Solvent effects on the structure and dipole moment of resorcinol

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Abstract

With the specific aim of explaining the dipole moment (DM) of resorcinol in water, we investigated the molecular conformations and solute–solvent interactions of resorcinol in ethanol, methanol and water. In this work, experimental dielectric procedures and theoretical ab initio and density functional methods were used. Basis sets at the levels of theory HF/6-31G(d) and B3LYP/6-31G(d) were used for calculations. Onsager's method was used to analyze the solvent effects on the conformers of resorcinol. A conformational equilibrium between the two main conformers of non-solvated resorcinol was proposed. The total energies, DMs, structural molecular and reactivity parameters of the conformers and transition states involved were calculated. These theoretical magnitudes were correlated with parameters of the solvating solvents. The properties of the solute–solvent association complexes formed by a molecule of resorcinol and two molecules of water by means of intermolecular hydrogen bonds were also calculated. It was concluded that the DM of resorcinol in water (8.66 D) is due to these solute–solvent association complexes, which are the predominant forms of resorcinol in aqueous solutions.
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Keywords: Resorcinol; Dipole moment; Conformations; Association complexes; Ab initio and DFT calculations

1. Introduction

Among polyphenolic compounds [1], flavonoids [2] constitute one of the most important groups due to their biological and physicochemical properties [3,4]. The structures of various classes of flavonoids show that the A-ring is a resorcinol, whereas the B-ring is a catechol derivative. In particular, resorcinol and their derivatives have numerous uses and applications in physical chemistry. For example, they are used in the synthesis of sugars [5] and tweezer-type compounds [6], in the determination of vanadium by ion-interaction reversed-phase liquid chromatography [7], of ascorbic acid in pharmaceuticals [8] and in the preparation of different organic and inorganic complexes [9,10]. The crystalline structure [11], ultrasonic behavior in protic and aprotic solvents [12], optic [13] and spectroscopic [14] characteristics, and polymorphism [15] of resorcinol have been investigated. However, there are few studies dealing with the molecular and electronic structures of resorcinol in the gaseous phase [16] or the molecular conformations and dipole moment (DM) of resorcinol in the hydroxylic solvents.

As a part of the research program aimed at investigating the stereochemical characteristics of compounds of biological importance, we investigated the structure and DM of sulfamethoxazole [17,18], flavone [19], catechol [20] and phloroglucinol [21] in hydroxylic solvents. The DM of highly diluted solutions of resorcinol in water at 25 °C was calculated using Buckingham's method [22], giving a DM average of 8.66 D [23]. With the objective of explaining this DM, in this paper we investigate the molecular conformations and solute–solvent interactions of resorcinol in ethanol, methanol and water by means of ab initio and density functional (DFT) methods.

2. Experimental

A series of complementary experiments were performed in order to confirm results obtained in previous dielectric

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measurements and determine the partial volume of the solute and the solvent.

White needles of pure resorcinol (mp = 101 °C) from Fluka (≥99%) were used for preparation of all solutions with conductivity water (2.87×10^{-6} μS). The working conditions and procedures for performing measurements were similar to those described previously [19,21].

3. Calculations

The structures of the conformers of resorcinol (Re), which we shall designate as Re1 and Re2, and the practical numbering system adopted for performing the calculations are shown in Fig. 1. The calculations were carried out following previously used procedures [21]. The potential energy surface minima obtained by the scan of Re in vacuum and water at the HF/6-31G(d) level of theory were optimized with the GAUSSIAN 98 [24] program packages, using basis sets at the HF/6-31G(d) and B3LYP/6-31G(d) levels of theory and the default convergence criteria.

Onsager's [25] method was used to analyze the solvent effects (ethanol, methanol and water) on Re1 and Re2. The equilibrium constant (K_C) and the energy of the transition state (TS) of the conformational reaction proposed were calculated at the B3LYP/6-31G(d) level of theory. Furthermore, to shed light on the experimental DM of Re in water, we proposed the formation of solute–solvent association complexes by means of intermolecular hydrogen bonds (IHBs) that involve one molecule of solute and some molecules of solvent.

4. Results and discussion

### 4.1. Conformational properties of resorcinol

Rotating the planes that contain the hydroxyl groups with respect to the plane containing the rest of the molecule around single bonds C–OH, the existence of two principal conformers of RE was detected (Fig. 1). In the same way as Rudyk et al. [21], the following conformational reaction was proposed

$$Re1 \rightleftharpoons Re2 \tag{1}$$

which is characterized by the conformational equilibrium constant K_C. Tables 1–3 give the calculated structural properties using Onsager's method at the B3LYP/6-31G(d) level of theory, for Re1 and Re2 and the corresponding activated complex (TS).

