chloride melts,[10,11] such a study would be of considerable value in its own right.

Assuming that spectroscopic studies fully confirm the conductance/structure relations that we seem to have established, the question will remain, how exactly does the presence of a large cation coordination number for the higher charged cation cause a generally smaller particle mobility than in a melt of the same composition in which the same cations have a lower coordination number. Our best explanation is that complexation effectively screens the charge on the cation so that the cohesion of the melt is determined by the Coulomb interaction between the lower charged cations and the complex anion. If the latter is of high coordination number than the residual negative charge on the complex is large (−4 for $[CoCl_6]$) and so the cohesion is large. By contrast, if the coordination number is smaller then the residual negative charge is smaller (−2 for $[CoCl_4]$) and the cohesion is correspondingly smaller. These effects were discussed in more detail in an earlier paper[12] in which the argument was supported by results from computer simulation experiments.

Conclusions

Comparison of conductivity changes on dissolution of divalent chlorides in solutions containing either all-chloride or mixed chloride–fluoride ligands are consistent with the notion that the conductivity and fluidity of solutions containing complex ions are greater if the complex ions formed are of low net charge than when they are of high net charge. The charge on such complexes is determined by the coordination number for fixed cation charges. Accordingly tetrahedral complexes favor high fluidities and conductances while octahedral or dodecahedral complexes produce higher viscosity, lower conductance, solutions.

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An Evaluation of Water–Water Analytical Potentials in the Region of Low-Energy Trifurcated Structures

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Several pairwise additive potentials, frequently used to describe liquid water, and a cooperative potential are examined with respect to their abilities to adequately describe the trifurcated water dimer structures recently reported to be of energies comparable to the best linear structures. All pairwise additive potentials were in error of at least 3 kcal/mol while the cooperative model was within 1 kcal/mol of the best quantum-mechanical results. It is suggested that, while these pairwise additive potentials may be of considerable use for the description of aqueous water, they should be used with caution where interactions involving individual water molecules or pairs are important.

Introduction

The correct description of water molecule interactions is of fundamental importance as it is essential to the critical study of biological systems. Both theoretical[1] and experimental[2] studies have indicated that a linear hydrogen-bonding structure corresponds to a minimum on the potential energy surface for the dimer water dimer. A recent report[3] has shown, however, that another dimer structure that forms trifurcated hydrogen bonds is within 0.2 kcal/mol of the best linear structure as calculated by using the MP4SDQ/6-311G** ab initio molecular orbital method,[4] after optimization at the HF/6-31G* or MP2/6-31G* level.

Several analytical potentials for water interactions have been developed in the past several years and used in computer simulations to describe liquid water. It is of significant interest to determine the extent to which they are able to describe this, and other, structures which have not been previously considered. In this note, we examine the water dimer potential energy surface in the region of these trifurcated and other structures. To this end, we compare several pairwise additive water–water potentials proposed in the literature[5-12] and frequently used in liquid studies, as well as the cooperative model of Campbell and Mezei[13] with the ab initio results.

Calculations

The calculations examined the six dimer structures considered in the ab initio study (see Figure 1 and Table I).[3] Structure I is the global minimum predicted by the AM1 semiempirical molecular orbital method;[14] II was obtained by a partial optimization starting from I using the GAUSSIAN-82 program[4] at the

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TABLE I: Geometrical Parameters for Various Structures of Water Dimer[a]

	a, Å	b, Å	c, Å	e, deg	water-1 O–H$_1$	water-1 O–H$_2$	water-1 HOH	water-2 O–H$_1$	water-2 O–H$_2$	water-2 HOH
I	2.23	2.23	2.31	86.0	0.960	0.964	104.1	1.962	0.963	103.4
II	2.53	2.52	2.79	98.2	0.960	0.961	105.0	0.963	0.963	101.6
III	2.68	2.68	2.11	128.8	0.968	0.973	105.3	0.972	0.972	103.0
IV	3.35	3.36	2.01	163.8	0.947	0.952	105.5	0.948	0.948	105.8
V	1.95	3.18	3.18	167.0	0.966	0.975	104.2	0.971	0.971	104.2
VI	2.09	3.48	3.47	180.0	0.961	0.963	103.3	0.961	0.961	103.8

[a] See Figure 1 for geometric definitions. Water-1 is the proton donor. OH_2 is the bond length for the H-bonding hydrogen.

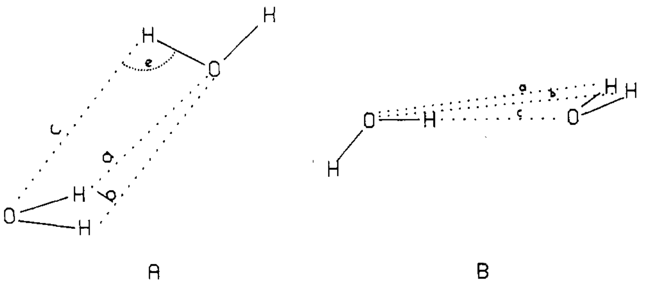

Figure 1. Two view of the water dimer: A represents a trifurcated and B a linear structure. A can be converted to B by rotating the H bond, *c*, counterclockwise, increasing the angle, *e*, and changing the relative lengths of the H bonds, *a*, *b*, and *c*.

