

# Solvation of alkane and alcohol molecules. Energy contributions

A. A. C. C. Pais,\* A. Sousa, M. E. Eusébio and J. S. Redinha

Departamento de Química, Universidade de Coimbra, P-3049 Coimbra Codex, Portugal

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In this work we conduct a systematic *ab initio* study of the solvation of small alkane, monoalcohol and diol molecules, in polar solvents with different properties. A choice of basis set suitable for the type of compounds under study is presented. The various components of the solvent–solute interaction and the cavitation energy are treated individually and their variation with chain length and introduction of hydroxy groups assessed. The use of solute molecules in which controlled changes are imposed allows for an estimation of the relative contributions, thus eliminating accidental error cancellation.

## 1 Introduction

Successful theoretical approaches to the study of solvation phenomena are essentially divided into two classes: those based on simulation techniques<sup>1</sup> and those based on effective Hamiltonian methods in which a continuum distribution of the solvent is assumed.<sup>2</sup> While results from the former are still considered to be severely limited by the number of solvent molecules used, the latter have proved to yield accurate overall solvation energies for a large number of solute molecule types and several standard solvents without much computational effort and at a low level of theory.

The decomposition of the interaction energy into its main components, as achieved by combination of the polarizable continuum model (PCM)<sup>2</sup> with the dispersion and repulsion contributions obtained by the Amovilli–Mennucci<sup>3</sup> procedure, added to a scaled particle theory (SPT)<sup>4–8</sup> cavitation term provides a picture adequate to describe the solvation processes and will be the methodological basis of the calculations in this work.

The alkane solute molecules present solute–solvent interactions dominated by the dispersion contribution and also non-negligible cavitation energies. They are, thus, very useful to assess the accuracy of the calculation of these contributions. On the other hand, each alcohol combines, relative to the corresponding alkane, similar dispersion contributions with substantially increased polarization effects.

Controlled changes in the solute molecular size, through the increase in the number of atoms in the carbon chain from methane to hexane, molecular shape, replacing linear by cyclic chains, and molecular polarity, considering alkanes, alcohols and dialcohols, thus provide a way to individually assess the accuracy of the different contributions in the systems dealt with here. These changes are complemented by varying the solvent. In this work water, formamide (FMD) and dimethylsulfoxide (DMSO) are the solvents considered. This choice is based on their different characteristics (size, electrical dipole, *etc.*) and on the fact that they are commonly used in experimental determinations such as those carried out in our laboratory.<sup>9,10</sup>

Most theoretical approaches to solvation phenomena allow for the direct calculation of Gibbs energy contributions. Experimentally, however, solvation enthalpy values are much commoner. It is thus desirable to theoretically estimate both thermodynamic quantities and identify the terms in which entropic contributions are dominant.

## 2 Methods

The solvation Gibbs energy is adequately described by

$$\Delta G_{\text{solv}}^{\circ} = \Delta G_{\text{pol}} + \Delta G_{\text{iec}} + \Delta G_{\text{disp}} + \Delta G_{\text{rep}} + \Delta G_{\text{cav}} \quad (1)$$

In this work, the electrostatic contribution,  $\Delta G_{\text{pol}}$ , is determined by the Miertuš–Scrocco–Tomasi polarizable continuum model.<sup>2</sup> In this quantum model the solute is represented by a charge distribution  $\rho(\mathbf{r})$  in a cavity placed in a polarizable dielectric medium with a certain permittivity. The molecular charge distribution induces in the dielectric a potential that, in turn, alters the initial charge distribution. The polarized dielectric is considered as a perturbation  $V_{\sigma}$  to the solute Hamiltonian  $H^{\circ}$

$$H = H^{\circ} + V_{\sigma} \quad (2)$$

that requires solution of a new Schrödinger equation. A technical difficulty caused by the penetration of the solute charge density outside this cavity is dealt with by a re-normalization. Several approaches have been proposed for this task.<sup>11</sup> In our case, we have chosen the standard procedure in which the same compensation factor is used for all tessera.

The term corresponding to the internal energy change<sup>3</sup>  $\Delta G_{\text{iec}}$  is simply given by

$$\Delta G_{\text{iec}} = \langle \Psi | H^{\circ} | \Psi \rangle - \langle \Psi^{\circ} | H^{\circ} | \Psi^{\circ} \rangle \quad (3)$$

where  $\Psi^{\circ}$  is the solute wavefunction in vacuum and  $\Psi$  the wavefunction in the presence of the dielectric.

The solute–solvent interaction dispersion term  $\Delta G_{\text{disp}}$  stems from the Amovilli–Mennucci<sup>3</sup> method. In this method, part of the dispersion energy is recovered from the basis set used to describe the solute wavefunction, denoted as W1 in the original work. A set of diffuse functions with exponents one third of the most diffuse W1 set may be added in complement and are denoted W2. These take the form of additional shells (s,p and/or d) placed in each solute atom.

The repulsion contribution  $\Delta G_{\text{rep}}$ , again based on the Amovilli–Mennucci formalism, results from the Pauli repulsion between solute and solvent, and may constitute a significant fraction of the total interaction for some of the systems studied here.

Finally, the cavitation term  $\Delta G_{\text{cav}}$  must be studied with some caution (see ref. 12 and 13 for recent analyses of this topic). We will address three variants of SPT and compare the

results. The first consists of the Pierotti approach<sup>6</sup> that considers molecules as being spheres (henceforth labeled ‘single sphere’) with radii taken from the respective total volume. Both Gibbs energies and enthalpies can be determined. Also taken into consideration is the Pierotti–Claverie method (labeled ‘sphere-by-sphere’)<sup>7</sup>

$$\Delta G_{\text{cav}} = \sum_i \frac{A_i}{4\pi R_i^2} \Delta G_{\text{cav}}(R_i) \quad (4)$$

where the expression for each single solute sphere of radius  $R_i$  is multiplied by the ratio between its surface exposed to the solvent,  $A_i$ , and its total surface. In the original work, enthalpies and entropies were also calculated using expressions equivalent to eqn. (4).

Finally, we test the SPT approach in which spherocylindric particles are assumed<sup>5</sup> for the description of the linear chain molecules. For linear hydrocarbons and alcohols the radius was taken from the ethane volume considering a spherocylindric length given by its carbon–carbon separation. The same radius was subsequently employed in longer solutes with characteristic lengths calculated from their respective van der Waals volumes. In the original article, the expression leading to the cavitation Gibbs energy is presented, from which the corresponding enthalpic term may be trivially derived.

The terms in expression (1) are Gibbs energy contributions and are combined with a corresponding Gibbs energy term for cavitation. As will be discussed later and for the systems considered in this work, the non-cavitation terms describe essentially enthalpic or internal energy contributions. Their use in conjunction with the enthalpic form of the cavitation energy produces thus an overall result that corresponds to an enthalpy of solvation. Other conceptually appealing approaches (see, *e.g.*, ref. 14) in which these two thermodynamic properties have been simultaneously calculated, have failed to reproduce experimental results for either or both.

### 3 Computational details

All *ab initio* calculations carried out in this work used the GAMESS<sup>15</sup> package, 00/03/25 version, and were performed at the Hartree–Fock level. Prior molecular mechanics and dynamics calculations resorted to the TINKER<sup>16</sup> set of programs, version 3.7. The results pertain to a temperature of 298 K.

