Hydrogen bonding in liquid alcohols: a computer simulation study

J.A. Padró[a], L. Saiz[a], E. Guàrdia[b]

[a]*Departament de Física Fonamental, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain*
[b]*Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Sor Eulàlia d'Anzizu s.n., B4-B5, 08034 Barcelona, Spain*

Abstract

A series of molecular dynamics simulations has been performed to investigate hydrogen bonding in liquid alcohols. The systems considered have been methanol, ethanol, ethylene glycol and glycerol at 298 K. The hydrogen bonding statistics as well as the mean lifetime of the hydrogen bonds are analyzed. The results are compared with those corresponding to liquid water. © 1997 Elsevier Science B.V.

Keywords: Molecular dynamics; Liquid alcohols; Hydrogen bonding; Lifetime

1. Introduction

The properties of associated liquids are largely determined by the characteristics of their hydrogen bonded network [1]. However, despite its interest, the detailed knowledge of hydrogen bonding in many H-bonded liquids is far from satisfactory. Experimental studies are rather indirect methods to investigate H-bonding. So, spectroscopic and relaxation measurements supply information on the dynamics of the H-bonds but the results of these experiments can be interpreted in only a qualitative way. Although limited to classical models, computer simulation methods can provide direct microscopic information on the statistics and the dynamics of H-bonds. Computer simulation studies of H-bonding have been mainly devoted to water [2–7] and methanol [8–12]. Fewer studies, and restricted to structural properties of the H-bonds, have been carried out for ethanol [12,13] and glycerol [14]. To our knowledge there are no computer simulation studies of H-bonding in other liquid alcohols.

In this paper, we apply the molecular dynamics (MD) simulation method to study the H-bonding statistics and the mean lifetime of H-bonds in different liquid alcohols including methanol, ethanol, ethylene glycol and glycerol. The results are compared with those obtained for liquid water. The H-bonded structures of these systems show marked differences. Methanol and ethanol have one hydroxyl group per molecule and they are characterized by H-bonding patterns which may be largely regarded as linear winding chains [12,13]. Ethylene glycol and glycerol have two and three hydroxyl groups per molecule, respectively, and they show three-dimensional H-bonding patterns which are not well-known. Liquid water shows a tetrahedral H-bonding pattern [1].

2. Computer simulations

MD simulations of methanol, ethanol, ethylene glycol and glycerol at room temperature $T = 298$ K and

Table 1
Characteristics of the simulated systems

System	Formula	Density (g cm^{-3})
Methanol	$(CH_3)-O-H$	0.78664
Ethanol	$(CH_3)-(CH_2)-O-H$	0.7873
Ethylene glycol	$H-O-(CH_2)-(CH_2)-O-H$	1.1101
Glycerol	$H-O-(CH_2)-[-(CH)-O-H]-(CH_2)-O-H$	1.2567
Water	H_2O	1.0

experimental densities at normal pressure were carried out (see Table 1). We considered 216 molecules in the case of methanol and 125 molecules for the other alcohols. The usual periodic boundary conditions were assumed. Molecules were modelled by site–site interaction potentials including torsional motion. There was one site on each atom except for the CH_n groups which were taken as single units centered on carbon. The geometrical parameters of molecules, intermolecular and intramolecular potential functions and potential parameters were those proposed by Jorgensen [12]. Bond length and bond angles were kept fixed during the simulations by using the SHAKE method [15]. To handle with the long-range coulombic interactions we used the Ewald summation technique [16]. We employed the integration algorithm proposed by Berendsen et al. [17] with a time step of 0.0025 ps. Each run consisted of an initial equilibration period of 50 ps and a production period of 150 ps. For the sake of comparison, we also performed a simulation of water at $T = 298$ K with the SPC model of Berendsen and coworkers [18]. In this case the number of molecules was 216 and the time step 0.0015 ps.

3. H-bond definition

Since in the MD simulations the intermolecular energy of the system is described by a continuous interaction potential we cannot distinguish with precision whether two molecules are H-bonded or not. Consequently, the adoption of a criterion to decide that one H-bond is established, is somewhat arbitrary. The H-bond definitions commonly used are based on either energetic or geometric criteria [3,5]. However, in the case of alcohols the choice of a criterion is less crucial than for water and both energetic and geometric criteria lead to similar results [8,13]. As in previous studies [7,11,13], we adopted a geometric

definition, i.e. we assumed that a H-bond exists between two oxygens of two different molecules if three conditions are fulfilled:

1. The distance R_{OO} between the oxygens is smaller than R_{OO}^c,
2. The distance R_{OH} between the "acceptor" oxygen and the hydrogen corresponding to the molecule of the "donor" oxygen is smaller than R_{OH}^c, and
3. The $H-O\cdots O$ angle is smaller than φ^c.

