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Hydrogen Bonding Interaction and Structural Change in Some Aliphatic Alcohol-Water Complexes: A Quantum Mechanical MP4 Study

MRINAL J. BEZBARUAH[1], BENZIR AHMED[1], IBRAHIM ALI[1], MADHAB UPADHYAYA[2] and BIPUL BEZBARUAH[1,*]

[1]Department of Applied Sciences, Gauhati University, Guwahati-781014, India
[2]Department of Chemistry, Chaiduar College, Gohpur-784168, India

*Corresponding author: E-mail: bipulbezbaruah@gmail.com

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Hydrogen bonding interaction in low molecular weight alcohols or lower alcohol (*viz*. methanol and ethanol) with water molecule is quite common. But, due to the presence of bulky groups in higher alcohols (*viz*. propanol, butanol and pentanol and their isomers) the hydrogen bonding interaction between alcohol and water molecule is significantly different. In alcohol-water heterodimer complexes, water plays an important role in the stability of such system, alcohol will be interacting with water molecule either as proton donor or proton acceptor mode. Quantum mechanical method, fourth degree Møller-Plesset (MP4) perturbation theory is an important tool for computing the interaction energy between the alcohol-water complexes. The interaction energy (IE) and natural bond orbital (NBO) calculations for some common aliphatic alcohol-water complexes (*e.g*. methanol, ethanol, propanol, butanol and pentanol) and their isomers were computed by using MP4 method.

Keywords: Alcohol, Water, MP4, Hydrogen bonding.

INTRODUCTION

Alcohols are capable of forming hydrogen bonds through polar hydroxyl groups either as donor or acceptor mode [1]. Hydrogen bonds between the aliphatic alcohols and water molecules have held a great interest in recent years due to its molecular recognition in both biological and artificial systems [2-5]. The polar hydroxyl groups are hydrophilic in nature whereas the non-polar carbon chain portion is hydrophobic and does not participate in the hydrogen bonding [6]. The presence of both hydrophilic and hydrophobic groups makes the alcohol-water system an interesting matter [7]. The characteristic of hydroxyl group present in the alcohols allows to form hydrogen bonds which is also responsible for the solubility of lower alcohols (methanol, ethanol and propanol). However, in case of higher alcohols (butanol, pentanol, *etc*.) are only partially soluble in aqueous medium. On the other hand, in lower alcohols (methanol and ethanol) the mixture of alcohol and water exhibits an entropy value less than their ideal values, which leads to the concept of negative excess entropy and believed to originate from incomplete mixing on the microscopic scale [8,9]. These explanations revealed that the hydrogen bonds formation in alcohol-water complex shows the greater stability of alcohols-water dimer [10,11]. Thermodynamics and structure of alcohol-water complexes are completely different in the alcohol-rich and water-rich region [12,13]. There is a general agreement that in the water rich region the hydrogen bonding strength of water is increased by presence of the hydrophobic head group of the alcohol. Coccia *et al*. [14] specified the three categories of water ethanol solutions; water rich, transitional or intermediate and ethanol rich [14].

Moreover, solvation of alcohols in aqueous medium has been studied extensively to understand the actual interaction between alcohol and water molecules [6]. Solvation of higher alcohols and study of alcohol-water complexes is still far from the normal hydrogen bonding in water-alcohol systems. The anomalous properties of alcohol-water mixtures are believed to be arise from the structuring of alcohol and water molecules around each other in solution. The molecular structure of alcohol and water in solution is not thoroughly understood; since both alcohol and water form complex hydrogen bonding but the hydrophobic alkyl groups present in alcohols completely changes the structure in the solution [15,16]. It is well known that the mixing of alcohol and water is controlled by excess entropy more than excess enthalpy. Earlier, it was believed that structure of water is enhanced around the hydrophobic group of alcohol which causes the negative excess entropy [17]. However, the recent scattering experiments have shown that there is no enhancement in the structure around the hydrophobic groups of alcohol [18-21]. Alcohol-water systems can have two possible isomers of hydrogen bonded structures where in one case alcohol is the proton acceptor $RHO–H_2O$ or a proton donor $ROH–OH_2$. However, the existence of these two possible isomers are easy to understand but it is quite difficult to find out their relative strength. For example, methanol-water system is amphoteric in nature where both methanol and water can act as proton donor and proton acceptor as well. But, the question arise between which of the two isomer is more stable has been controversial [22-24]. Detailed microwave rotation tunneling spectroscopy has established that the complex where methanol is the proton acceptor and water is the proton donor, $CH_3HO–H_2O$, is the more stable isomer in gas phase [25-28]. In current investigation, the hydrogen bonding interaction is studied between some aliphatic alcohol and their isomers with water molecule for different alcohol-water interacting mode and also the relative stability of such conformers by using computational method is established. Here, the minute details like different path of interactions, relative binding energy, and orientation of molecules were also emphasized by calculating a single point energy and natural bond orbital (NBO) by MP4 methods.

EXPERIMENTAL

Calculation of interaction energy: All the models were constructed by using GaussView 5.0. The hydrogen bonding interactions were studied between some aliphatic alcohol-water complexes by computational methods. Several alcohol-water complexes were constructed in such a way that they have different orientation with respect to each other and optimized these complexes in gas phase at room temperature. The molecular structures were optimized by using Møller-Plesset perturbation methodology *i.e.* MP2 level of theory and double zeta basis set 6-311++G(d,p) at 298 K and 1 atmospheric pressure. After optimization it gives a constant intermolecular hydrogen bond distances and then interaction energies were calculated by changing the intermolecular hydrogen bond distances for every alcohol-water complexes. The single point energies were calculated by the MP4 level of theories with 6-311++G(d,p) basis set using Gaussian09 software package [29].