#### 3.1 Geometry optimization

All solute geometries were optimized in the gas phase at the respective basis set Hartree–Fock level from an initial molecular mechanics energy minimized geometry, corresponding to the most stable conformers. This was chosen from those arising from successive molecular dynamics trajectories at 1000 and 2000 K. For the compounds treated in this work it is usually assumed that the geometries in solution are similar to the gas phase ones. However, in cases where more than one conformer is found with similar energies, results are presented for each of these conformers.

#### 3.2 Solvent and solute data

The systems treated in this work were described essentially through the default data in GAMESS. For water as solvent, this corresponds to a relative permittivity  $\epsilon_r = 78.390$ , solvent radius,  $R_{\text{solv}} = 1.385 \text{ \AA}$  and thermal expansion coefficient  $\alpha_p = 0.257 \times 10^{-3} \text{ K}^{-1}$ , ionization potential  $\text{IE} = 0.4510 E_h$  and relative refractive index,  $n_D = 1.32$ . In the case of FMD, GAMESS does not provide built-in constants, and we have used  $\epsilon_r = 109$ ,  $R_{\text{solv}} = 1.97 \text{ \AA}$ ,  $\alpha_p = 0.746 \times 10^{-3}$ ,  $\text{IE} = 0.3734 E_h$  and  $n_D = 1.447$ .<sup>17–19</sup> For the solvent DMSO the defaults  $\epsilon_r = 46.7$  and  $R_{\text{solv}} = 2.455 \text{ \AA}$  were used in conjunction with  $\alpha_p = 0.982 \times 10^{-3} \text{ K}^{-1}$ ,  $\text{IE} = 0.3344 E_h$  and  $n_D = 1.477$ .<sup>18,19</sup>

The reference states for the solute in the gas phase and in solution are those suggested by Ben-Naim,<sup>20</sup> which implies in some cases that the experimental values used for comparison were corrected accordingly.

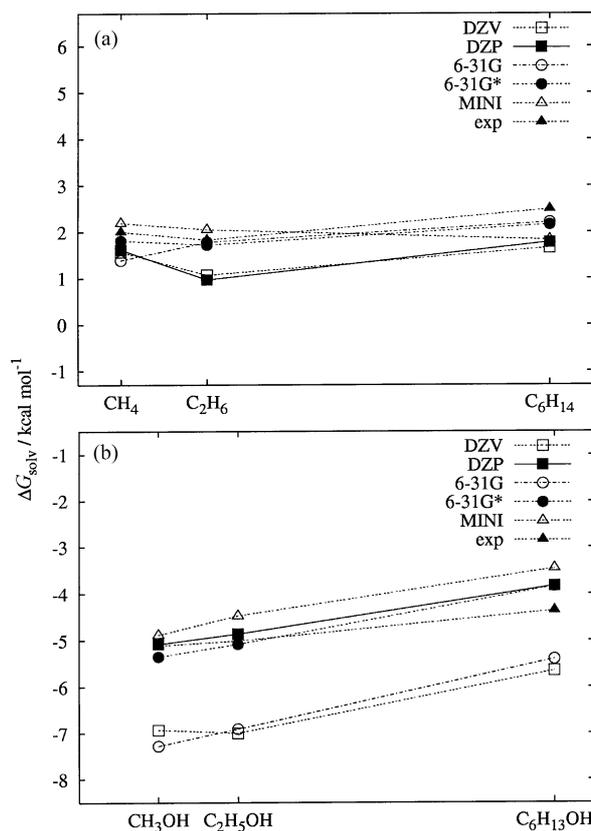
In what concerns the definition of the radius of each solute atom, we have chosen to use GAMESS defaults except for hydrogens bonded to oxygen in which  $1.0 \text{ \AA}$  is used as a starting point, irrespective of the solvent, see the next section for further details. A scaling factor of 1.2 was employed in all cases for the PCM, dispersion and repulsion calculations.

#### 3.3 Basis sets

We have performed some preliminary studies to choose one suitable basis set able to describe the solvation properties of all the compounds considered. These studies were conducted in water as solvent and focused on the most stable conformers. Comparison with the experimental values is made using the spherocylindric approach in the cavitation term, except for methane and methanol where a description based on a single sphere is adopted. This choice will be justified in subsequent sections.

The choice of water as solvent is based on the fact that there is a wealth of experimental data available. Also, the *ab initio* methods used focus essentially on a description of the solute wavefunction. Results for other solvents are assured directly through parametric transposition.

The tests presented include the MINI,<sup>21</sup> DZV,<sup>22</sup> 6-31G,<sup>23</sup> 6-31G(d)<sup>24</sup> and DZP<sup>22</sup> with additional spd shells, and have suggested some general trends (see Fig. 1). First, the DZV and 6-31G basis sets tend to overestimate the polarization contribution, which is too negative in comparison to the corresponding DZP and 6-31G(d) ones. This is consistent with the fact that they also significantly overestimate the gas phase dipole moment of the alcohol molecules considered. Such effects are, obviously, not relevant in alkanes, as seen in Table 1. The MINI basis set shows a different behavior and, in spite



**Fig. 1** Experimental and calculated hydration energies of (a) alkanes and (b) alcohols with different basis sets.

**Table 1** Results for different basis sets in the calculation of the solvation Gibbs energy (in kcal mol<sup>-1</sup>) of alkanes in water and its components

Solute	W1	W2	iec	pol	disp	rep	cav	Total	Exp.
CH <sub>4</sub>	DZV	spd	0.00	-0.19	-5.50	1.90	5.36	1.57	2.00 <sup>a</sup>
C <sub>2</sub> H <sub>6</sub>	DZV	spd	0.01	-0.17	-8.57	2.65	7.15	1.07	1.83 <sup>a</sup>
n-C <sub>6</sub> H <sub>14</sub>	DZV	spd	0.02	-0.26	-17.71	5.39	14.22	1.66	2.49 <sup>a</sup>
CH <sub>4</sub>	DZP	spd	0.01	-0.19	-5.49	1.93	5.36	1.62	
C <sub>2</sub> H <sub>6</sub>	DZP	spd	0.01	-0.18	-8.71	2.71	7.14	0.97	
n-C <sub>6</sub> H <sub>14</sub>	DZP	spd	0.02	-0.30	-17.65	5.51	14.20	1.78	
CH <sub>4</sub>	6-31G	spd	0.01	-0.18	-5.56	1.76	5.36	1.39	
C <sub>2</sub> H <sub>6</sub>	6-31G	spd	0.02	-0.16	-7.71	2.50	7.13	1.78	
n-C <sub>6</sub> H <sub>14</sub>	6-31G	spd	0.04	-0.26	-16.73	4.96	14.20	2.21	
CH <sub>4</sub>	6-31G(d)	spd	0.02	-0.19	-5.15	1.77	5.36	1.81	
C <sub>2</sub> H <sub>6</sub>	6-31G(d)	spd	0.02	-0.18	-7.78	2.53	7.13	1.72	
n-C <sub>6</sub> H <sub>14</sub>	6-31G(d)	spd	0.04	-0.30	-16.77	4.99	14.20	2.16	
CH <sub>4</sub>	MINI	spd	0.00	-0.23	-4.08	1.13	6.70	2.19	
C <sub>2</sub> H <sub>6</sub>	MINI	spd	0.00	-0.26	-6.47	1.62	7.16	2.05	
n-C <sub>6</sub> H <sub>14</sub>	MINI	spd	0.00	-0.51	-15.04	3.06	14.32	1.83	

<sup>a</sup> Ref. 25.

of some over-estimation of the dipole moments in the polar compounds, the value of the polarization contribution is lower in absolute value (see Table 2). The 6-31G(d) and DZP functions have a very similar behavior in what concerns this electrostatic term, yielding results for polar compounds that are more negative than those corresponding to the MINI basis and less negative than those of the basis without polarization functions. For these solutes the 6-31G(d) and DZP values are closer to the MINI ones than those corresponding to the DZV and 6-31G basis sets.