As cut-off distances R_{OO}^c and R_{OH}^c we selected the positions of the first minima of the radial distribution functions $g_{OO}(r)$ and $g_{OH}(r)$. As can be seen in Fig. 1, the positions of these minima do not show important changes, specially in the case of the $g_{OH}(r)$ which defines the most critical cut-off value. Thus we used the same cut-off distances for the four alcohols, $R_{OO}^c = 3.5$ Å and $R_{OH}^c = 2.6$ Å. The cut-off distances for water were $R_{OO}^c = 3.4$ Å and $R_{OH}^c = 2.4$ Å. As in other studies [6] we have chosen $\varphi^c = 30°$ since the number of pairs of oxygens which satisfying conditions 1 and 2 form an angle $\varphi > 30°$ is almost negligible for all the simulated systems.

One of the advantages of the use of the geometrical definition is that we can identify which H and O atoms participate in each H-bond. Hence, in a given configuration, we can classify the hydrogen atoms into two groups: the H-bonded and the non-H-bonded hydrogens. Moreover, we can classify the oxygen atoms according to the total number of H-bonds in which they participate. Finally, in the case of molecules with more than one oxygen, we can classify the molecules according to the total number of H-bonds in which they participate.

4. H-bond statistics

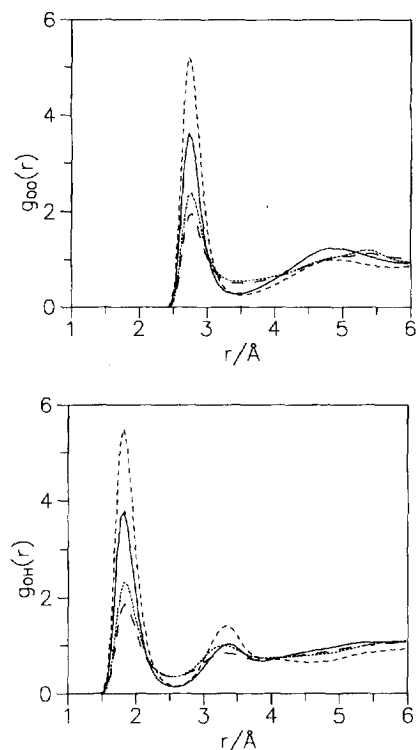We define f_n^H, f_n^O and f_n as the percentages of

Fig. 1. Oxygen–oxygen (top) and oxygen–hydrogen (bottom) radial distribution functions: ——————, methanol; – – –, ethanol; - - -, ethylene glycol; — — —, glycerol.

hydrogens (of the OH groups), oxygens and molecules in the system with n ($n = 0,1,2,3,...$) H-bonds. The results for f_n^H and f_n^O are given in Table 2. f_n and the mean number of H-bonds per molecule n_{HB} are summarized in Table 3. The results obtained for water are similar to those of Ref. [7], calculated with a flexible SPC model and slightly different cut-off distances.

The majority of molecules in liquid methanol and ethanol have two H-bonds which indicates that their structure is basically constituted by linear chains of H-bonded molecules [11,13] (in these systems, with one

hydroxyl group per molecule, $f_n^O = f_n$). Molecules with one H-bond are at the end of the chains whereas those with three H-bonds should be associated with branching. The situation is very different for ethylene glycol and glycerol. For these systems, the largest part of oxygens have also two H-bonds but the differences between f_2^O, f_1^O and f_3^O are smaller than for methanol and ethanol. We observe that f_2^O diminishes, while f_1^O and f_3^O increase, as the number of hydroxyl groups per molecule increases. Moreover, oxygen atoms with $n = 2$ in ethylene glycol and glycerol molecules should be associated with branching. Results in Table 3 show that branching is very important in liquid ethylene glycol and glycerol. The percentage of ethylene glycol molecules with two H-bonds is very low and still smaller in the case of glycerol. In both liquids, $f_1 = 0$. These findings show that, unlike in alcohols with one hydroxyl group, there are no linear H-bonded chains in ethylene glycol and glycerol. Despite these differences the mean number of H-bonds per oxygen atoms is very close (≈ 1.9) for the four alcohols and n_{HB} is proportional to the number of OH groups per molecule.

