^-(- - -) ion and DMF (— — —) molecules.

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REFERENCES

[1] a) R. M. Meighan, R. H. Cole, J. Phys. Chem. 68, 503 (1964)

b) A.L. Mc Clellan, Tables of Experimental Dipole moments; Rahara Enterprises, El Cerrito,CA (1989)

[2] A.D. Buckingham, "Intermolecular Interactions from Diatomics to Biopolymers", B. Pallman - Willey, New York (1978)

[3] a) E.I Du Pont "DMF Product Bulletin", Wilmington, DE (1971)

b)S.W. Benson, 'Thermodynamic Kinetics", Willey, New York (1976)

c) M. Holtz, X. Mao , D.Seiferling, J. Chem. Phys. 104, 675 (1996)

[4] V.M. Shelley, A. Talintyre, J. Yarwood, R. Buchner, Faraday Discuss.Chem. Soc. 85, 211 (1988)

[5] V.M. Shelley, J. Yarwood, Molecular Physics, 71, 65 (1990)

[6] R. Konrat, S. H. Sterk, J. Phys. Chem. 94, 1291 (1990)

[7] Y. J. Chang, E. W. Castner, J. Phys. Chem. 98, 9712 (1994)

[8] X. Mao, M. Holz, Z. Naturforrsch. 49a, 1016 (1994)

[9] a) J. Gao, J. Am Chem. Soc. 115, 2930 (1993)

b) X. Zhou, J.A. Krauser, D.R. Tato, A.S. VanBuren, J.A. Clark, P.R. Mody and R. Lim, J.Phys. Chem. 100, 2689 (1996)

[10] H. Ohtaki, S. Itoh, T. Yamaguchi, S. Ishiguro, B.H. Rode, Bull. Chem. Soc. Jpn. 56, 3406 (1983)

[11] T. Radnai, S.Itoh and H. Ohtaki, Bull. Chem. Soc. Jpn. 61, 3845 (1988)

[12] W. L. Jorgensen, C.J. Swenson, J. Am. Chem. Soc. 107, 569 (1985)

[13] S. Yasonath, C.N.R. Rao, Chem. Phys. 155, 351 (1991)

[14] J. Gao, J. Am. Chem. Soc. 115, 2930 (1293)

[15] P.C. Schoester, M.D. Zeidler, P.A. Bopp, Z. Naturforsh 50, 38 (1995)

[16] J. Gao, J.J. Parelites, D. Habibollazadeh, J. Phys. Chem. 100, 2689 (1996)

[17] a) K. Ozutsumi, S. Ishiguro, H. Ohtaki, Bull. Chem. Soc. Jpn. 61, 945 (1988)

b) K. Ozutsumi, T. Takamuku, S. Ishiguro, H. Ohtaki, Bull. Chem. Soc. Jpn. 62, 1875 (1989)

[18] a) K. Ozutsumi, K. Tohji, Y. Udagawa, S. Ishiguro, Bull. Chem. Soc. Jpn. 65, 1528 (1991)

b) K. Ozutzumi, T. Takamuku, S. Ishiguro, H. Ohtaki, Bull. Chem. Soc. Japan 65, 214 (1992)

[19] a) K. Ozutzumi, M. Kuide, H. Suzuki, S. Ishiguro, J. Phys. Chem. 97, 500 (1993)

b) T. Radnai, S. Ishiguro, H. Ohtaki, Bull. Chem. Soc. Jpn. 65, 1445 (1992)

[20] J. Ishiguro, Pure Appl. Chem. 66, 393 (1994)

[21] M. Yamagami, H. Wakita, T. Yamaguchi, J. Chem. Phys. 103, 8174 (1995)

[22] R. Impey, M. Sprik, M. Klein, J. Am. Chem. Soc 109, 5900 (1987)

[23] B. Guillot, Y. Guissani, D. Borgis, S. Bratos. Proceedings of the NATO ASI Series C vol. 291, p47 on " Reactive and flexible Molecules in Liquids", Edit. Th. Dorfmueller, Nafplion Greece (1988).

[24] M. Mathusoodanan and B. L. Tembe, J. Phys. Chem. 99, 44 (1995)

[25] G. Sese', E. Guardia, J. A. Padro', J. Chem. Phys. 105, 8826 (1996)

[26] a) G.S. Fanourgakis, S.C. Farandos, J. Phys. Chem. 100, 3900 (1996)

b) G.S. Fanourgakis, S.C. Farandos, P. Parneix, P. Brechignac, J. Phys. Chem. 106, 4954 (1997)

[27] A. Luzar, D. Chandler, J. Chem. Phys.. 98, 8160 (1993)

[28] a) J. Brodholt, M. Sampoli, R. Vallauri, Molecular Physics 86, 149 (1995)

b) M. Hlouca, K.U. Deiters, Molecular Physics 90, 593 (1997)

[29] J. W. Essex, W. l. Jorgensen, J. Phys. Chem. 99, 17956 (1995)

[30] a) M. Neumann, Molecular Physics, 50, 841 (1983)

b) P.E. Smith, W.F. van Gusteren, J. Chem. Phys. 100, 3169 (1994)

[31] D.R. Line (Ed.), CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, 75th edition (1994)

[32] S.H. Lee, J.C. Rasaiah, J. Phys. Chem., 100, 1420 (1996)

[33] M.P.Allen and D.J. Tildesley, "Computer Simulation of Liquids", Clarendon, Oxford (1987)

[34] J.E. Enderby, S. Gummings, G.S. Herdreman, G. W. Neilson, P.S. Salmon, N. Skipper, J. Phys. Chem. 91, 5851 (1987)

[35] R. W. Impey, M. Sprik, M.L. Klein, J. Am. Chem. Soc. 109, 5900 (1987)

[36] P.Chieux, H. Bertagnolli, J. Phys. Chem. 88, 5802 (1985)

[37] a)T. Cartailler, W. Kunz, P. Turq and M.-C. Bellisent-Funel, J. Phys.: Condens. Matter 3, 1133 (1991)

b) J. Barthel, M. Kleebauer and R. Buchner, J. Solution Chem. 24, 1(1995)

c) J. Barthel and R. Deser, J. Solution Chem. 23, 1133 (1994)

d) I.S. Perelygin and M.A. Klimchuk, Russ. J. Phys. Chem. 47, 1138, 1402 (1973)

[38] Y. Marcus, Ion Solvation, John Wiley and Sons Ltd., Chiechester, (1985)

[39] S. Chang, P.P. Schmidt, and M.W. Severson, J. Phys. Chem. 90, 1046 (1986)

[40] M. Chalaris, J. Samios (to be published)