The dispersion contribution is, for the systems considered, a substantial fraction of the overall solvation Gibbs energy and the use of additional (W2) spd diffuse functions is mandatory if agreement with the experimental values is to be obtained. The differences among the basis sets are not so clear as for the other energy terms. The only relevant observation is that the MINI set with spd additional shells corresponds to the smallest dispersion contributions, which may indicate an overall under-estimation of the absolute value of the solvation energy. This basis set may still be a suitable candidate for dealing with larger systems, as previously suggested<sup>3</sup> having in mind the computational effort, but at the expense of some accuracy.

These and other basis sets have been used in previous work, but there was no attempt to select one to encompass compounds of the same type, irrespective of the size. The DZP + spd results have been shown to compare well with

experimental values for a significant number of small compounds,<sup>3</sup> but it seems not so adequate as the size of the molecule increases. Our results indicate that the 6-31G(d) + spd yields Gibbs energy solvation values closer to the experimental ones. We have chosen to use this basis for the whole set of calculations.

The results of PCM related methods were considered<sup>26</sup> to be somewhat dependent on the basis set chosen for the calculation. We have found this to have some relevance only when comparing basis with and without polarization functions. In what concerns the calculation of the dispersion (and repulsion) terms in the Amovilli–Mennucci formalism, differences among these basis sets are much smaller if corresponding spd additional diffuse functions are used for W2.

## 4 Results and discussion

**Linear chain alkanes and monoalcohols.** The results for the total solvation Gibbs energies and its components are shown in Tables 3 and 4 for the linear chain alkanes and monoalcohols in the three solvents considered. The results were obtained by resorting to the three definitions of the cavity, namely, single sphere from total volume, multicavity based on solute atomic spheres and spherocylinders.

**Table 2** As Table 1 for monoalcohols in water

Solute	W1	W2	iec	pol	disp	rep	cav	Total	Exp.
CH <sub>3</sub> OH	DZV	spd	0.87	-8.67	-7.21	2.04	6.04	-6.93	-5.11 <sup>a</sup>
C <sub>2</sub> H <sub>5</sub> OH	DZV	spd	0.90	-8.58	-10.02	2.85	7.85	-7.00	-5.01 <sup>a</sup>
n-C <sub>6</sub> H <sub>13</sub> OH	DZV	spd	0.90	-8.52	-18.51	5.56	14.92	-5.65	-4.36 <sup>a</sup>
CH <sub>3</sub> OH	DZP	spd	0.73	-6.73	-7.16	2.05	6.03	-5.08	
C <sub>2</sub> H <sub>5</sub> OH	DZP	spd	0.76	-6.66	-9.69	2.89	7.84	-4.86	
n-C <sub>6</sub> H <sub>13</sub> OH	DZP	spd	0.96	-6.85	-18.45	5.62	14.89	-3.83	
CH <sub>3</sub> OH	6-31G	spd	0.84	-8.42	-7.50	1.76	6.04	-7.28	
C <sub>2</sub> H <sub>5</sub> OH	6-31G	spd	0.87	-8.32	-9.77	2.46	7.85	-6.91	
n-C <sub>6</sub> H <sub>13</sub> OH	6-31G	spd	0.50	-7.83	-17.90	4.93	14.90	-5.40	
CH <sub>3</sub> OH	6-31G(d)	spd	0.71	-6.50	-7.35	1.76	6.03	-5.35	
C <sub>2</sub> H <sub>5</sub> OH	6-31G(d)	spd	0.73	-6.43	-9.70	2.49	7.83	-5.08	
n-C <sub>6</sub> H <sub>13</sub> OH	6-31G(d)	spd	0.74	-6.47	-17.90	4.91	14.88	-3.84	
CH <sub>3</sub> OH	MINI	spd	0.38	-5.82	-6.76	1.22	6.10	-4.88	
C <sub>2</sub> H <sub>5</sub> OH	MINI	spd	0.37	-5.69	-8.75	1.65	7.95	-4.47	
n-C <sub>6</sub> H <sub>13</sub> OH	MINI	spd	0.34	-5.86	-16.11	3.07	15.10	-3.46	

<sup>a</sup> Ref. 25.

**Table 3** Gibbs energy of solvation (in kcal mol<sup>-1</sup>) for alkanes in water, FMD and DMSO. The results for cavitation Gibbs energy using a unique sphere, a solute atom by atom multisphere and a spherocylinder are referred to, respectively, as ss, sbs and sc

Solvent	Solute	iec	pol	disp	rep	cav			Total			Exp.
						ss	sbs	sc	ss	sbs	sc	
Water	CH <sub>4</sub>	0.02	-019	-5.15	1.77	5.36	6.68		1.81	3.13		2.00 <sup>a</sup>
	C <sub>2</sub> H <sub>6</sub>	0.02	-018	-7.78	2.53	6.93	9.81	7.13	1.52	4.40	1.72	1.83 <sup>a</sup>
	n-C <sub>3</sub> H <sub>8</sub>	0.03	-0.22	-9.45	3.14	8.31	12.87	8.90	1.81	6.37	2.40	1.96 <sup>a</sup>
	n-C <sub>4</sub> H <sub>10</sub>	0.03	-0.24	-12.49	3.76	9.54	15.94	10.68	0.60	7.00	1.74	2.08 <sup>a</sup>
	n-C <sub>5</sub> H <sub>12</sub>	0.03	-0.28	-14.55	4.37	10.66	19.01	12.43	0.23	8.58	2.00	2.33 <sup>a</sup>
	n-C <sub>6</sub> H <sub>14</sub>	0.04	-0.30	-16.77	4.99	11.72	22.08	14.20	-0.32	10.04	2.16	2.49 <sup>a</sup>
FMD	CH <sub>4</sub>	0.02	-0.19	-5.88	1.80	5.64			1.39			
	C <sub>2</sub> H <sub>6</sub>	0.02	-0.18	-8.87	2.58	7.25		7.44	0.80		0.99	
	n-C <sub>3</sub> H <sub>8</sub>	0.02	-0.21	-10.71	3.19	8.64		9.26	0.93		1.55	
	n-C <sub>4</sub> H <sub>10</sub>	0.03	-0.24	-14.14	3.79	9.89		11.06	0.67		0.50	
	n-C <sub>5</sub> H <sub>12</sub>	0.03	-0.28	-16.43	4.38	11.03		12.85	-1.27		0.55	
	n-C <sub>6</sub> H <sub>14</sub>	0.04	-0.30	-18.90	4.99	12.11		14.65	-2.06		0.48	-0.84 <sup>b</sup>
	n-C <sub>7</sub> H <sub>16</sub>	0.05	-0.34	-21.37	5.59	13.11		16.44	-2.96		0.37	-0.90 <sup>b</sup>
DMSO	CH <sub>4</sub>	0.02	-0.19	-5.73	1.46	4.98			0.54			1.16 <sup>c</sup>
	C <sub>2</sub> H <sub>6</sub>	0.02	-0.18	-8.65	2.09	6.34		6.51	-0.38		-0.21	0.07 <sup>c</sup>
	n-C <sub>3</sub> H <sub>8</sub>	0.02	-0.21	-10.41	2.57	7.53		8.06	-0.50		0.03	-0.36 <sup>c</sup>
	n-C <sub>4</sub> H <sub>10</sub>	0.02	-0.23	-13.70	3.05	8.58		9.59	-2.28		-1.27	-0.99 <sup>c</sup>
	n-C <sub>5</sub> H <sub>12</sub>	0.00	-0.26	-15.91	3.54	9.55		11.12	-3.08		-1.51	-1.25 <sup>c</sup>
	n-C <sub>6</sub> H <sub>14</sub>	0.02	-0.29	-18.28	4.01	10.46		12.65	-4.08		-1.89	-1.79 <sup>c</sup>