The interaction energies (E_{IE}) were calculated by using the following equation;

$$E_{IE} = E_{Alcohol\text{-}water} - E_{Alcohol} - E_{water}$$

where, $E_{Alcohol\text{-}water}$ = Energy for alcohol-water complex; $E_{Alcohol}$ = energy of alcohol; and E_{water} = energy of water

Natural bond orbital (NBO) calculation: The natural bond orbital (NBO) analysis were carried out for all possible hydrogen bonding interactions (O-H) of alcohol-water complexes. This interaction is taking place between "filled" Lewis-type NBOs (donor) and "empty" non-Lewis NBOs (acceptor) and calculating their energetic importance by perturbation theory. Since these interactions lead to donation of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals, they are referred to as "delocalization" corrections to the zeroth-order natural Lewis structure. For each donor NBO (i) and acceptor NBO (j), the stabilization energy E(2) associated with delocalization (2e-stabilization) i to j is estimated as:

$$E(2) = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i}$$

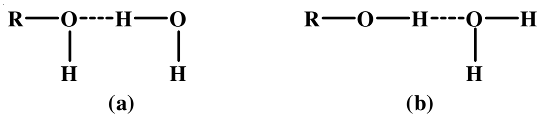
where q_i is the donor orbital occupancy; ε_i, ε_j are diagonal elements (orbital energies) and F(i,j) is the off-diagonal NBO Fock matrix element [30].

RESULTS AND DISCUSSION

Bonding mode and steric effect: Experimental observation shows that alcohol forms strong hydrogen bond within themselves and can also form strong hydrogen bonds with water molecules. All the studied alcohol-water complexes and their isomers are shown in Table-1. There are two different modes of alcohol-water hydrogen bonding interaction, one is proton acceptor and other is proton donor. The first model depicts the interaction due to hydrogen bonding between the oxygen atom of the alcohol molecule and hydrogen atom of water molecule, whereas the second model depicts the interaction between the oxygen atom of the water molecule and hydrogen atom of the alcohol molecule (Fig. 1). In other words, model-I of alcohol-water complex, the oxygen atom of –OH group in alcohol is acted as proton acceptor ($RHO\cdots\cdots H_2O$) whereas, in model-II oxygen atom of -OH group in alcohol is proton donor ($ROH\text{-}\cdots\cdots OH_2$). It has been observed that among all the alcohol-water complexes the interaction energy value is always more negative in model-I than that of model-II (Table-2). Therefore, model-I is found to be more favourable than that of model-II. This can be revealed by the comparison of Mulliken charge density for the interacting sites of alcohol, water and alcohol-water complexes (Table-3).

TABLE-1
INVESTIGATED ALCOHOLS AND THEIR ISOMERS

S. No.	Alcohol	Class	Isomers
1	Methanol	1°	–
2	Ethanol	1°	–
3	Propanol	1°	Propanol or *n*-propyl alcohol
4	Propanol	2°	Propan-2-ol or *iso*-propyl alcohol
5	Butanol	1°	Butanol or *n*-butyl alcohol
6	Butanol	1°	2-Methylpropanol or *iso*-butyl alcohol
7	Butanol	2°	Butan-2-ol or *sec*-butyl alcohol
8	Butanol	3°	2-Methylpropan-2-ol or *tert*-butyl alcohol
9	Pentanol	1°	Pentanol or *n*-pentyl alcohol
10	Pentanol	1°	3-Methylbutanol or *iso*-pentyl alcohol
11	Pentanol	1°	2- Methylbutanol
12	Pentanol	1°	2,2-Dimethylpropanol or *neo*-pentyl alcohol
13	Pentanol	2°	2-Pentanol
14	Pentanol	2°	3-Pentanol
15	Pentanol	2°	3-Methylbutan-2-ol
16	Pentanol	3°	2-Methylbutan-2-ol



(a) (b)

Fig. 1. Mode of hydrogen bonding in alcohol-water complexes (a) proton acceptor and (b) proton donor

TABLE-2
EQUILIBRIUM H-BOND DISTANCES AND O···H INTERACTION ENERGIES FOR ALCOHOL-WATER COMPLEXES

Alcohol	Models	Equilibrium H-Bond distances (Å)	Interaction energies (kcal/mol)
Methanol	I	1.89	-6.653
	II	1.94	-6.160
Ethanol	I	1.90	-6.983
	II	1.94	-6.162
n-Propyl alcohol	I	1.90	-7.019
	II	1.94	-6.520
iso-Propyl alcohol	I	1.90	-8.426
	II	1.96	-7.468
n-Butyl alcohol	I	1.90	-6.501
	II	1.94	-6.184
iso-Butyl alcohol	I	1.89	-6.593
	II	1.94	-6.444
tert-Butyl alcohol	I	1.89	-7.406
	II	1.97	-6.420
2-Butanol	I	1.88	-6.866
	II	1.95	-5.545
1-Pentanol	I	1.90	-6.589
	II	1.95	-6.187
2-Pentanol	I	1.88	-7.459
	II	1.96	-6.283
3-Pentanol	I	1.89	-7.144
	II	1.94	-6.194
iso-Pentyl alcohol	I	1.89	-6.729
	II	1.95	-6.228
neo-Pentyl alcohol	I	1.89	-6.558
	II	1.94	-6.363
2-Methylbutanol	I	1.91	-5.648
	II	1.99	-6.243
2-Methylbutan-2-ol	I	1.89	-7.400
	II	1.96	-6.504
3-Methylbutan-2-ol	I	1.96	-6.389
	II	1.95	-6.252