Results for water are very different from those for alcohols. It could be expected some similarity between the structure of water and that of ethylene glycol because in both cases the molecules have two H atoms which may participate in H-bonds. Although for both water and ethylene glycol the greater part of molecules have four H-bonds the percentages for other n values are markedly different. The percentage of non H-bonded hydroxyl hydrogens is similar for methanol, ethanol and ethylene glycol whereas for glycerol is somewhat higher and closer to that for water.

5. H-bond lifetimes

The study of the temporal evolution of the H-bonds

Table 2
Percentages of oxygens and hydrogens with n H-bonds

System	f_0^O	f_1^O	f_2^O	f_3^O	f_4^O	f_5^O	f_0^H	f_1^H
Methanol	1	16.5	75.5	7	0	0	6.0	94.0
Ethanol	1	13	81	5	0	0	5.5	94.5
Ethylene glycol	1	18	67	13.5	0.5	0	5.5	94.5
Glycerol	2.5	24	58	15	0.5	0	9.5	90.5
Water	0	2	13.5	37.5	42	5	11.5	88.5

Table 3
Percentages of molecules with n H-bonds and mean number of H-bonds per molecule

System	f_0	f_1	f_2	f_3	f_4	f_5	f_6	f_7	f_8	f_9	n_{HB}
Methanol	1	16.5	75.5	7	0	0	0	0	0	0	1.9
Ethanol	1	13	81	5	0	0	0	0	0	0	1.9
Ethylene glycol	0	0	3.5	24	55.5	15	2	0	0	0	3.9
Glycerol	0	0	0.5	2.5	12.5	30	34.5	16	3.5	0.5	5.7
Water	0	2	13.5	37.5	42	5	0	0	0	0	3.3

is complicated because of the fast intermolecular vibrational motions which rearrange the H-bonds patterns producing the breaking and subsequent reformation of H-bonds in short intervals of time. We have calculated the survival probability or lifetime of the H-bonds in a similar way than Rapaport [2] and Matsumoto and Gubbins [9]. We have defined a variable $\eta_{ij}(t)$ that takes the values 0 or 1 depending on the H-bond state of a given pair of oxygens:

$$\eta_{ij}(t) = \begin{cases} 1, & \text{if oxygens } i \text{ and } j \text{ are H−bonded at} \\ & \text{time } 0 \text{ and time } t, \text{ and the bond has} \\ & \text{not been broken for any period longer} \\ & \text{than } t^* \\ 0, & \text{otherwise} \end{cases} \quad (1)$$

We have calculated the normalized autocorrelation function of $\eta_{ij}(t)$, that we call $C_{HB}(t)$. It represents the probability that a given H-bond existing between two molecules at the instant $t = 0$ remains alive at the instant t, independently whether the H-bond has been broken for a time less than t^* during that time interval. If we assume an asymptotic exponential relaxation behavior we can calculate the H-bond lifetime τ_{HB}

$$C_{HB}(t) \approx \exp\left(-\frac{t}{\tau_{HB}}\right) \quad \text{(at long times)} \quad (2)$$

The limiting cases $t^* = 0$ and $t^* = \infty$ correspond to the continuous H-bond lifetime (τ_{HB}^C) and the intermittent H-bond lifetime (τ_{HB}^I) proposed in Ref. [2]. In the former case, $C_{HB}^C(t)$ is calculated by allowing to $\eta_{ij}(t)$ to make just one transition from 1 to 0 whereas in the latter case, $C_{HB}^I(t)$ is determined by considering that the value of $\eta_{ij}(t)$ is 1 or 0 independently whether the H-bond was broken between 0 and t. We have also considered an intermediate case ($C_{HB}^R(t), \tau_{HB}^R$) by

taking a reasonable value of t^*, namely $t^* = \tau_{HB}^C$. Thus, the transition of $\eta_{ij}(t)$ from 0 to 1 is restricted to those cases in which the H-bond was broken during an interval smaller than τ_{HB}^C.