<sup>a</sup> Ref. 25. <sup>b</sup> Ref. 27. <sup>c</sup> Ref. 28.

Considering water, it is patent that the theoretical approach yields values close to those experimentally determined, except in the case of the multisphere description for cavitation. In our view, the major cause for this poor performance relies on the fact that the area ratio of eqn. (4), that scales the contribution of each sphere, is based on atomic spheres. The amount of excluded volume is thus insufficient in terms of the solvent-accessible surface, with the error increasing with the size of the molecule. The results based on a single sphere do not significantly deviate from the experimental ones, but the trend is not correct as the chain length increases. The cavitation energies provided do not grow sufficiently with the size of the molecule. Roughly, if the total volume of a linear chain molecule doubles, this will lead to no more than a 30% increase in the cavitation contribution. In contrast, the use of the spherocylinder description provides an adequate shape that ultimately leads to a more correct behavior in terms of chain length.

cylinder description provides an adequate shape that ultimately leads to a more correct behavior in terms of chain length.

Considering formamide as solvent, the experimental values are scarce. Once data became available for n-heptane in this solvent, the series was enlarged so as to encompass this solute and assess the correctness of the trend obtained. Deviations from these two experimental values are not excessive and the experimental trend was verified. The sphere-by-sphere approach for cavitation increases drastically these deviations and we will omit the corresponding results.

For DMSO there are no experimental data concerning solvation Gibbs energies for the alcohol molecules. We have considered the radius of the hydrogen bonded to oxygen as 0.84 Å in the results of Tables 4 and 5, for reasons that will be explained in Section 4.1.

**Table 4** As Table 3 for monoalcohols

Solvent	Solute	iec	pol	disp	rep	cav		Total		Exp.
						ss	sc	ss	sc	
Water	CH <sub>3</sub> OH	0.71	-6.50	-7.35	1.76	6.03		-5.35		-5.11 <sup>a</sup>
	C <sub>2</sub> H <sub>5</sub> OH	0.73	-6.43	-9.70	2.49	7.50	7.83	-5.41	-5.08	-5.01 <sup>a</sup>
	n-C <sub>3</sub> H <sub>7</sub> OH	0.73	-6.31	-11.23	3.14	8.80	9.60	-4.87	-4.07	-4.83 <sup>a</sup>
	n-C <sub>4</sub> H <sub>9</sub> OH	0.75	-6.39	-13.44	3.77	9.98	11.35	-5.83	-4.46	-4.72 <sup>a</sup>
	n-C <sub>5</sub> H <sub>11</sub> OH	0.72	-6.31	-16.16	4.41	11.07	13.10	-6.27	-4.24	-4.47 <sup>a</sup>
	n-C <sub>6</sub> H <sub>13</sub> OH <sup>b</sup>	0.74	-6.47	-17.90	4.91	12.11	14.88	-6.61	-3.84	-4.36 <sup>a</sup>
		0.72	-6.04	-18.19	4.89	12.14	14.91	-6.48	-3.71	
FMD	CH <sub>3</sub> OH	0.71	-6.54	-8.39	1.79	6.32		-6.11		
	C <sub>2</sub> H <sub>5</sub> OH	0.73	-6.45	-11.03	2.54	7.82	8.16	-6.39	-6.05	
	n-C <sub>3</sub> H <sub>7</sub> OH	0.73	-6.33	-12.76	3.18	9.14	9.96	-6.04	-5.22	
	n-C <sub>4</sub> H <sub>9</sub> OH	0.50	-6.15	-15.23	3.82	10.34	11.75	-6.72	-5.31	
	n-C <sub>5</sub> H <sub>11</sub> OH	0.72	-6.34	-18.26	4.43	-11.45	13.54	8.00	-5.91	
	n-C <sub>6</sub> H <sub>13</sub> OH	0.73	-6.44	-20.18	4.91	-12.51	15.35	8.47	-5.63	
		0.72	-6.04	-20.52	4.91	-12.53	15.38	8.40	-5.55	
DMSO	CH <sub>3</sub> OH	0.94	-8.05	-8.33	1.54	5.51		-8.39		
	C <sub>2</sub> H <sub>5</sub> OH	0.93	-7.87	-10.93	2.15	6.79	7.07	-8.93	-8.65	
	n-C <sub>3</sub> H <sub>7</sub> OH	0.95	-7.91	-12.56	2.71	7.91	8.61	-8.90	-8.20	
	n-C <sub>4</sub> H <sub>9</sub> OH	0.96	-7.89	-14.93	3.14	8.93	10.13	-9.79	-8.59	
	n-C <sub>5</sub> H <sub>11</sub> OH	0.91	-7.72	-17.85	3.60	9.87	11.65	-11.19	-9.41	
	n-C <sub>6</sub> H <sub>13</sub> OH	0.94	-7.90	-19.70	4.05	10.76	13.18	-11.85	-9.43	
		0.92	-7.56	-20.04	4.07	10.78	13.22	-11.83	-9.39	

<sup>a</sup> Ref. 25. <sup>b</sup> The results presented for hexanol refer to the lowest energy conformers found with the 6-31G(d) basis set. These conformers are almost isoenergetic.

In Fig. 2 and 3 we depict the various contributions for the solvation energy in water as a function of the number of carbon atoms in the molecules considered so far.

It is noteworthy that the polarization contribution to solvation varies by approximately the same amount when we switch from an alkane to the corresponding alcohol, irrespective of the length of the carbon chain. In the same way, almost constant differences can be found when the chain length is increased in alkanes by the insertion of additional  $\text{CH}_2$  fragments. These variations are, however, numerically not significant. In alcohols, the small differences in polarization energy are obscured by the large contribution corresponding to the hydroxy group.

Also, the absolute value of the dispersion energy increases with the number of carbons in the solute molecule, as expected, but this increase is somewhat irregular (exceeding 2 kcal mol<sup>-1</sup> per  $\text{CH}_2$  in the three solvents).

The repulsion term always constitutes a significant portion of the overall solvation energy, especially in the case of alkane molecules. It increases systematically ( $\approx 0.7$  kcal mol<sup>-1</sup> per  $\text{CH}_2$  in water and FMD, slightly less in DMSO).