TABLE-3a
COMPUTED MULLIKEN CHARGE DENSITIES FOR THE INDIVIDUAL ALCOHOL AND WATER MOLECULE

Alcohols	Alcohol		Water		
	O	H	O	H	H
Methanol	-0.382	0.256	-0.508	0.254	0.254
Ethanol	-0.335	0.262	-0.508	0.258	0.254
n-Propyl alcohol	-0.326	0.256	-0.508	0.254	0.254
iso-Propyl alcohol	-0.284	0.270	-0.508	0.254	0.254
n-Butyl alcohol	-0.312	0.253	-0.507	0.254	0.254
iso-Butyl alcohol	-0.310	0.274	-0.508	0.254	0.254
tert-Butyl alcohol	-0.232	0.257	-0.508	0.254	0.254
2-Butanol	-0.250	0.254	-0.508	0.254	0.254
1-Pentanol	-0.305	0.251	-0.508	0.254	0.254
2-Pentanol	-0.246	0.244	-0.508	0.254	0.254
3-Pentanol	-0.250	0.266	-0.508	0.254	0.254
iso-Pentyl alcohol	-0.304	0.250	-0.508	0.254	0.254
neo-Pentyl alcohol	-0.305	0.272	-0.508	0.254	0.254
2-Methylbutanol	-0.313	0.264	-0.508	0.254	0.254
2-Methylbutan-2-ol	-0.228	0.261	-0.508	0.258	0.258
3-Methylbutan-2-ol	-0.255	0.253	-0.508	0.254	0.254

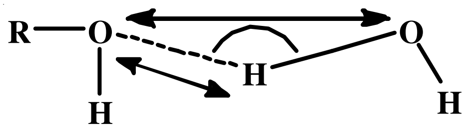


Fig. 2. Representation of bond length $R_{O\cdots H}$ and $R_{O\cdots O}$ (Å) and bond angle $R_{O\cdots H\cdots O}$(°)

On the other hand, due to the proton accepting nature of model-I, water molecule comes closer to the alcohol molecule which experiences more repulsive forces by alkyl group of alcohol which results significant deviation of O-H-O bond angle in the alcohol-water complex (Fig. 2). Generally, in alcohol-water complex for model-I, the ideal O-H-O bond angle should be 180º, but due to the repulsive forces exist between the alkyl group of alcohol and water molecule there exist a characteristics deviation from the ideal bond angle (180º). Thus, more is the repulsive forces between the alkyl group and water in alcohol-water complex, more will be the deviation of O-H-O bond angle. In present investigation, the bond angle deviation for model-I within a range of 8-16º is obtained. On the other hand, in model-II *i.e.* proton donor alcohol-water complex shows a minimum repulsion between alkyl group of alcohol and water molecule. Therefore, it shows minimum deviation of O-H-O bond angle (approximately 2º) in alcohol-water complex, as it has been established from the optimized model of alcohol-water complexes (Table-4). Isomers of alcohols also plays an important role in the deviation of O-H-O bond angle in alcohol-water complexes, bulky alkyl group occurs more repulsion to the water molecule in alcohol-water complexes which reduces the O-H-O bond angle than that of the ideal condition.

Lower alcohols such as methanol or ethanol-water complexes, model-I always shows more O-H-O bond angle deviations than model-II as explained above. Propanol has two isomeric forms *iso*-propyl and *n*-propyl alcohol. In case of propanol-water complexes, *iso*-propyl alcohol-H_2O complex shows more deviation in O-H-O bond angle (167.4º) than in *n*-propyl alcohol-H_2O complex (172.78º). This is due to the bulkiness of *iso*-propyl group than that of *n*-propyl group. Again, butanol exist as four isomers and forms four different types of complexes with water. In butanol-H_2O complexes of model-I, both *n*-butyl alcohol-H_2O and *iso*-butyl alcohol-H_2O complexes show almost similar type of deviation in O-H-O bond angle (~172º), due to their less bulky alkyl group. But in *tert*-butyl alcohol-H_2O complex, the deviation in O-H-O bond angle (168.04º) is more than that of above two isomers, this is due to the bulky and symmetrical *tert*-butyl group. Interestingly, present investigations revealed that 2-butanol-H_2O complex exhibits high deviations in the O-H-O bond angle (164.17º) than that of all of its isomers because of unsymmetrical repulsions brought about by the -CH_3 and -C_2H_5 groups (Fig. 4g). On the other hand, pentanol has eight different isomers, O-H-O bond angle