The rotamers Re1 and Re2 have a totally planar structure, while the calculated TS in ethanol, methanol and water has non-planar structures. As an example, Fig. 2 shows the structure of the TS computed in water. From Tables 1–3 it can be observed that the thermodynamic stability of Re1 is slightly higher than that of Re2. Also, that the dihedral angle D-$H_{14}O_8C_3C_4$, which measures the non-planarity of the TS molecule, practically does not change with the solvent.

On the other hand, the K_C values increase according to the following sequence

$$K_C(\text{ethanol}) < K_C(\text{methanol}) < K_C(\text{water}) \tag{2}$$
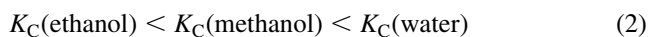
This indicates that the K_C constants increase when the permittivity (D) of the reaction medium increases. This conclusion agrees with the experimental observations, which show that the equilibria are shifted toward the formation of species with major DM [26].

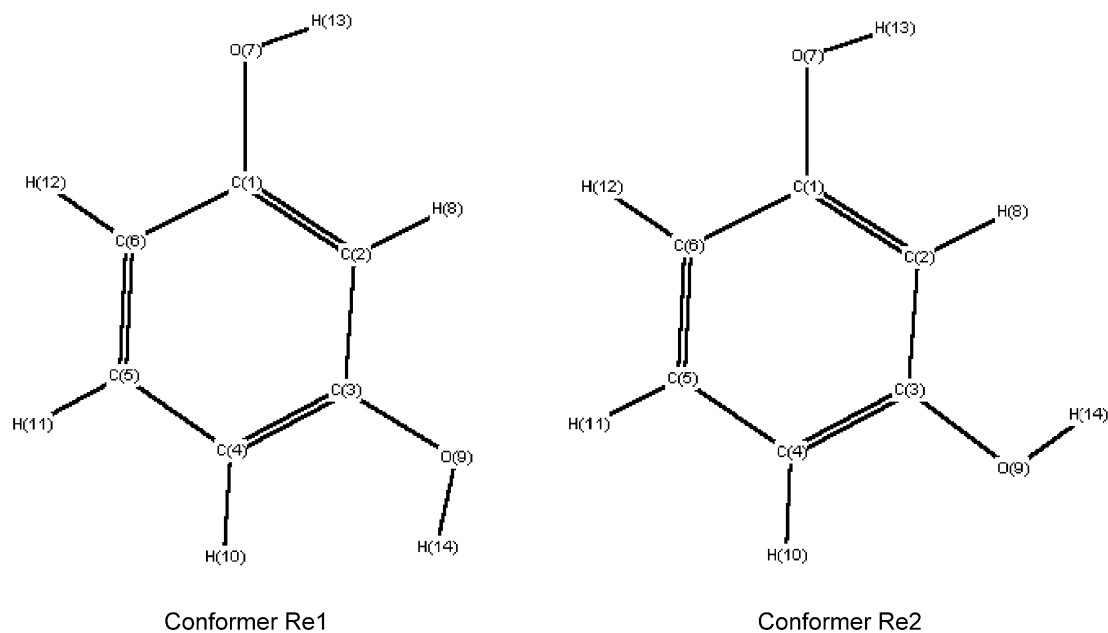Conformer Re1   Conformer Re2

Fig. 1. Structures of conformers of resorcinol and practical numbering system adopted for carrying out the calculations.

Table 1
Calculated structural magnitudes using Onsager's method at the B3LYP/6-31G(d) level of theory for the conformers (Re1 and Re2) and activated complex (TS) of resorcinol in ethanol, at 25 °C

Molecular properties	Ethanol		
	Re1	Re2	TS
TE	−240147.63	−240147.37	−240143.44
K_C	0.645		
DM	1.68	2.83	2.09
RBE	4.19	3.93	–
A_o	4.13	4.20	4.20
D-$H_{14}O_8C_3C_4$	0	0	91.9
qO_7	−0.565	−0.559	−0.561
qO_8	−0.558	−0.559	−0.588
qH_{13}	0.317	0.321	0.320
qH_{14}	0.322	0.321	0.324
rH_{13}-O_7	0.966	0.966	0.966
A-$H_{13}O_8C_1$	108.8	109.6	109.1

TE, total energy including solvent energy (kcal/mol); K_C, conformational equilibrium constant; RBE, energy of the rotation barrier (kcal/mol); DM, dipolar moment (Debye); A_o, molecular radius (Å); D-$H_{14}O_8C_3C_4$, dihedral angle $H_{14}O_8C_3C_4$ (°); q, total atomic charge (a.u.); rH_{13}-O_7, bond length between the indicated atoms (Å) (Figs. 1 and 2); A-$H_{13}O_8C_1$, bond angle (°).