**Cyclohexane, cyclohexanol and 1,2-cyclohexanediol.** For the first two compounds, several conformers were used in our solvation studies (see Table 5). For cyclohexane, we present results for both the chair and boat conformers, while for cyclohexanol the chair conformer with equatorial and axial hydroxy groups and the boat conformer with an equatorial group were considered. A single sphere was considered in the cavitation term, for obvious reasons, in all cyclic compounds.

The most stable cyclohexane geometry yields energy components systematically lower in absolute value than those found for n-hexane, as should have been anticipated. We note that the available surface area for the PCM calculation corresponds to 148.4 Å<sup>2</sup> in the cyclic compound as compared with

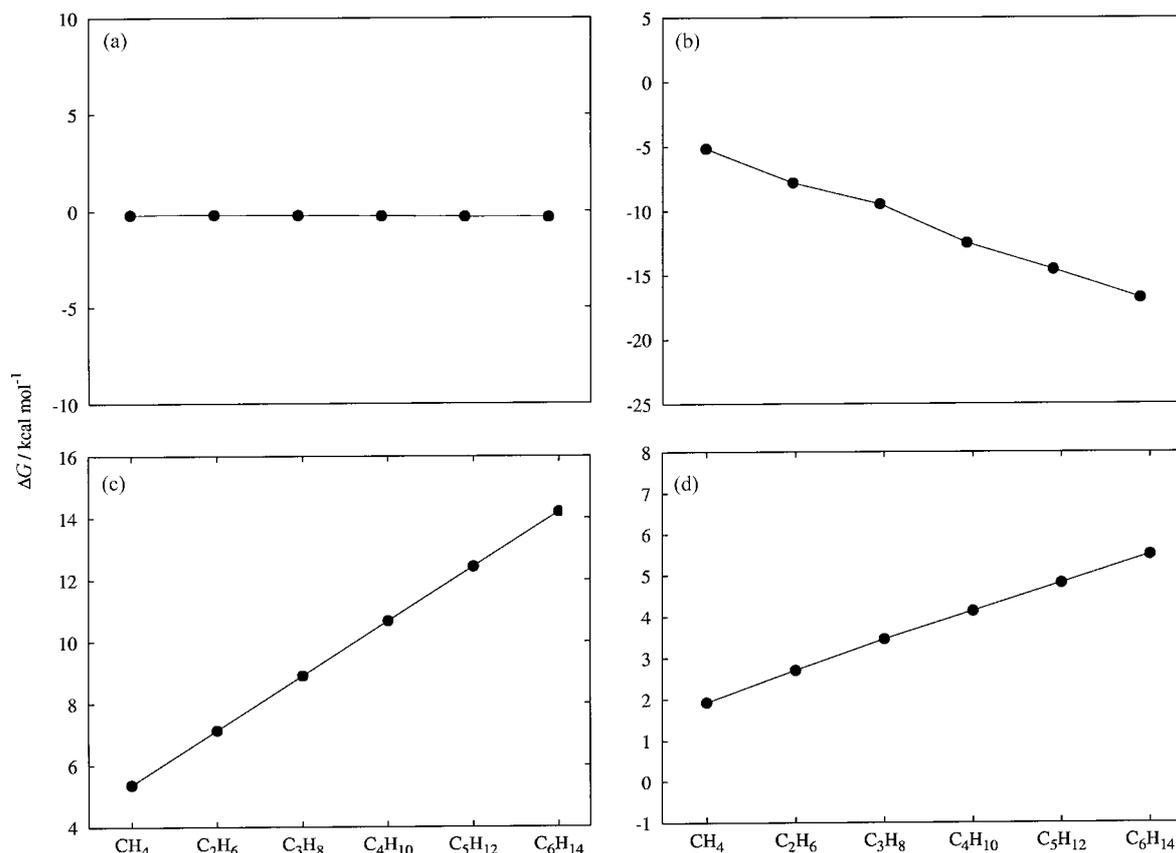
173.7 Å<sup>2</sup> for the linear one. When we compare cyclohexane with the most stable geometry for cyclohexanol, the difference in solvation energy is related essentially to the increase in the absolute value of the polarization energy (*ca.* 6 kcal mol<sup>-1</sup>, comparable to what is found on going from n-hexane to n-hexanol). If we now look at the differences between the several cyclohexanol conformers studied, it comes as no surprise that the positioning of the hydroxy groups plays a greater role than the overall shape of the molecule. Thus, the equatorial OH chair and boat conformers present similar results, both closer to the experimental findings than the axial OH chair conformer.

For the study of 1,2-cyclohexanediol we have considered the *cis* and *trans* isomers in the chair conformation. As shown in Table 5, these produce clearly distinct results, the latter being characterized by the largest (more negative) solvation energies. We note that the existence of two (close) hydroxy groups poses particular problems in this compound. The representation of the total electronic density around the hydroxy hydrogens indicates that each one should be treated differently in terms of the effective radius that is imposed, *i.e.*, the calculation of the polarization contribution may be refined.

Tests conducted on other diols, such as butanediols, have indicated that solvation energies are strongly dependent on the relative orientation of the two hydroxy groups. The calculated values tend to approach the experimental ones when this orientation inhibits the formation of intramolecular hydrogen bonds. A detailed appreciation of the role of this bond as described in continuum methods thus requires further efforts.

#### 4.1 Gibbs energies vs. enthalpies

The available experimental data for solvation entropies are presented in Table 6 along with the values corresponding to calculated cavitation entropies. The similitude of these values



**Fig. 2** Contributions to the solvation energy of linear alkanes in water. (a) Polarization energy; (b) dispersion energy; (c) cavitation energy and (d) repulsion energy.