TABLE-3b
COMPUTED MULLIKEN CHARGE DENSITIES FOR ALCOHOL-WATER COMPLEXES

Alcohols	Models	Alcohol		Water		
		O	H	O	H	H
Methanol	I	-0.434	0.276	-0.574	0.252	0.323
	II	-0.464	0.372	-0.575	0.278	0.278
Ethanol	I	-0.393	0.284	-0.563	0.251	0.312
	II	-0.460	0.425	-0.581	0.277	0.279
n-Propyl alcohol	I	-0.368	0.276	-0.552	0.251	0.308
	II	-0.457	0.446	-0.578	0.278	0.278
iso-Propyl alcohol	I	-0.302	0.269	-0.548	0.254	0.296
	II	-0.400	0.423	-0.580	0.279	0.283
n-Butyl alcohol	I	-0.370	0.276	-0.556	0.251	0.310
	II	-0.456	0.430	-0.579	0.279	0.279
iso-Butyl alcohol	I	-0.353	0.266	-0.573	0.254	0.325
	II	-0.455	0.446	-0.578	0.279	0.279
tert-Butyl alcohol	I	-0.274	0.273	-0.548	0.255	0.302
	II	-0.352	0.412	-0.581	0.283	0.283
2-Butanol	I	-0.292	0.263	-0.545	0.252	0.307
	II	-0.404	0.428	-0.579	0.279	0.281
1-Pentanol	I	-0.368	0.276	-0.552	0.251	0.308
	II	-0.453	0.429	-0.580	0.280	0.280
2-Pentanol	I	-0.281	0.265	-0.538	0.250	0.308
	II	-0.401	0.428	-0.581	0.282	0.282
3-Pentanol	I	-0.333	0.280	-0.581	0.251	0.348
	II	-0.324	0.375	-0.568	0.274	0.287
iso-Pentyl alcohol	I	-0.349	0.267	-0.565	0.253	0.319
	II	-0.443	0.419	-0.578	0.278	0.283
neo-Pentyl alcohol	I	-0.315	0.281	-0.543	0.243	0.321
	II	-0.451	0.467	-0.577	0.280	0.280
2-Methylbutanol	I	-0.334	0.289	-0.517	0.247	0.275
	II	-0.457	0.450	-0.576	0.280	0.280
2-Methylbutan-2-ol	I	-0.270	0.278	-0.551	0.253	0.313
	II	-0.367	0.432	-0.581	0.283	0.285
3-Methylbutan-2-ol	I	-0.282	0.250	-0.558	0.257	0.299
	II	-0.418	0.457	-0.579	0.280	0.280

TABLE-4
COMPUTED O···H (Å) BOND DISTANCES AND
O···H···O (°) BOND ANGLE CALCULATION FOR
ALCOHOL-WATER COMPLEXES

Alcohol	Models	$R_{O\cdots H}$ (Å)	$R_{O\cdots O}$ (Å)	$R_{O\cdots H\cdots O}$ (°)
Methanol	I	1.89	2.85	172.11
	II	1.94	2.91	178.91
Ethanol	I	1.90	2.86	172.66
	II	1.94	2.91	179.97
n-Propyl alcohol	I	1.90	2.87	172.78
	II	1.94	2.91	179.09
iso-Propyl alcohol	I	1.90	2.85	167.41
	II	1.96	2.93	178.69
n-Butyl alcohol	I	1.90	2.87	172.33
	II	1.94	2.91	178.84
iso-Butyl alcohol	I	1.89	2.85	172.16
	II	1.94	2.91	178.93
tert-Butyl alcohol	I	1.89	2.85	168.04
	II	1.97	2.93	179.04
2-Butanol	I	1.88	2.83	164.17
	II	1.95	2.92	178.57
1-Pentanol	I	1.90	2.87	172.19
	II	1.95	2.91	179.1
2-Pentanol	I	1.88	2.83	163.97
	II	1.96	2.93	178.18
3-Pentanol	I	1.89	2.86	175.46
	II	1.94	2.9	172.48
iso-Pentyl alcohol	I	1.89	2.85	171.31
	II	1.95	2.91	179.12
neo-Pentyl alcohol	I	1.89	2.83	164.65
	II	1.94	2.90	178.63
2-Methyl-butan-1-ol	I	1.92	2.87	164.28
	II	1.99	2.92	162.56
2-Methyl-butan-2-ol	I	1.89	2.84	167.49
	II	1.96	2.93	178.85
3-Methyl-butan-2-ol	I	1.96	2.91	167.95
	II	1.95	2.91	178.49

deviations in primary pentanol-water complex depends on the presence of alkyl branch at α-carbon of alcohol, it is because of such alkyl group exert more steric repulsion on water molecule (Fig. 3). Therefore, neo-pentyl alcohol-water and 2-methyl butanol-water complexes shows more O-H-O bond angle deviations than that of pentan-1-ol water and 3-methyl butanol water complexes (Table-4). Again, in secondary pentanol-water complex O-H-O bond angle deviation depends on the alkyl group linked to α-carbon of alcohol, *i.e.* due to the presence of two ethyl group in pentan-3-ol water complex, it shows symm-

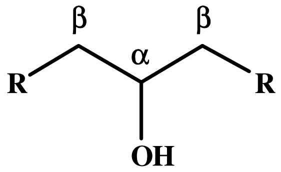
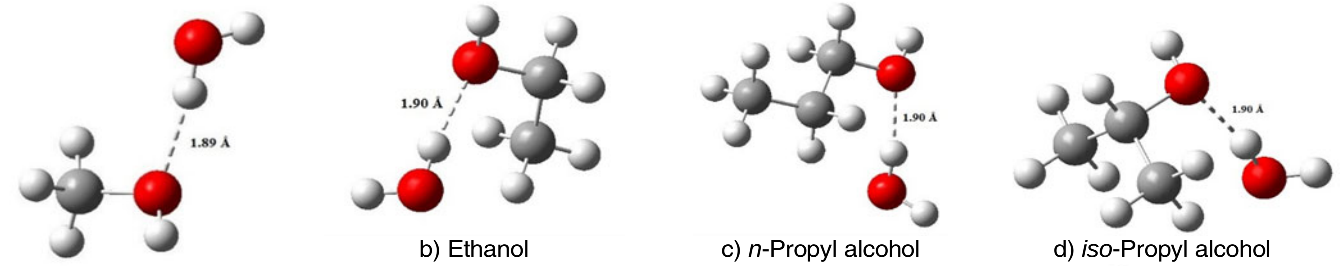