It is well known that Kirkwood's equation [27,28] permits to analyze the influence of the solvents upon the specific rate dipole–dipole reactions. Recently [20], Eq. (3) was obtained using the Kirkwood's equation

$$\ln K_C = \ln K_\infty + \frac{3}{4kT}\left[\frac{DM_{Re1}^2}{A_{o_{Re1}}^3} - \frac{DM_{Re2}^2}{A_{o_{Re2}}^3}\right]\frac{1}{D} \qquad (3)$$

Table 2
Calculated structural magnitudes using Onsager's method at the B3LYP/6-31G(d) level of theory for the conformers (Re1 and Re2) and activated complex (TS) of resorcinol in methanol, at 25 °C

Molecular properties	Methanol		
	Re1	Re2	TS
TE	−240147.67	−240147.46	−240143.48
K_C	0.696		
DM	1.75	2.91	2.11
RBE	4.19	3.98	–
A_o	3.96	4.07	4.10
D-$H_{14}O_8C_3C_4$	0	0	91.7
qO_7	-0.566	-0.559	-0.561
qO_8	-0.557	-0.559	-0.588
qH_{13}	0.316	0.322	0.320
qH_{14}	0.322	0.322	0.324
rH_{13}-O_7	0.966	0.966	0.966
A-$H_{13}O_8C_1$	108.7	109.6	109.2

TE, total energy including solvent energy (kcal/mol); K_C, conformational equilibrium constant; RBE, energy of the rotation barrier (kcal/mol); DM, dipolar moment (Debye); A_o, molecular radius (Å); D-$H_{14}O_8C_3C_4$, dihedral angle $H_{14}O_8C_3C_4$ (°); q, total atomic charge (a.u.); rH_{13}-O_7, bond length between the indicated atoms (Å) (Figs. 1 and 2); A-$H_{13}O_8C_1$, bond angle (°).

Table 3
Calculated structural magnitudes using Onsager's method at the B3LYP/6-31G(d) level of theory for the conformers (Re1 and Re2) and activated complex (TS) of resorcinol in water, at 25 °C

Molecular properties	Water		
	Re1	Re2	TS
TE	−240147.73	−240147.61	−240143.53
K_C	0.817		
DM	1.83	3.02	2.14
RBE	4.20	4.08	–
A_o	3.81	3.90	4.00
D-$H_{14}O_8C_3C_4$	0	0	91.4
qO_7	−0.567	−0.559	−0.561
qO_8	−0.557	−0.559	−0.588
qH_{13}	0.316	0.323	0.320
qH_{14}	0.323	0.323	0.325
rH_{13}-O_7	0.966	0.967	0.966
A-$H_{13}O_8C_1$	108.6	109.6	109.2

TE, total energy including solvent energy (kcal/mol); K_C, conformational equilibrium constant; RBE, energy of the rotation barrier (kcal/mol); DM, dipolar moment (Debye); A_o, molecular radius (Å); D-$H_{14}O_8C_3C_4$, dihedral angle $H_{14}O_8C_3C_4$ (°); q, total atomic charge (a.u.); rH_{13}-O_7, bond length between the indicated atoms (Å) (Figs. 1 and 2); A-$H_{13}O_8C_1$, bond angle (°).

This equation is very useful to determine the dependence of the equilibrium constant of a reaction that involves polar molecules, as the conformational equilibrium described by Eq. (1), with the permittivity of the medium. In Eq. (3), K_∞ is the conformational equilibrium constant for a medium with infinite D; k is Boltzmann's constant; T is the absolute temperature; DM stands for the dipolar moments; and A_o is the molecular radius of the involved species. The K_C values calculated for Re were plotted against $1/D$ according to Eq. (3), as shown in Fig. 3.