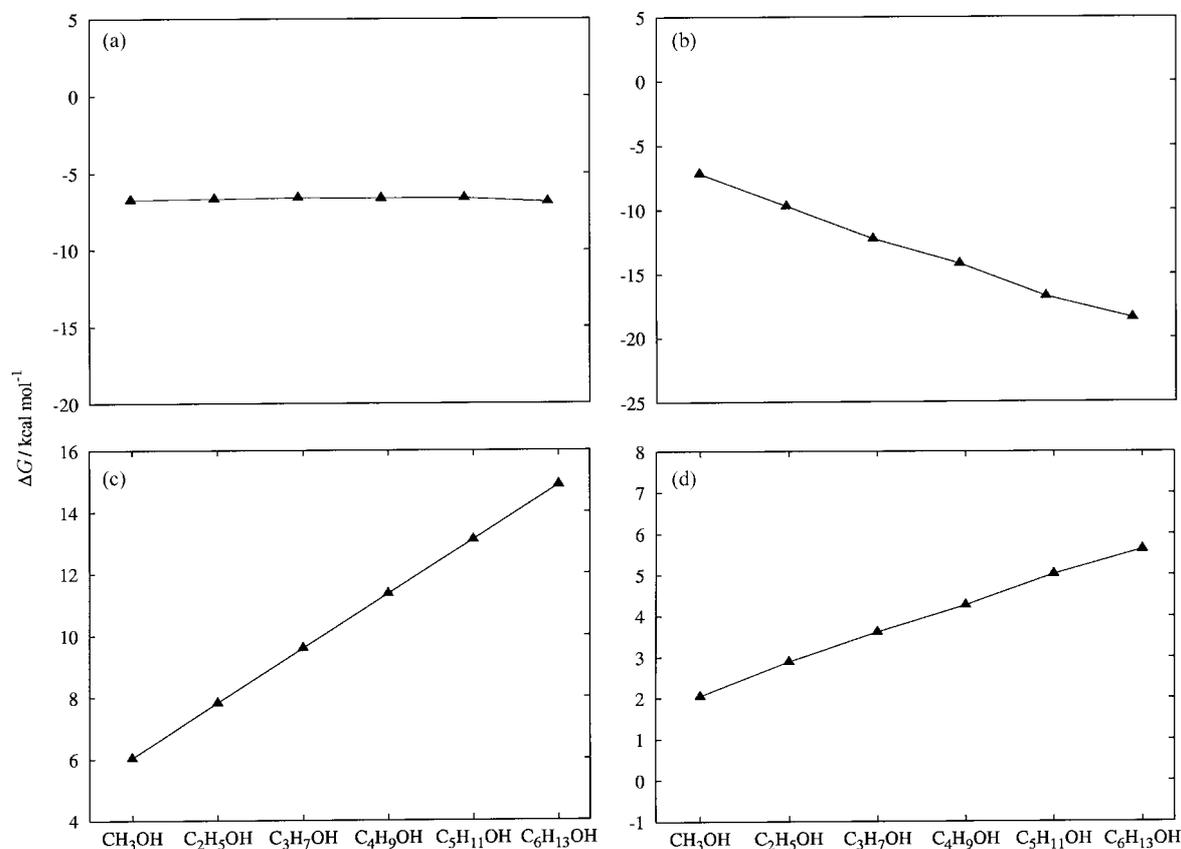


Fig. 3 As Fig. 2 for monoalcohols.

indicates that most of the entropic contribution for the Gibbs energy resides in this term for the type of systems studied. This is also illustrated in Fig. 4 for the alkanes and monoalcohols in water.

An attempt was made to determine the contribution of the non-cavity terms to the solvation entropy, by estimating the variation in the corresponding Gibbs energy components with temperature. Taken into consideration were the temperature dependence of the relative permittivity and refractive index,<sup>19</sup> and cavity volume (other parameters in the model are almost

temperature insensitive). The latter was estimated on the basis of the variation with temperature of the partial molar volume of some of the solutes at infinite dilution in the respective solvent.<sup>32</sup> An overall result typically much less than 6 cal mol<sup>-1</sup> K<sup>-1</sup> is obtained for water. This order of magnitude is consistent with previous determinations.<sup>33</sup> When the other solvents (FMD and DMSO) are considered this contribution is slightly higher for some solutes and almost nil in others, due to different thermal expansion coefficients.<sup>34</sup> The entropic contribution associated with the property-based parameters is

Table 5 As Table 3 for cyclohexane, cyclohexanol and 1,2-cyclohexanediol

Solute	Solvent	iec	pol	disp	rep	cav	Total	Exp.
Cyclohexane (chair)	Water	0.03	-0.22	-14.24	4.25	11.03	0.85	1.23 <sup>a</sup>
	FMD	0.03	-0.22	-16.13	4.29	11.40	-0.63	-1.63 <sup>b</sup>
	DMSO	0.02	-0.21	-15.65	3.47	9.86	-2.51	-2.42 <sup>c</sup>
Cyclohexane (boat)	Water	0.02	-0.24	-15.09	4.35	11.03	0.07	
	FMD	0.02	-0.24	-17.15	4.42	11.40	-1.55	
	DMSO	0.02	-0.23	-16.67	3.58	9.86	-3.44	
Cyclohexanol (chair) equatorial OH	Water	0.71	-6.05	-15.60	4.29	11.43	-5.22	-5.48 <sup>a</sup>
	FMD	0.72	-6.09	-17.66	4.31	11.81	-6.91	
	DMSO	0.92	-7.50	-17.31	3.58	10.17	-10.14	
Cyclohexanol (chair) axial OH	Water	0.67	-5.49	-15.55	4.22	11.42	-4.73	
	FMD	0.66	-5.45	-17.58	4.25	11.80	-6.32	
	DMSO	0.84	-6.81	-17.22	3.54	10.17	-9.48	
Cyclohexanol (boat) equatorial OH	Water	0.74	-6.17	-15.49	4.35	11.44	-5.13	
	FMD	0.74	-6.19	-17.59	4.41	11.82	-6.81	
	DMSO	0.92	-7.50	-17.25	3.64	10.18	-10.01	
<i>trans</i> -1,2-Cyclohexanediol	Water	1.10	-9.79	11.83	-17.56	4.19	-10.23	
	FMD	1.09	-9.70	12.22	-19.85	4.22	-12.02	
	DMSO	1.39	-12.06	10.49	-19.59	3.57	-16.20	
<i>cis</i> -1,2-Cyclohexanediol	Water	0.96	-8.69	11.82	-17.52	4.21	-9.22	
	FMD	0.94	-8.62	12.20	-19.82	4.24	-11.06	
	DMSO	0.74	-10.57	10.48	-19.58	3.64	-15.29	

<sup>a</sup> Ref. 25. <sup>b</sup> Ref. 27. <sup>c</sup> Ref. 28.

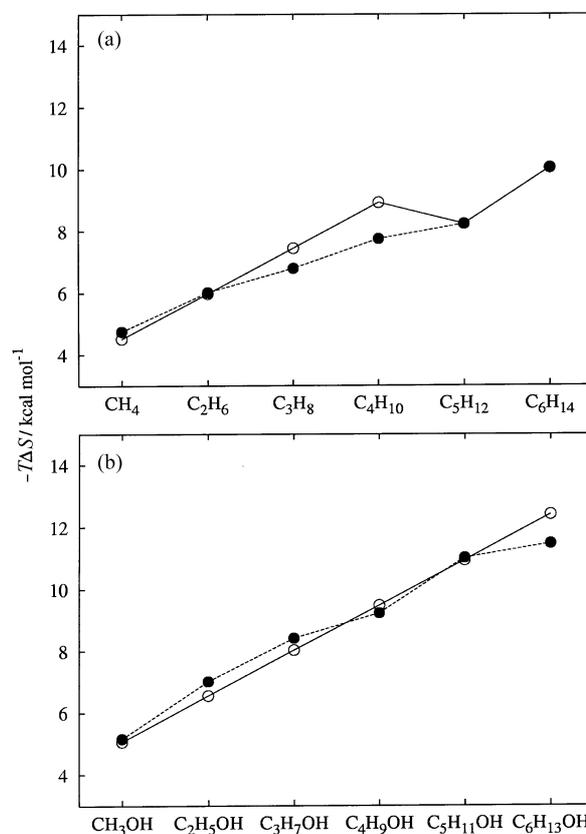
**Table 6** Entropic contributions in the Gibbs energy of solvation (kcal mol<sup>-1</sup>)