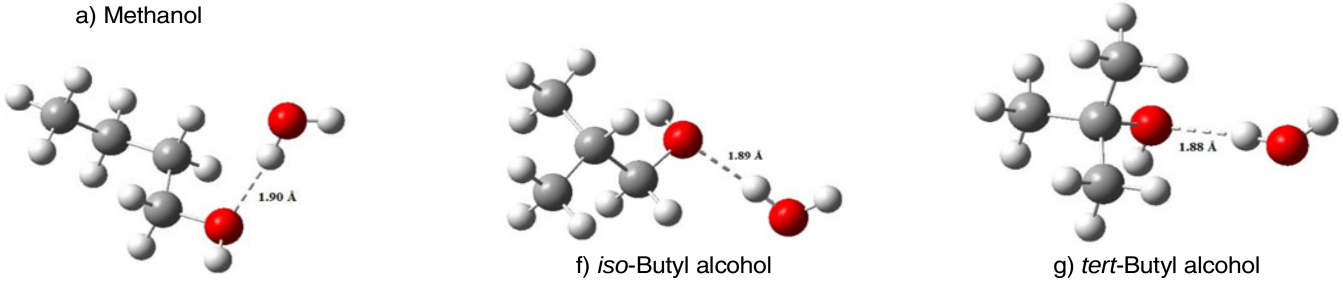
Fig. 3. Representation of α and β carbon in alcohols

etrical repulsion and hence least O-H-O bond angle deviations (175°) than all other pentanol-water complexes. But, 3-methylbutan-2-ol-water and pentan-2-ol water complexes show more O-H-O bond angle deviations than that of pentan-3-ol water complex due to the presence of different alkyl group linked to α-carbon atom (Fig. 4j & l). *tert*-Pentanol-water complex (*i.e.* 2-methylbutan-2-ol-water) also shows highest O-H-O bond



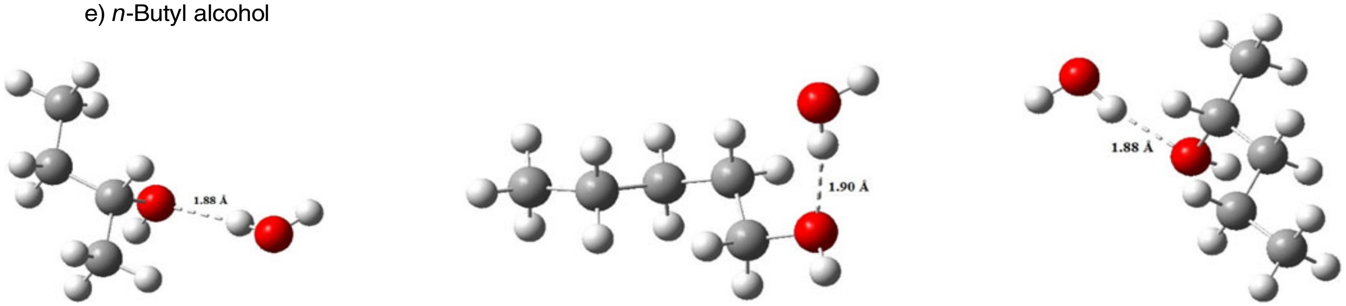
b) Ethanol c) *n*-Propyl alcohol d) *iso*-Propyl alcohol

a) Methanol

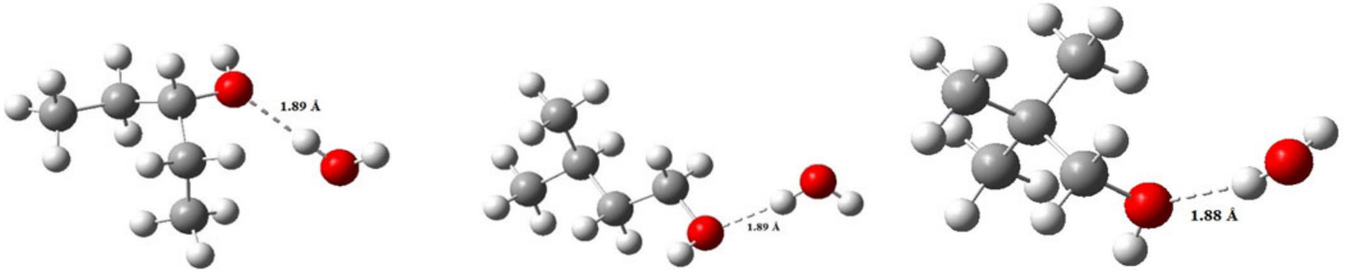


f) *iso*-Butyl alcohol g) *tert*-Butyl alcohol

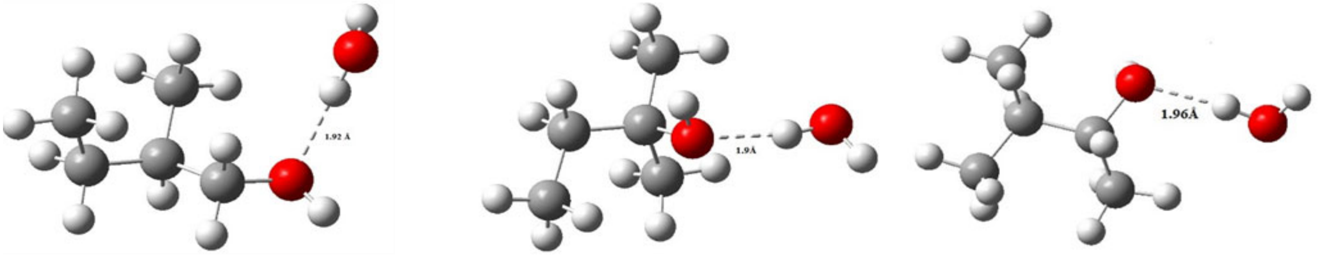
e) *n*-Butyl alcohol



h) *sec*-Butyl alcohol i) *n*-Pentyl alcohol j) 2-Pentanol



k) 3-Pentanol l) *iso*-Pentyl alcohol m) *neo*-Pentyl alcohol



n) 2-Methylbutanol o) 2-Methylbutan-2-ol p) 3-Methylbutan-2-ol

Fig. 4. Optimized models for isomers of alcohol-water complexes with proton acceptor hydrogen bonding mode

angle deviations (~164°) this is because of the presence of three alkyl groups attached to α-carbon atom (Fig. 4p).