The following expression was obtained

$$\ln K_C = -8.5373(1/D) - 0.0951 \qquad (r = 0.9990) \qquad (4)$$

Eq. (4) indicates that the solvents with the highest polarity favor the conformational reaction described in Eq. (1). From Tables 1–3, it is observed that the difference between the thermodynamic stability of Re1 and Re2 decreases when the D of the medium increases and therefore, the K_C constants increase. On the other hand, from Eq. (4) it was calculated that in a solvent with $D = \infty$, K_∞ is 0.909. Furthermore, using Eq. (3) and the data of Tables 1–3, the following values of K_∞ were obtained

$K_\infty(\text{ethanol}) = 0.678$

$K_\infty(\text{methanol}) = 0.726$

$K_\infty(\text{water}) = 0.835$

From the mean of the above three values, we obtained $K_\infty(\text{average}) = 0.746$. The difference between the numerically calculated K_∞ constant and that obtained from Eq. (4) ($K_\infty = 0.909$) is lower than 25%. This fact proves the applicability of Eq. (3) previously proposed by us [20]
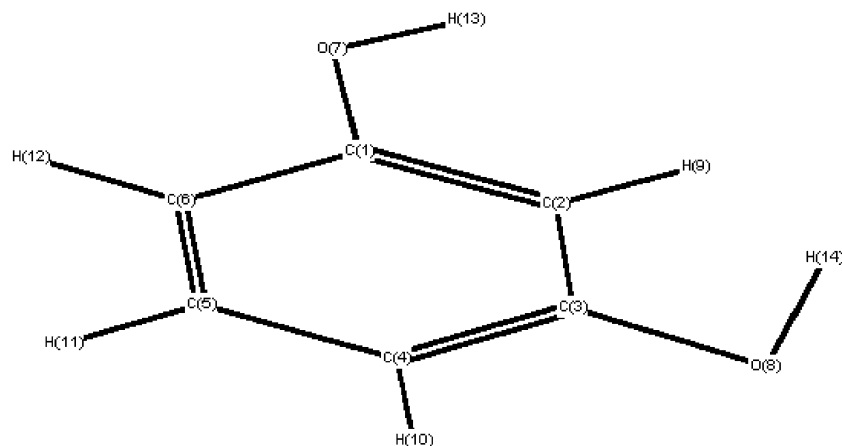
Fig. 2. Calculated conformational transition state at the B3LYP/6-31G(d) level of theory for resorcinol in water at 298 K.

and the utility of the theoretical magnitudes obtained for Re, to 298 K.

It is evident that in solutions of hydroxylic solvents, polar solutes as Re undergo specific solvent–solute interactions such as IHBs. Therefore, for describing in our system the interactions that involve solute–solvent IHBs [29,30], we selected the solvation parameters α [31] and Acity [32]. These parameters are very useful for measuring the hydrogen bond donating ability (HBD capability) of a solvent, this is to say, the capability of the solvent to provide a proton. The values of α and Acity determined for ethanol, methanol and water are 0.86, 0.98, 1.17 and 0.66, 0.75, 1.00, respectively.

Several relationships were obtained between theoretical magnitudes of Re1, Re2 and TS with the α and Acity parameters of solvating solvents. Fig. 4 shows the changes of the DMs of Re1, Re2 and TS with the α-parameter of the solvents used. The variations of the rotation barrier energy (RBE) of Re with the parameters α and Acity of the solvents are shown in Fig. 5.

From Figs. 4 and 5, it is observed that the linear equations obtained have very good correlation coefficients $(r > 0.98)$, with error bars of $1–2\%$. The equations of Fig. 4 indicate that the greater HBD capability of a solvent increases the polarization of the species and, consequently, their DMs. The equations of Fig. 5 show that the RBEs of the forward and reverse reactions (Eq. (1)), increase with the α and Acity parameters of the hydroxylic solvents (Tables 1–3). This fact implies that the solvents with highest polarity and HBD ability increase the corresponding RBEs and consequently, do not favor the conformational reaction described in Eq. (1).

From an analysis of all the equations included in Figs. 3–5, it can be concluded that the degree of conversion Re1 → Re2 increases with the HBD capability and polarity of the reaction medium. It was also concluded that considering the DMs of the non-solvated conformers, it is not possible to explain the experimental DM of Re in water. This is due to the fact that the values obtained for the DM of
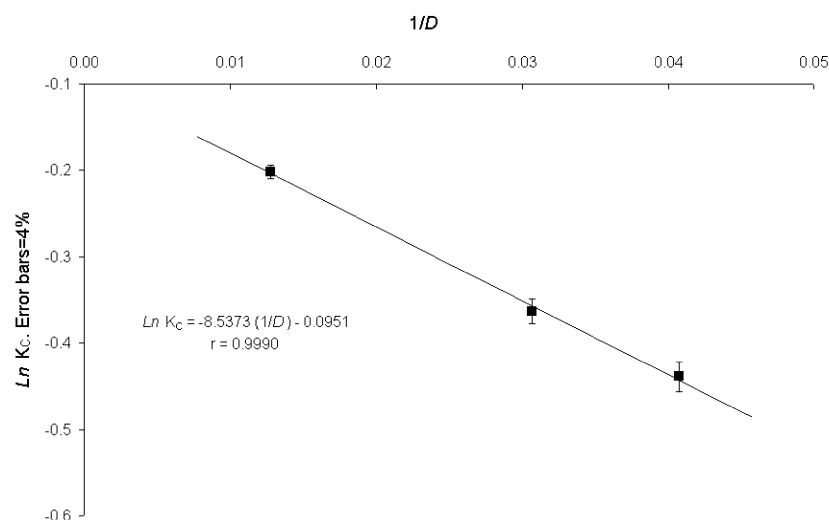