Solvent	Solute	$-T\Delta S(\text{cav})$		$-T\Delta S(\text{exp})$
		ss	sc	
Water	CH <sub>4</sub>	4.51		4.75 <sup>a</sup>
	C <sub>2</sub> H <sub>6</sub>	5.81	5.97	6.01 <sup>a</sup>
	n-C <sub>3</sub> H <sub>8</sub>	6.95	7.44	6.79 <sup>a</sup>
	n-C <sub>4</sub> H <sub>10</sub>	7.97	8.92	7.74 <sup>a</sup>
	n-C <sub>5</sub> H <sub>12</sub>	8.90	10.38	8.23 <sup>b</sup>
	n-C <sub>6</sub> H <sub>14</sub>	9.77	11.85	10.04 <sup>b</sup>
	c-C <sub>6</sub> H <sub>12</sub>	11.03		9.17 <sup>b</sup>
	CH <sub>3</sub> OH	5.06		5.16 <sup>a</sup>
	C <sub>2</sub> H <sub>5</sub> OH	6.28	6.55	7.01 <sup>a</sup>
	n-C <sub>3</sub> H <sub>7</sub> OH	7.36	8.03	8.42 <sup>b</sup>
	n-C <sub>4</sub> H <sub>9</sub> OH	8.33	9.48	9.23 <sup>b</sup>
	n-C <sub>5</sub> H <sub>11</sub> OH	9.24	10.93	11.01 <sup>b</sup>
	n-C <sub>6</sub> H <sub>13</sub> OH	10.10	12.41	11.47 <sup>b</sup>
	FMD	n-C <sub>6</sub> H <sub>14</sub>	4.63	5.61
n-C <sub>7</sub> H <sub>16</sub>		4.98	6.27	5.74 <sup>c,d,e</sup>
DMSO	n-C <sub>5</sub> H <sub>12</sub>	1.15	1.34	1.97 <sup>f</sup>
	n-C <sub>6</sub> H <sub>14</sub>	1.20	1.46	2.15 <sup>f</sup>
	c-C <sub>6</sub> H <sub>12</sub>	1.17		2.34 <sup>f</sup>

<sup>a</sup> Ref. 29. <sup>b</sup> Ref. 25. <sup>c</sup> Ref. 27. <sup>d</sup> Ref. 30. <sup>e</sup> Ref. 31. <sup>f</sup> Ref. 28.

negligible. The above results indicate that the non-cavity Gibbs energy terms are essentially enthalpic, as pointed out before for water and some other solvents.<sup>3,13,37</sup> We have thus used the approximation of combining these terms with the enthalpic form for cavitation to represent the total enthalpy of solvation in Tables 7–9. In all cases, the calculated values are in close agreement with the experimental determinations, although deviations tend to increase with chain length for the larger alkanes. The cyclic compounds seem to pose no particular problems.

When DMSO is considered as solvent, the solvation enthalpies calculated as described above deviate for alcohols, by *ca.* 2 kcal mol<sup>-1</sup> from the experimental determinations, both in the single sphere and spherocylinder approaches. This deviation is not found in alkanes, although in that case experimental information is scarce. This behaviour seems to indicate that at least one of the input properties (related to the solvent or to the solute in this solvent) is either inaccurate or ineffi-

**Fig. 4** Entropic contributions of (a) alkanes and (b) alcohols in water. (○) Experimental; (●) cavity calculations.

cient in parametrization. It is possible that the problem resides in the effective solvent radius, but we have discarded this diagnosis on the basis of the alkane results, Table 7. We have thus taken the option of considering the radius of the hydrogen bonded to oxygen as 0.84 Å, as already mentioned. This option is additionally substantiated by the fact that, using the 6-31G(d) basis set, the distance between the hydroxy hydrogen and the DMSO oxygen in a solute–solvent complex is shorter than that corresponding to water. Once again, the atomic multisphere approach yields values of the cavitation energy that are consistently excessive and cause major disagreement with the experimental results for the larger chains. The

**Table 7** Enthalpies of solvation (kcal mol<sup>-1</sup>) for alkanes in water, FMD and DMSO

Solvent	Solute	$\Delta H_{\text{cav}}$		non-cav	$\Delta H_{\text{tot}}$		$\Delta H_{\text{exp}}$
		ss	sc		ss	sc	
Water	CH <sub>4</sub>	0.85		-3.55	-2.70		-2.75 <sup>a</sup>
	C <sub>2</sub> H <sub>6</sub>	1.12	1.16	-5.41	-4.29	-4.25	-4.17 <sup>a</sup>
	n-C <sub>3</sub> H <sub>8</sub>	1.36	1.46	-6.50	-5.14	-5.04	-4.83 <sup>a</sup>
	n-C <sub>4</sub> H <sub>10</sub>	1.57	1.76	-8.94	-7.37	-7.18	-5.66 <sup>a</sup>
	n-C <sub>5</sub> H <sub>12</sub>	1.76	2.05	-10.43	-8.67	-8.38	-5.90 <sup>b</sup>
	n-C <sub>6</sub> H <sub>14</sub>	1.95	2.35	-12.04	-10.09	-9.69	-7.55 <sup>b</sup>
FMD	CH <sub>4</sub>	3.30		-4.25	-0.95		
	C <sub>2</sub> H <sub>6</sub>	4.33	4.45	-6.45	-2.12	-2.00	
	n-C <sub>3</sub> H <sub>8</sub>	5.23	5.60	-7.71	-2.48	-2.11	
	n-C <sub>4</sub> H <sub>10</sub>	6.04	6.76	-10.56	-4.52	-3.80	
	n-C <sub>5</sub> H <sub>12</sub>	6.78	7.89	-12.00	-5.52	-4.41	
	n-C <sub>6</sub> H <sub>14</sub>	7.48	9.04	-14.17	-6.69	-5.13	-5.72 <sup>c,d</sup>
DMSO	CH <sub>4</sub>	4.14		-4.44	-0.30		
	C <sub>2</sub> H <sub>6</sub>	5.40	5.55	-6.72	-1.32	-1.17	
	n-C <sub>3</sub> H <sub>8</sub>	6.50	6.97	-7.56	-1.53	-1.06	
	n-C <sub>4</sub> H <sub>10</sub>	7.50	8.39	-9.97	-3.36	-2.47	
	n-C <sub>5</sub> H <sub>12</sub>	8.40	9.78	-11.25	-4.23	-2.85	-3.22 <sup>e</sup>
	n-C <sub>6</sub> H <sub>14</sub>	9.26	11.19	-12.61	-5.28	-3.35	-3.94 <sup>e</sup>

<sup>a</sup> Ref. 29. <sup>b</sup> Ref. 25. <sup>c</sup> Ref. 30. <sup>d</sup> Ref. 31. <sup>e</sup> Ref. 28.