The resulting $C_{HB}^C(t)$ and $C_{HB}^R(t)$ functions for the different systems are shown in Figs. 2 and 3, respectively. The $C_{HB}^I(t)$ functions, which are not shown in these figures, are very close to the corresponding $C_{HB}^R(t)$ functions. This suggests that the reformation of H-bonds which remain broken during a period of
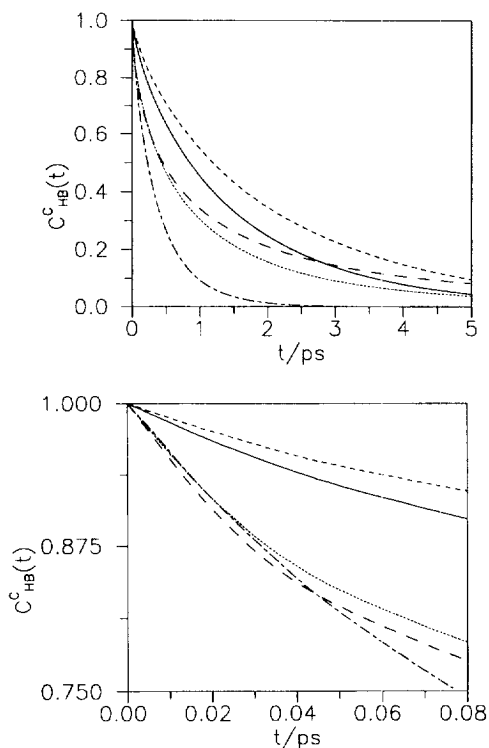

Fig. 2. H-bond lifetime autocorrelation functions for $t^* = 0$ ($C_{HB}^C(t)$): ————, methanol; – – –, ethanol; - - -, ethylene glycol; — — —, glycerol; — – — – –, water. The bottom drawing shows the short-time behavior of the $C_{HB}^C(t)$ funcions.
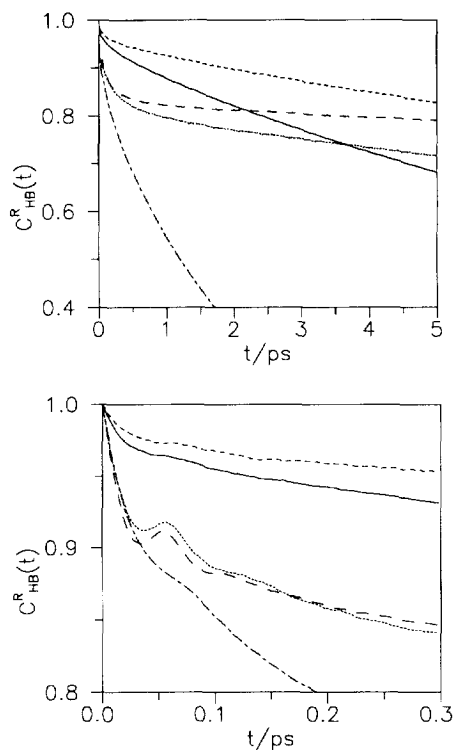
Fig. 3. H-bond lifetime autocorrelation functions for $t^* = \tau_{HB}^C$ ($C_{HB}^R(t)$): ————, methanol; – – –, ethanol; - - -, ethylene glycol; — — —, glycerol; – – – –, water. The bottom drawing shows the short-time behavior of the $C_{HB}^R(t)$ functions.

Table 4
Lifetime of the H-bonds and molecular dipole moment reorientational times

System	τ_{HB}^C (ps)	τ_{HB}^R (ps)	τ_{HB}^l (ps)	τ_μ (ps)
Methanol	1.5	16	16.5	10 [a]
Ethanol	2.5	36	37	27 [b]
Ethylene glycol	2.0	39	44	97 [c]
Glycerol	3.0	110	115	450 [c]
Water	0.5	2.5	3	3.2 [d]

[a] Ref. [19].
[b] Ref. [13].
[c] Ref. [20].
[d] Ref. [21].

glycerol show marked oscillations at about 0.06 ps (for the other systems we can also observe a very small increase of $C_{HB}^R(t)$ at the same position). These oscillations, which are absent in $C_{HB}^C(t)$, should be associated with the reform of broken H-bonds.