Fig. 3. Relationship between the conformational equilibrium constant of resorcinol and the permittivity of hydroxylic solvents.
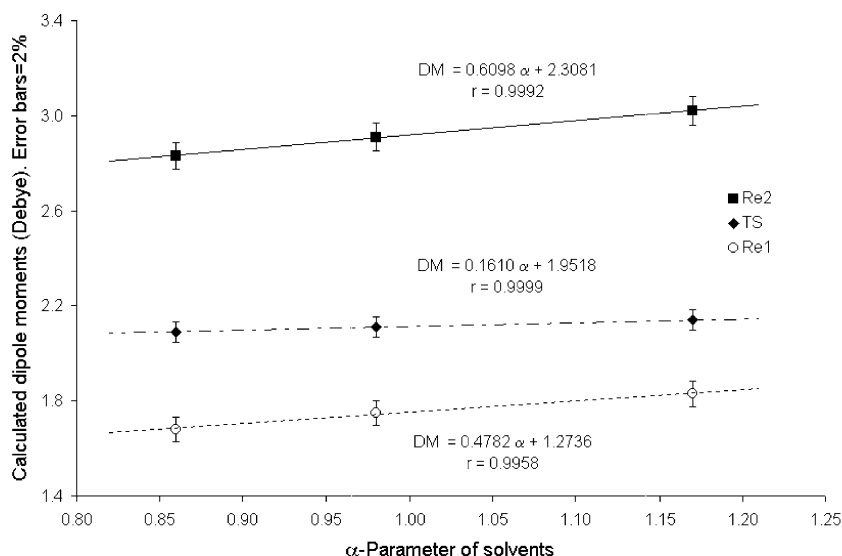
Fig. 4. Changes of the dipole moments of conformers and transition state of resorcinol with the α-parameter of solvents.

Re1 (1.83 D) and Re2 (3.02 D) were lower than the experimental DM of Re (8.66 D) [23].

4.2. Dipole moment and molar partial volume of resorcinol

The data for specific volume v (ml/g), refraction index n and D, measured in Re aqueous solutions, were analyzed as in previous works [19]. The values of the form factor and refraction index determined for Re were 0.24 and 1.6319, respectively. For each of the prepared solutions, the molar polarization of the solvent and the solute were calculated with Buckingham's equation and the corresponding DM was calculated with Debye's equation. An average value of the DM of Re in water (DM_{Re}) thus obtained was 8.66 D. On the other hand, the total volumes (V_T) of Re aqueous solutions were obtained (Table 4).

It was observed that the variation of V_T with molality (m) follows the linear equation:

$$V_T = 1003.35 + 82.94m \tag{5}$$

With M standing for molecular weight and V_{TPM} for the theoretical partial molar volume, the following equation

$$V_{TPM} = Mv \tag{6}$$

was used for calculating the V_{TPM} of the solute (V_{TPM2}) and the solvent (V_{TPM1}). On the other hand, the experimental partial molar volume of the solute (V_{EPM2}) was determined by means of expression [33]

$$V_{EPM2} = (dV_T/dm) \tag{7}$$

The experimental partial molar volume of the solvent (V_{EPM1}) was obtained dividing the intersection of the straight line of Eq. (5) by factor 55.5, this is to say, by
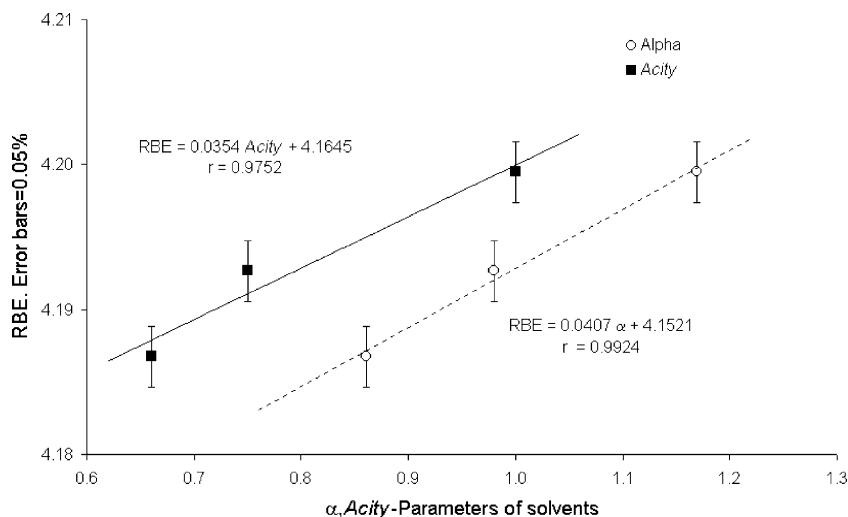