Calculation of interaction energy of alcohol-water complex also reveals the stability of such system. Interestingly, it has also been observed that the interaction energy value for normal chain alcohol-water complex gives more negative interaction energy value in lower alcohols (*i.e.* methanol, ethanol and propanol) and then suddenly decreases in higher alcohol (*i.e.* butanol and propanol) (Table-1). It happens because as the number of carbon atom increases in the alkyl group of an alcohol, the hydrophobicity of alkyl part of the molecule also increases, which also results in the increase of electron donating effect of alkyl group in alcohol-water complex. Therefore, in lower alcohols *viz.* in methanol, ethanol and propanol, an inductive effect outweighs the overall increase in hydrophobic nature of alkyl group of alcohol molecule and as a result of which stronger hydrogen bond forms in such systems. This results more negative interaction energy values and strong hydrogen bond in alcohol-water complex from methanol to propanol. Therefore, the sequence of stability in alcohol-water complex and interaction energy values in lower alcohols show, methanol·····H_2O < ethanol····· H_2O < propanol·····H_2O (Table-2). It is well established that alcohols with more than three carbon atoms (*viz.* butanol and pentanol), the overall hydrophobic nature of alkyl groups of alcohol molecule increases and it is predominant over the electron releasing effect of the alkyl group. Thus in alcohol-water complex, the alcohol molecules minutely start repelling water molecule. This is why the decrease in the interaction energy as well as weakening of hydrogen bonding in higher alcohol-water complexes as compared to the lower alcohol-water complexes.

In case of the isomeric alcohols for propanol, butanol and pentanol, the alcohol with more branches has more negative interaction energy than the normal alcohol with less branches. In such isomeric alcohols (chain and positional isomers), if the alkyl group has more branches, then it gets more spherical shape. These spherical alkyl groups always have a lower surface area then that of normal alkyl chain and hence are less hydrophobic in nature. Since, the hydrogen bond formed by the less hydrophobic isomers are stronger than the more hydrophobic ones, hence the branched chain alcohol-water complexes have more negative interaction energy than that of straight chain alcohol-water complexes. In the above studied isomeric alcohol-water complexes, the sequence of stability and interaction energies in the isomers of propanol, butanol, pentanol are given below:

i) *n*-Propyl alcohol-H_2O < *iso*-Propyl alcohol-H_2O

ii) *n*-Butyl alcohol-H_2O < *iso*-Butyl alcohol-H_2O < *sec*-Butyl alcohol-H_2O < *tert*-Butyl alcohol-H_2O

iii) 2-Methylbutanol-H_2O < 3-Methylbutan-2-ol-H_2O < *neo*-Pentyl alcohol-H_2O < Pentanol-H_2O < *iso*-Pentyl alcohol-H_2O < 3-Pentanol-H_2O < 2-Methylbutan-2-ol-H_2O < 2-Pentanol-H_2O

Interaction energy plots: Again, we are trying to change the hydrogen bond distances of all the alcohol-H_2O optimized models within a range from 1.2 to 3.0 Å to compute the actual alcohol-water interaction energies. By this way we can easily predict the strength of hydrogen bond, stability, bond dissociation energies as well as the chemical behaviour of these complexes. Generally, if we plot interaction energies (kcal/mol) for each model with respect to the change in hydrogen bond distances then we can get an exponentially decreasing curve. The minimum point in curve results the more negative interaction energy value, which gives the most favored point with a stable alcohol-water complex. It has been observed that on increasing the hydrogen bond length after a certain point, the interaction energy becomes steady and they behave as two individual molecules rather than an alcohol-water complex. Moreover, further decreasing the hydrogen bond distances after minimize point of alcohol-water complexes, it gives the less negative or positive interaction energy value and it may also form covalent bond if they get closer than the minimum intermolecular distances *i.e.* 1.2 Å. Since, we have to determine the minimized interaction energy between alcohol-water complexes; therefore only one minimized point with more negative interaction energy value is considered. Here, we have shown the interaction energy plot for methanol-water complexes for both model-I and II (Fig. 5) and all the other alcohol-water complexes also show almost similar type of plots.

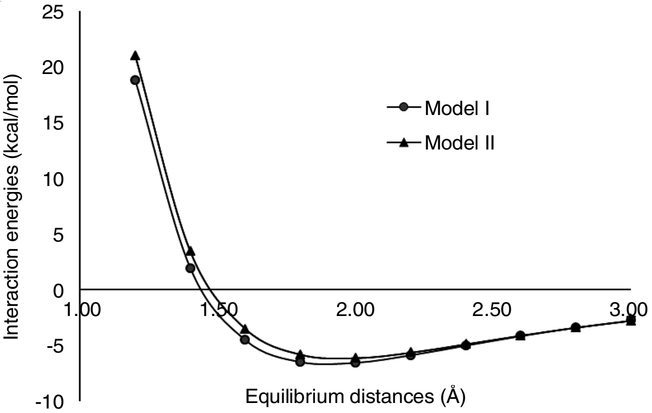


Fig. 5. Interaction energy plot for methanol-water complex

Natural bond orbital (NBO) analysis: Natural bond orbital (NBO) analysis performed by Gaussian09 to understand the electron charge delocalization during the course of interaction. From the value of electronic stabilization energy E(2), we could have an idea about how much interaction is taking place between the interacting counterparts of a molecule. Delocalization of electron charge density between occupied Lewis type (bonding or lone pair) NBO orbitals and formally unoccupied (anti-bonding or Rydberg) non-Lewis NBO orbitals corresponds to a stabilizing donor-acceptor interaction. All the above mentioned alcohol-water complexes show that the hydrogen bonding is taking place through the -OH of alcohol with water. The two possibilities of shifting of electron charge density depending upon their molecular conformations were observed *i.e.* either from alcohol to water or from water to alcohol. The donor-acceptor electronic stabilization energy (E2) of the hydrogen bonding sites (O-H) for all the alcohol-water complexes are shown in Table-5. From the hydrogen bonding sites in alcohol-water complex, it is clearly observed that the lone pair (LP) of