**Table 8** As Table 7 for monoalcohols

Solvent	Solute	$\Delta H_{\text{cav}}$			$\Delta H_{\text{tot}}$		$\Delta H_{\text{exp}}$
		ss	sc	non-cav	ss	sc	
Water	CH <sub>3</sub> OH	0.97		-11.38	-10.41		-10.25 <sup>a</sup>
	C <sub>2</sub> H <sub>5</sub> OH	1.22	1.28	-12.91	-11.69	-11.63	-12.05 <sup>a</sup>
	n-C <sub>3</sub> H <sub>7</sub> OH	1.44	1.57	-13.67	-12.23	-12.10	-13.25 <sup>a</sup>
	n-C <sub>4</sub> H <sub>9</sub> OH	1.65	1.87	-15.31	-13.66	-13.44	-13.95 <sup>a</sup>
	n-C <sub>5</sub> H <sub>11</sub> OH	1.83	2.17	-17.34	-15.51	-15.17	-14.93 <sup>b</sup>
	n-C <sub>6</sub> H <sub>13</sub> OH	2.01	3.56	-18.72	-16.71	-15.16	-15.28 <sup>b</sup>
		2.02	2.48	-18.62	-16.60	-16.14	
FMD	CH <sub>3</sub> OH	3.74		-12.43	-8.69		-8.15, <sup>c,a</sup> 8.28 <sup>a,d</sup>
	C <sub>2</sub> H <sub>5</sub> OH	4.70	4.91	-14.21	-9.51	-9.30	-9.02, <sup>c,d</sup> -9.08 <sup>c,d</sup>
	n-C <sub>3</sub> H <sub>7</sub> OH	5.55	6.06	-15.18	-9.63	-9.12	-10.04 <sup>c,d</sup>
	n-C <sub>4</sub> H <sub>9</sub> OH	6.33	7.19	-17.06	-10.73	-9.87	-11.09, <sup>c,d</sup> -11.12 <sup>c,d</sup>
	n-C <sub>5</sub> H <sub>11</sub> OH	7.05	8.33	-19.45	-12.40	-11.12	-12.04 <sup>c,d</sup>
	n-C <sub>6</sub> H <sub>13</sub> OH	7.74	9.48	-20.98	-13.24	-11.50	-12.76 <sup>e</sup>
		7.75	9.50	-20.93	-13.18	-11.43	
DMSO	CH <sub>3</sub> OH	4.63		-13.90	-9.27		-9.62, <sup>c</sup> -9.76 <sup>c</sup>
	C <sub>2</sub> H <sub>5</sub> OH	5.81	6.06	-15.72	-9.91	-9.66	-9.24, <sup>c</sup> -9.31 <sup>c</sup>
	n-C <sub>3</sub> H <sub>7</sub> OH	6.87	7.48	-16.81	-9.94	-9.33	-10.16 <sup>c</sup>
	n-C <sub>4</sub> H <sub>9</sub> OH	7.28	8.87	-18.72	-10.90	-9.85	-11.05, <sup>c</sup> -11.08 <sup>c</sup>
	n-C <sub>5</sub> H <sub>11</sub> OH	8.71	10.27	-21.06	-12.35	-10.74	-11.92 <sup>c</sup>
	n-C <sub>6</sub> H <sub>13</sub> OH	9.54	11.68	-22.61	-13.04	-10.93	
		9.57	11.72	-22.61	13.07	-10.89	

<sup>a</sup> Ref. 29. <sup>b</sup> Ref. 25. <sup>c</sup> Ref. 30. <sup>d</sup> Ref. 31. <sup>e</sup> Ref. 35.

approach is thus discarded for this large radius solvent in the compounds considered. As for the former solvents, the cyclic compounds are conveniently described as a single sphere for the cavitation term.

An additional comment on the differences in solvation enthalpies amongst the three solvents. The interaction terms differ from solvent to solvent as might have been anticipated from solvent properties such as the dipole moment and molecular polarizability. However, the effect of these properties is damped by the numerical density. Most of the differences stem from the energy for opening the solute cavity, smaller for water and increasing for FMD and, again, for DMSO.

## 5 Conclusions

In this work we have shown that the combination of SPT with the Miertuš–Scrocco–Tomasi PCM approach and the

Amovilli–Mennucci description for the dispersion and Pauli repulsion terms provides an accurate means to calculate the solvation energy of alkanes, monoalcohols up to 6 carbon atoms and diols, with solvation enthalpies ranging from -3 to -20 kcal mol<sup>-1</sup>, with a much smaller range for the respective Gibbs energies. This applies both to linear and cyclic forms and is true for the three solvents tested. Also, an increase in the chain length does not lead to increased deviation from the experimental results, thus substantiating some size consistency in the calculations. This does not fully apply to the longer alkylic chains in which some deviation from the experimental results can be found. Note that the experimental solvation enthalpies for n-alkanes present a damped growth as the chain increases in length, while the theoretical calculations tend to increase steadily by *ca.* 2 kcal mol<sup>-1</sup> in absolute value.

Problems related to conformational changes in the solute molecule from gas phase to solution have also been addressed,

**Table 9** As Table 7 for cyclohexane, cyclohexanol and 1,2-cyclohexanediol

Solute	Solvent	$\Delta H_{\text{cav}}$	non-cav	$\Delta H_{\text{tot}}$	$\Delta H_{\text{exp}}$
Cyclohexane (chair)	Water	1.83	-10.18	-8.35	-7.30 <sup>a</sup>
	FMD	7.02	-12.03	-5.01	-5.72 <sup>c</sup>
	DMSO	8.69	-12.37	-3.68	-4.76 <sup>d</sup>
Cyclohexane (boat)	Water	1.85	-10.96	-9.13	
	FMD	7.02	-10.95	-5.93	
	DMSO	8.70	-13.30	-4.60	
Cyclohexanol (chair) equatorial OH	Water	1.89	-16.65	-14.76	-16.34 <sup>e</sup>
	FMD	7.28	-18.72	-11.44	-13.21 <sup>e</sup>
	DMSO	8.99	-20.31	-11.32	-12.94 <sup>e</sup>
Cyclohexanol (chair) axial OH	Water	1.89	-16.15	-14.26	
	FMD	7.28	-18.12	-10.84	
	DMSO	8.99	-19.65	-10.66	
Cyclohexanol (boat) equatorial OH	Water	1.90	-16.57	-14.67	
	FMD	7.29	-18.63	-11.34	
	DMSO	9.00	-20.19	-11.19	
<i>trans</i> -1,2-Cyclohexanediol	Water	1.96	-22.06	-20.10	-20.23 <sup>f</sup>
	FMD	7.55	-24.24	-16.69	-17.23 <sup>f</sup>
	DMSO	9.29	-26.69	-17.40	-17.74 <sup>f</sup>
<i>cis</i> -1,2-Cyclohexanediol	Water	1.96	-21.04	-19.08	-19.14 <sup>e</sup>
	FMD	7.54	-23.26	-15.72	-16.35 <sup>e</sup>
	DMSO	9.28	-25.77	-16.49	-16.24 <sup>e</sup>

<sup>a</sup> Ref. 25. <sup>b</sup> Ref. 27. <sup>c</sup> Ref. 30. <sup>d</sup> Ref. 28. <sup>e</sup> Ref. 10. <sup>f</sup> Ref. 36.

showing that in most cases the gas phase structure is sufficient to provide an adequate estimate of this solvation energy (for a recent approach to this problem see ref. 38). In compounds where there is the possibility of formation of intramolecular hydrogen bonds we believe that the differences in electronic density around the hydroxy hydrogens should be taken into account (as they would be in a much more expensive SCI-PCM approach<sup>39</sup>).

The description of the type of cavity used to calculate the work necessary to exclude the solvent particles in order to introduce the solute molecule has been shown to be dependent on the solute characteristics, especially its shape.

We have also concluded that the electrostatic, dispersion and repulsion terms are not so strongly dependent on the choice of basis set as has been suggested,<sup>26</sup> for the basis range analyzed in this work.

In systems studied, it has been shown that the entropic component of the Gibbs energy is present in the cavitation work rather than in the interaction terms. This allows for the use of the latter terms as enthalpic contributions that, combined with the corresponding form of the cavitation energies, provide direct estimates of the total enthalpy of solvation.

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