Fig. 5. Variations of the rotation barrier energy of resorcinol with the α, Acity—parameters of hydroxylic solvents.

Table 4
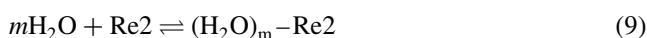Total volume (V_T) of aqueous solutions of resorcinol, at 25 ± 0.1 °C

Solution	m	v	V_T
1	0.018448	1.002747	1004.78
2	0.027759	1.002536	1005.60
3	0.036403	1.002365	1006.38
4	0.046524	1.002136	1007.31
5	0.064783	1.001809	1008.95
6	0.083184	1.001245	1010.42
7	0.092851	1.001267	1010.70
8	0.138500	1.000476	1015.73

m, molality; v, specific volume (ml/g); V_T, total volume of the solution (ml).

the number of water moles per kilogram of water. Table 5 summarizes the values of the theoretical and experimental partial molar volumes (ml/mol) obtained. It can be observed that the values of V_{EPM1} and V_{TPM1} are practically the same, while the magnitudes of the solute, V_{EPM2} and V_{TPM2}, differ by 4.2–4.4%.

4.3. Solvent–solute association complexes

In Sections 4.1 and 4.2, it was concluded that: (a) it is not possible to explain the experimental DM_{Re} of Re in water using only the DMs of the non-solvated conformers; (b) the excellent relationships obtained between the parameters of the solvents and the theoretical magnitudes of the solute suggest the existence of specific solvent–solute interactions; (c) the lower value of V_{EPM2} as compared to V_{TPM2} in the studied range of Re concentrations supports the existence of possible solute–solvent associations. Therefore, in order to explain the experimental DM_{Re} (8.66 D) of Re in water, we proposed the following solute–solvent association reactions

$$n\text{H}_2\text{O} + \text{Re1} \rightleftharpoons (\text{H}_2\text{O})_n-\text{Re1} \qquad (8)$$

$$m\text{H}_2\text{O} + \text{Re2} \rightleftharpoons (\text{H}_2\text{O})_m-\text{Re2} \qquad (9)$$

In the above equations, n and m are the number of water molecules associated to Re1 or Re2, respectively. Several calculations were performed by shifting the coefficients n and m. The most satisfactory results were obtained with $n = m = 2$. This fact implies that both the association complexes, which we shall designate as $(\text{H}_2\text{O})_2-\text{Re1}$ and $(\text{H}_2\text{O})_2-\text{Re2}$, respectively, are formed by two molecules of solvent and one of solute. In both cases, of the whole Re molecule, only the regions that include the OH groups

Table 5
Theoretical and experimental partial molar volumes (ml/mol)

Resorcinol		Water	
V_{TPM2}	V_{EPM2}	V_{TPM1}	V_{EPM1}
86.58	82.94	18.069	18.078

participate in the formation of the complex. Taking into account these complexes, the conformational equilibrium of Eq. (1) was reformulated as follows:

$$(\text{H}_2\text{O})_2-\text{Re1} \rightleftharpoons (\text{H}_2\text{O})_2-\text{Re2} \qquad (10)$$
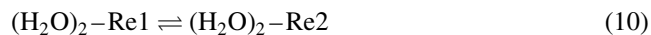
We shall designate the equilibrium constant of the above reaction as K_{CW}. Table 6 gives optimized values of molecular properties of the proposed association complexes, obtained at the B3LYP/6-31G(d) level of theory with Onsager's method. Figs. 6 and 7 show the structure of the association complexes $(\text{H}_2\text{O})_2-\text{Re1}$ and $(\text{H}_2\text{O})_2-\text{Re2}$, respectively, in water at 298 K. In association complexes, the solute molecules practically maintain the planar structure that characterizes the non-solvated solute molecules (Table 3). In addition, when the molecules of Re1 and Re2 are solvated, the electronic densities of the oxygen atoms and the electronic deficiencies of the hydrogen atoms of their hydroxyl groups increase (Table 6). Consequently, the MDs of the association complexes are higher than those of their non-solvated conformers (Table 3).