The H-bond lifetimes have been obtained by fitting an exponential function to $C_{HB}(t)$ in a given time interval (see Eq. (2)), i.e. between 1 and 5 ps for alcohols and between 0.5 and 3 ps for water. The resulting τ_{HB} values reflect the long time behavior of the corresponding $C_{HB}(t)$ functions. The differences among τ_{HB}^C for the different alcohols are not significant whereas τ_{HB}^R is markedly higher than τ_{HB}^C in all cases and increases with the size of molecules. τ_{HB}^R is notoriously greater for glycerol than for the other alcohols which indicates the higher stability of the H-bonds in this liquid. τ_{HB}^l is similar but slightly higher than τ_{HB}^R for all systems. The H-bond lifetimes for water are markedly lower than those for alcohols. This is consistent with the fact that water molecules show faster reorientation motions than alcohol molecules. The reorientation times of the molecular dipole moments for all the analyzed systems are reported in Table 4. It must be noticed that both τ_{HB}^R and τ_μ increase with the size of the alcohol molecules. In all cases, τ_{HB}^C is markedly smaller than τ_μ.

time longer than τ_{HB}^C has a very low probability. As expected, the decay of $C_{HB}^R(t)$ is slower than that of $C_{HB}^C(t)$. The large differences between $C_{HB}^C(t)$ and $C_{HB}^R(t)$ suggest that the dynamical process of breaking and making H-bonds is very fast (with a characteristic time smaller than τ_{HB}^C) and highly probable. The decays of the $C_{HB}(t)$ functions for water are markedly faster than those for alcohols.

The behavior of the $C_{HB}(t)$ functions at short times is very interesting. The simulated systems can be divided into two groups according to the initial decay of $C_{HB}^C(t)$. For methanol and ethanol the initial decay is slower than for ethylene glycol, glycerol and water. These differences may be related to the corresponding H-bonding patterns. At short times, the linear H-bonded chains of methanol and ethanol are more stable than the three-dimensional H-bond networks of ethylene glycol, glycerol and water. Moreover, the $C_{HB}^R(t)$ functions for ethylene glycol and

Acknowledgements

References

[1] See for instance M.C. Bellisent-Funel, J.C. Dore (Eds.), Hydrogen-Bond Networks, Kluwer, Dordrecht, 1994.

[2] D.C. Rapaport, Mol. Phys. 50 (1983) 1151.

[3] D. Bertolini, M. Cassettari, M. Ferrario, P. Grigolini, G. Salvetti, Adv. Chem. Phys. 62 (1985) 277.

[4] F. Sciortino, S.L. Fornili, J. Chem. Phys. 90 (1989) 2786.

[5] A. Geiger, P. Mausbach, in: J.C. Dore, J. Teixeira (Eds.), Hydrogen-Bonded Liquids, Kluwer, Dordrecht, 1991, pp. 171–183, and references therein.

[6] A. Luzar, D. Chandler, J. Chem. Phys. 98 (1993) 8160; Phys. Rev. Lett. 76 (1996) 928.

[7] J. Martí, J.A. Padró, E. Guàrdia, J. Chem. Phys. 105 (1996) 639.

[8] M. Haughney, M. Ferrario, I.R. McDonald, J. Phys. Chem. 91 (1987) 4935.

[9] M. Matsumoto, K.E. Gubbins, J. Chem. Phys. 93 (1990) 1981.

[10] J. Alonso, F.J. Bermejo, M. García-Hernández, J.L. Martínez, W.S. Howells, J. Mol. Struct. 250 (1991) 147.

[11] J. Martí, J.A. Padró, E. Guàrdia, J. Mol. Liq. 64 (1995) 1.

[12] W.L. Jorgensen, J. Phys. Chem. 90 (1986) 1276.

[13] L. Saiz, J.A. Padró, E. Guàrdia, J. Phys. Chem. 101 (1997) 78.

[14] L.J. Root, F.H. Stillinger, J. Chem. Phys. 90 (1989) 1200.

[15] J.P. Ryckaert, Mol. Phys. 55 (1985) 549.

[16] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Clarendon Press, Oxford, 1987, Chapter 5.

[17] H.J.C. Berendsen, J.P.M. Postma, W.F.van Gunsteren, A. DiNola, J.R. Haak, J. Chem. Phys. 81 (1984) 3684.

[18] H.J.C. Berendsen, J.P.M. Postma, W.F.van Gunsteren, J. Hermans, in: B. Pullman (Eds.), Intermolecular Forces, Reidel, Dordrecht, 1981.

[19] E. Guàrdia, G. Sesé, J.A. Padró, J. Mol. Liq. 62 (1994) 1.

[20] L. Saiz, J.A. Padró, E. Guàrdia, to be published.

[21] E. Guàrdia, J.A. Padró, J. Phys. Chem. 94 (1990) 6049.