MP2/6-31G* level. Both I and II are in orientations that allow trifurcated hydrogen bonds. Structure III, an intermediate between the trifurcated and the linear structure that still contains two hydrogen bonds, was found to be lower in energy than II at the MP2/6-31G* level. Structure IV represents a minimum at the HF/6-31G* level with the O–O distance restricted to 2.964 Å. Structure V is the completely optimized structure at the MP2/6-31G* level obtained by starting from structure IV. Structure VI is the optimal linear dimer obtained by the AM1 method. It has the lowest energy of the five at the MP4SDQ/6-311G** level.

For the pairwise additive analytical potentials, we examined the ab initio potentials by Matsuoka, Clementi, and Yoshemine (MCY),[5] Clementi and Hatibz (CH),[6] and Yoon, Morokuma, and Davidson (YMD)[7] as well as the empirical potentials of Stillinger, Rahman, and Ben Naim (ST2),[8] Berendsen, Postma, Van Gunsteren, and Hermans (SPC)[9] and the family of potentials by Jorgensen and Madura, TIPS2,[10] TIP3P,[11] and TIP4P.[12] The cooperative model of Campbell and Mezei (CM)[13] (containing a permanent electrostatic term, a cooperatively calculated induced dipole term, and an empirical correction to reproduce Hartree–Fock energies), supplemented by an empirical dispersion term,[14] was also examined. Due to the high-order multipole expansion used in the CM model it is too expensive to use it in computer simulation.

The energy calculations were based on atomic coordinates that were obtained by replacing the monomer geometries contained in I–VI by the geometries used in the various water models in a manner that conserved the centers of mass and orientations of the waters. Additional charge centers were placed where required. For the pairwise additive potentials, structures II and VI were also used as the starting point of a minimization (by a Monte Carlo computer simulation at 1 K temperature) to obtain the nearest significant local minimum.

Results and Discussion

The calculated energies of structures I–VI are given in Table II, along with the best quantum-mechanical results from ref 3. It is clear from the table that none of the pairwise additive potentials described adequately either of the trifurcated structures, I and II. Particularly bad results were obtained for structure I which was found to be repulsive by all pairwise additive models. For the well-studied linear dimer conformation, however, their performance is remarkably good and consistent. The cooperative CM potential, on the other hand, gave very good results uniformly: the trifurcated conformations were described within 1 kcal/mol and its performance on the linear dimers was consistently better than any of the pairwise additive models tested.

TABLE II: Calculated Water–Water Binding Energies[a]

		I (3)	II (3)	III (2)	IV (1)	V (1)	VI (1)
		configurn (no. of H bonds)					
quantum-mechanical pair potential energies	MCY	0.41	−3.33	−3.72	−5.50	−5.26	−5.24
	CH	1.42	−3.39	−4.52	−5.52	−5.47	−5.28
	YMD	0.92	−3.59	−3.75	−5.34	−4.93	−5.16
empirical pair potential energies	ST2	1.80	−3.05	−2.97	−6.44	−5.66	−5.99
	SPC	5.16	−3.10	−3.91	−5.59	−5.36	−5.11
	TIPS	6.94	−2.85	−4.22	−5.70	−5.70	−5.30
	TIP3P	3.86	−3.45	−3.91	−5.48	−5.25	−5.10
	TIP4P	5.07	−3.05	−4.29	−5.57	−5.60	−5.14
cooperative energies	CM	−3.70	−5.09	−5.89	−6.03	−6.06	−5.76
ab initio (MP4SDQ/6-311G**)		−3.08	−6.02	−5.84	−6.23	−6.14	−6.40

[a] The symbols for the models are defined in the Calculations section. Energies are in kcal/mol. Ab initio energies are from ref 3.

The minimization of the trifurcated structure (structure II) led to the linear dimer for the MCY, YMD, ST2, SPC, TIP3P, and TIP4P potentials. However, for the CH model, the minimization lead to a trifurcated minimum with −4.15 kcal/mol and for the TIPS2 model to a bifurcated minimum with −4.60 kcal/mol.

The apparent failure of the pairwise additive potentials tested to properly describe the trifurcated conformations is in marked contrast with their general success in reproducing structural and thermodynamic properties of liquid water, suggesting that the trifurcated conformations have very low statistical weight in the liquid state. This can intuitively by justified by remarking that in general the multiple bonds restrict the freedom of the dimer and thus create an entropically unfavorable situation. In the case of liquid water, they would also prevent formation of hydrogen-bonded networks.

The present work suggests that, while several of the pairwise additive models considered here have been shown to be adequate for the description of water in its liquid state, they should be used with caution when interactions with individual water molecules are important, for example, when considering the effects of individual water molecules or pairs trapped in an enzyme–substrate complex.

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