On the other hand, it must be noted that in the formation of the association complexes, the two OH groups of the solute take part in an IBH with the solvent molecules. The complexes are formed by two IBHs, which are of two classes. In one of them, the solvent acts as a hydrogen-bond donor (HBD capability), while in the other the solvent acts as a hydrogen-bond acceptor (HBA capability).

Table 6
Calculated structural magnitudes using Onsager's method at the B3LYP/6-31G(d) level of theory for the solute–solvent association complexes of resorcinol in water, at 25 °C

Molecular properties	Water	
	$(\text{H}_2\text{O})_2-\text{Re1}$ complex	$(\text{H}_2\text{O})_2-\text{Re2}$ complex
TE	-336076.09	-336075.97
K_{CW}	0.804	
DM	9.34	9.13
A_o	4.85	4.85
D-$\text{H}_{13}\text{O}_7\text{C}_1\text{C}_2$	3.7	0
D-$\text{H}_{14}\text{O}_8\text{C}_3\text{C}_4$	0.6	0.6
$q\text{O}_7$	-0.594	-0.593
$q\text{O}_8$	-0.588	-0.588
$q\text{H}_{13}$	0.320	0.327
$q\text{H}_{14}$	0.353	0.348
$r\text{H}_{13}\text{-O}_7$	0.966	0.966
$r\text{H}_{14}\text{-O}_8$	0.984	0.983
$d\text{H}_{16}\text{-O}_7$	1.960	1.999
A-$\text{O}_7\text{H}_{16}\text{O}_{15}$	163.3	156.6
$d\text{H}_{14}\text{-O}_{18}$	1.763	1.783
A-$\text{O}_8\text{H}_{14}\text{O}_{18}$	178.0	178.7

TE, total energy including solvent energy (kcal/mol); K_{CW}, conformational equilibrium constant; DM, dipolar moment (Debye); A_o, molecular radius (Å); D-$\text{H}_{13}\text{O}_7\text{C}_1\text{C}_2$, dihedral angle $\text{H}_{13}\text{O}_7\text{C}_1\text{C}_2$ (°); D-$\text{H}_{14}\text{O}_8\text{C}_3\text{C}_4$, dihedral angle $\text{H}_{14}\text{O}_8\text{C}_3\text{C}_4$ (°); q, total atomic charge (a.u.); $rd\text{H}_{13}\text{-O}_7$ and $d\text{H}_{14}\text{-O}_8$, bonds lengths between the indicated atoms (Å) (Figs. 6 and 7); $d\text{H}_{16}\text{-O}_7$ and $d\text{H}_{14}\text{-O}_{18}$, interaction distance between the indicated atoms (Å) (Figs. 6 and 7); A-$\text{O}_7\text{H}_{16}\text{O}_{15}$ and A-$\text{O}_8\text{H}_{14}\text{O}_{18}$, H-bond angles (°).

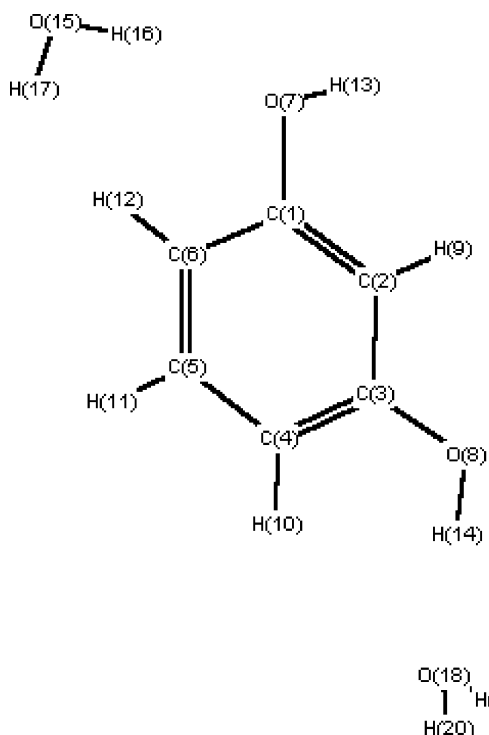Fig. 6. Structure of the association complex $(H_2O)_2$–Re1 of resorcinol calculated at the B3LYP/6-31G(d) level of theory, in water at 298 K.