TABLE-5
COMPUTED NBO AND DONOR-ACCEPTOR SITES FOR ALCOHOL-WATER COMPLEXES

Alcohol	Models	Donor	Acceptor	Stabilization energy (kcal/mol)
Methanol	I	LP(2) O5(A)	BD*(1) O7-H9(W)	3.97
	II	LP(2) O7(W)	BD*(1) O5-H6(A)	6.31
Ethanol	I	LP(2) O4(A)	BD*(1) O6-H8(W)	4.20
	II	LP(2) O6(W)	BD*(1) O4-H5(A)	6.20
n-Propyl alcohol	I	LP(2) O4(A)	BD*(1) O6-H8(W)	4.22
	II	LP(2) O6(W)	BD*(1) O4-H5(A)	6.24
iso-Propyl alcohol	I	LP(2) O3(A)	BD*(1) O5-H7(W)	4.81
	II	LP(2) O5(W)	BD*(1) O3-H4(A)	6.40
n-Butyl alcohol	I	LP(2) O4(A)	BD*(1) O6-H8(W)	4.51
	II	LP(2) O6(W)	BD*(1) O4-H5(A)	6.21
iso-Butyl alcohol	I	LP(2) O2(A)	BD*(1) O4-H6(W)	4.15
	II	LP(2) O6(W)	BD*(1) O4-H5(A)	6.23
tert-Butyl alcohol	I	LP(2) O2(A)	BD*(1) O4-H6(W)	5.02
	II	LP(2) O4(W)	BD*(1) O2-H3(A)	6.49
2-Butanol	I	LP(2) O3(A)	BD*(1) O5-H7(W)	4.59
	II	LP(2) O5(W)	BD*(1) O3-H4(A)	6.39
1-Pentanol	I	LP(2) O4(A)	BD*(1) O6-H8(W)	4.55
	II	LP(2) O6(W)	BD*(1) O4-H5(A)	6.20
2-Pentanol	I	LP(2) O3(A)	BD*(1) O5-H7(W)	4.53
	II	LP(2) O5(W)	BD*(1) O3-H4(A)	6.43
3-Pentanol	I	LP(1) O3(A)	BD*(1) O5-H7(W)	3.62
	II	LP(2) O5(W)	BD*(1) O3-H4(A)	6.22
iso-Pentyl alcohol	I	LP(2) O4(A)	BD*(1) O6-H8(W)	4.49
	II	LP(2) O6(W)	BD*(1) O4-H5(A)	6.22
neo-Pentyl alcohol	I	LP(2) O2(A)	BD*(1) O4-H6(W)	2.63
	II	LP(2) O6(W)	BD*(1) O4-H5(A)	6.25
2-Methylbutanol	I	LP(2) O6(A)	BD*(1) O4-H5(W)	2.09
	II	LP(2) O6(W)	BD*(1) O4-H5(A)	6.23
2-Methylbutan-2-ol	I	LP(2) O2(A)	BD*(1) O4-H6(W)	4.98
	II	LP(2) O4(W)	BD*(1) O2-H3(A)	6.49
3-Methylbutan-2-ol	I	LP(2) O3(A)	BD*(1) O5-H7(W)	5.80
	II	LP(2) O5(W)	BD*(1) O3-H4(A)	6.39

LP = lone pair, BD* = Antibonding orbital, A = Alcohol molecule, W = Water molecule

oxygen (either from alcohol or water) behaves as electron donor whereas the O-H antibonding (BD*) orbital behaves as electron pair acceptor. Higher value of computed electronic stabilization energy E(2) in alcohol-water complexes result favorable donor-acceptor complex through hydrogen bonding (Table-5). Therefore, a lower alcohol-water complex shows effective hydrogen bonding interaction in gas phase but the steric effect of higher alcohols may restrict the stability of such hydrogen bond.

Conclusion

All alcohol-water complexes can form hydrogen bond either through proton accepting or proton donor mode of interaction. Calculation of interaction energy of such complexes reveal that the proton acceptor (RHO–H_2O) hydrogen bonding mode is always more favourable than that of proton donor (ROH–H_2O) mode of interaction. For lower molecular weight alcohol-water complexes, the order of interaction energy and stability is methanol-water < ethanol-water < propanol-water. But, for higher alcohols the mode of interaction is significantly affected by the bulky alkyl groups of such alcohols. During the hydrogen bonding interaction, the O-H-O bond angle of alcohol-water complexes also showed some deviation. It has been observed that among all isomers of lower alcohol-water complexes, propan-2-ol-water shows more deviation of O-H-O bond angle than others. But, for higher alcohol (butanol and pentanol)-water complexes, butan-2-ol-water, butan-2-ol-water, 2,2-dimethylpropanol and 2-methylbutan-2-ol-water shows high deviation of O-H-O bond angle than other alcohol-water complexes. NBO analysis also showed that donor-acceptor mode of interaction in the alcohol-water complexes.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. Y. Marcus, The Properties of Solvents, John Wiley & Sons: Chichester (1998).
2. A.J. Kirby, *Acc. Chem. Res.*, **30**, 290 (1997); https://doi.org/10.1021/ar960056r
3. G.R. Desirajau, Crystal Engineering: The Design of Organic Solids, Elsevier: Amsterdam (1989).