For example, in the formation of the $(H_2O)_2$–Re1 complex (Fig. 6) IBH H_{16}–O_7 belongs to the first class while IBH H_{14}–O_{18} corresponds to the second type. The distances and angles that characterize these interactions in both the complexes, allow concluding that they belong to the class of moderate IHBs [34].
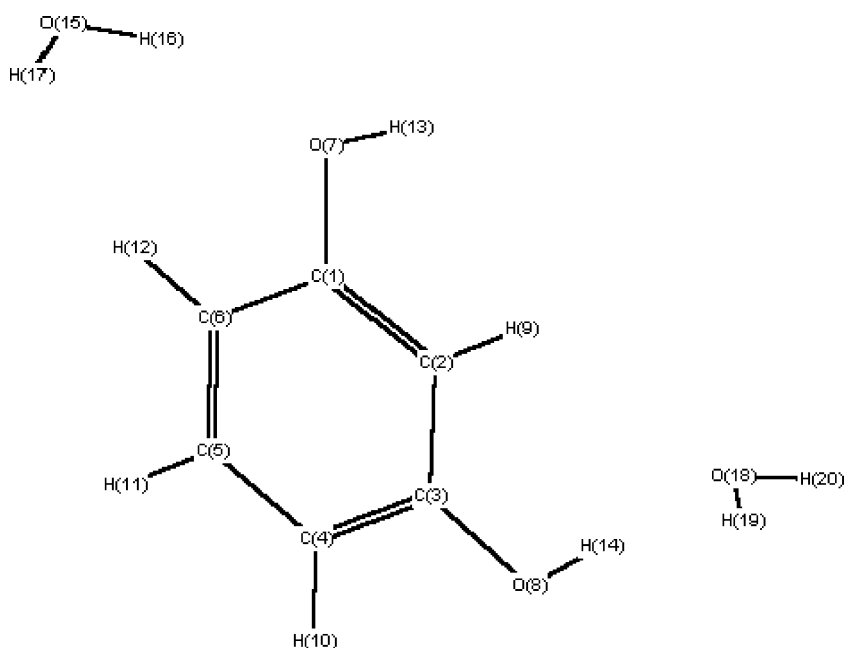
Taking into account the calculated value of K_{CW} (0.804) we determined that in the conformational reaction described in Eq. (10) there exists 55.4% of $(H_2O)_2$–Re1 and 44.6% of $(H_2O)_2$–Re2 in equilibrium. Therefore, it is reasonable to propose that

$$DM_{Re} = P \times DM_{Theo}(H_2O)_2-Re1 + (1 - P)$$
$$\times DM_{Theo}(H_2O)_2-Re2 \qquad (11)$$

where DM_{Theo} is the theoretical DM of the complexes and P is the percentual fraction. Using the DM_{Theo} data of Table 6, it was determined that $DM_{Re} = 9.25$. The difference between this value and the experimental DM_{Re} (8.66 D) is less than 7%, which permits to say that there is a reasonable agreement between the two values. Thus, it can be inferred that the experimental DM_{Re} in water is the result of the contribution of the DMs of two solvent–solute association complexes that are in equilibrium (Eq. (10)).

5. Conclusions

The solvent effects on the conformational equilibrium between the conformers of resorcinol were studied. These two conformers determine the major dielectric properties of aqueous solutions of resorcinol. We applied a recently proposed equation to explain the changes of K_C with the medium permittivity. We also related different theoretical magnitudes of the solute (DMs, RBEs) with parameters of the solvating solvents (α and Acity). In this paper, we have demonstrated the possibility of explaining the DM of resorcinol in water (8.66 D). To do this, it was necessary to propose that a conformational equilibrium takes place in

Fig. 7. Structure of the association complex $(H_2O)_2$–Re2 of resorcinol calculated at the B3LYP/6-31G(d) level of theory, in water at 298 K.

aqueous solutions, which involves two association complexes that include the solvent and the solute. These complexes have 2:1 stoichiometry, i.e. they are formed by two molecules of water and one of resorcinol. In their formation, there participate the regions of solute that include the hydroxyl groups. The calculations performed at the B3LYP/6-31G(d) level of theory using Onsager's method allowed to prove that the association complexes are formed by two IHBs. In one of them, the water acts as a hydrogen-bond donor, while in the other it acts as a hydrogen-bond acceptor. It was concluded that the DM of resorcinol in water is due to a contribution of 55.4% of $(H_2O)_2$–Re1 complex and 44.69% of $(H_2O)_2$–Re2 complex. These results imply that the equilibrium constant that characterizes the conformational reaction proposed is 0.804.

Acknowledgements

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