4. G.A. Jeffrey and W. Saenger, Hydrogen Bonding in Biological Structures, Springer-Verlag: New York (1991).
5. J.A. Gerlt, M.M. Kreevoy, W.W. Cleland and P.A. Frey, *Chem. Biol.*, **4**, 259 (1997); https://doi.org/10.1016/S1074-5521(97)90069-7
6. F. Franks, Water: A Comprehensive Treatised, Plenum Press, vol. 2 (1973).
7. E.E. Fileti, P. Chaudhuri and S. Canuto, *Chem. Phys. Lett.*, **400**, 494 (2004); https://doi.org/10.1016/j.cplett.2004.10.149
8. F. Franks and J.E. Desnoyers, ed: F. Franks, Water Science Reviews, Cambridge University Press, Cambridge, vol. 1, p. 171 (1985).
9. I. Juurinen, K. Nakahara, N. Ando, T. Nishiumi, H. Seta, N. Yoshida, T. Morinaga, M. Itou, T. Ninomiya, Y. Sakurai, E. Salonen, K. Nordlund, K. Hämäläinen and M. Hakala, *Phys. Rev. Lett.*, **107**, 197401 (2011); https://doi.org/10.1103/PhysRevLett.107.197401
10. S. Dixit, J. Crain, W.C.K. Poon, J.L. Finney and A.K. Soper, *Nature*, **416**, 829 (2002); https://doi.org/10.1038/416829a
11. J.-H. Guo, Y. Luo, A. Augustsson, S. Kashtanov, J.-E. Rubensson, D.K. Shuh, H. Ågren and J. Nordgren, *Phys. Rev. Lett.*, **91**, 157401 (2003); https://doi.org/10.1103/PhysRevLett.91.157401
12. R.K. Lam, J.W. Smith and R.J. Saykally, *J. Chem. Phys.*, **144**, 191103 (2016); https://doi.org/10.1063/1.4951010
13. T. Sato, A. Chiba and R. Nozaki, *J. Chem. Phys.*, **112**, 2924 (2000); https://doi.org/10.1063/1.480865
14. A. Coccia, P.L. Indovina, F. Podo and V. Viti, *Chem. Phys.*, **7**, 30 (1975); https://doi.org/10.1016/0301-0104(75)85022-1
15. Peter I. Nagy, *Int. J. Mol. Sci.*, **15**, 19562 (2014); https://doi.org/10.3390/ijms151119562
16. T.A. Dolenko, S.A. Burikov, S.A. Dolenko, A.O. Efitorov, I.V. Plastinin, V.I. Yuzhakov and S.V. Patsaeva, *J. Phys. Chem. A*, **119**, 10806 (2015); https://doi.org/10.1021/acs.jpca.5b06678
17. F. Franks and D.J.G. Ives, *Q. Rev. Chem. Soc.*, **20**, 1 (1966); https://doi.org/10.1039/QR9662000001
18. S. Dixit, A. Soper, J. Finney and J. Crain, *Europhys. Lett.*, **59**, 377 (2002); https://doi.org/10.1209/epl/i2002-00205-7
19. J.L. Finney, D.T. Bowron, R.M. Daniel, P.A. Timmins and M.A. Roberts, *Biophys. Chem.*, **105**, 391 (2003); https://doi.org/10.1016/S0301-4622(03)00104-2
20. T.S. van Erp and E.J. Meijer, *J. Chem. Phys.*, **118**, 8831 (2003); https://doi.org/10.1063/1.1567258
21. J. Fidler and P. Rodger, *J. Phys. Chem. B*, **103**, 7695 (1999); https://doi.org/10.1021/jp9907903
22. J.E. Del Bene, *J. Chem. Phys.*, **55**, 4633 (1971); https://doi.org/10.1063/1.1676800
23. S. Kim, M.S. Jhon and H.A. Scheraga, *J. Phys. Chem.*, **92**, 7216 (1988); https://doi.org/10.1021/j100337a012
24. N. Bakkas, Y. Bouteiller, A. Loutellier, J.P. Perchard and S. Racine, *Chem. Phys. Lett.*, **232**, 90 (1995); https://doi.org/10.1016/0009-2614(94)01318-P
25. P.A. Stockman, G.A. Blake, F.J. Lovas and R.D. Suenram, *J. Chem. Phys.*, **107**, 3782 (1997); https://doi.org/10.1063/1.474736
26. L. González, O. Mó and M. Yáñez, *J. Chem. Phys.*, **109**, 139 (1998); https://doi.org/10.1063/1.476531
27. K.N. Kirschner and R.J. Woods, *J. Phys. Chem. A*, **105**, 4150 (2001); https://doi.org/10.1021/jp004413y
28. E.E. Fileti, K. Coutinho and S. Canuto, *Adv. Quantum Chem.*, **47**, 51 (2004); https://doi.org/10.1016/S0065-3276(04)47004-X
29. M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewaki, J.V. Ortiz, J.B. Foresmann, J. Ciolowski, A. Namayakkara, M. Challacombe, C.Y. Peng, B.B. Stefanov, P.Y. Ayala, M.W. Wong, J.L. Andres, E.S. Replogle, W. Chen, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez and J.A. Pople, Gaussian 09, Gaussian Inc., Pittsburgh (2009).
30. M. Szafran, A. Komasa and E. Bartoszak-Adamska, *J. Mol. Struct. THEOCHEM*, **827**, 101 (2007); https://doi.org/10.1016/j.molstruc.2006.05.012