Ab Initio and Density Functional Predictions of Solvation Free Energies of Cyclic Polyethers $(CH_2CH_2O)_n$ (n=2,6) in Aqueous and Tetrachloromethane Solutions

B. Ariche[1,2,*], A. Rahmouni[1], H. Brahim[1], A. Guendouzi[1] and K. Alali[1]

[1]*Modeling and Calculation Methods Laboratory, Taher Moulay University, B.P. 138, En-Nasr Avenue, Mascara Road, 20002 Saida, Algeria*

[2]*Department of Chemistry, University of Oran 1, PO Box 1524 Elmnaouer, Oran 31000, Algeria*

Abstract: Solvation free energies ΔG^{sol}_{tot} of cyclic polyethers $(CH_2CH_2O)_n$ (n=2,6) in aqueous and tetrachloromethane solutions have been calculated at HF, MP2 and B3LYP/6-311G (d,p) levels of theory using CPCM, IEFPCM and SMD implicit solvation models. It has been found that ΔG^{sol}_{tot} are negative for both solvents, they increase linearly with system sizes and they are more important in water solution. The electrostatic contributions to the solvation free energies ΔG^{sol}_{ele} are also more important in water because of their polar nature. In water, CPCM and IEFPCM models give a close values, which are slightly different from SMD values. In tetrachloromethane solvent CPCM model seems overestimate ΔG^{sol}_{ele}. For both solvents the non-electrostatic contributions to the solvation free energies ΔG^{sol}_{n-ele} provided by SMD are remarkably different to those given by CPCM and IEFPCM models.

Keywords: Continuum model, Solvation free energy, Cyclic polyether, Water, Tetrachloromethane.

1. INTRODUCTION

Many theoretical studies have been performed to understand the solvation of crown ethers in liquid phases [1-5]. Continuum solvation model is one of the powerful tools to provide accurate estimates of solvation free energies at a reasonable computational cost [6-22]. Compared to the explicit solvation model arranging a few solvent molecules around the solute, the continuum model places a solute molecule in a solvent cavity surrounded by a polarizable continuum, whose reaction field modifies the energy and properties of the solute. Hence, the calculations using the continuum solvation model are cheaper, simpler, and more convenient than those using the explicit solvation model [23].

Conductor-like polarizable continuum model (CPCM) [13,16] and integral equation formalism polarizable continuum model (IEFPCM) [7-12] are two of many successful solvation models. In their approaches, the solute interacts with the solvent represented by a dielectric continuum model. The solute molecule is embedded into a cavity surrounded by a dielectric continuum of a given permittivity. CPCM and IEFPCM define the cavities as envelopes of spheres centered on atoms or atomic groups. Inside the cavity the dielectric constant is the same as in vacuo, outside it takes the value of the desired solvent.

Once the cavity has been defined, the surface is smoothly mapped by small regions, called tesserae. Each tessera is characterized by the position of its centre, its area, and the electrostatic vector normal to the surface passing through its centre. Unlike the previous models, universal solvation model based on solute electron density (SMD) [20,21] is based on the quantum mechanical charge density of a solute molecule interacting with continuum description of the solvent. The SMD bulk electrostatic contribution to the free energy of solvation arises from a self-consistent reaction field treatment that involves solution of the nonhomogeneous Poisson equation by the Integral-Equation-Formalism Polarizable Continuum Model [20].

Cyclic polyethers $(CH_2CH_2O)_n$, commonly known as crown ethers [24], are synthesized originally by Pederson in 1967 [25]. They exhibit conformational mobility and have the structure of a cavity that is lined inside with the electron pairs of the donor atoms and surrounded from the outside by the hydrocarbon framework [26]. The principal interest of crown ethers arises from their potential to form stable complexes with a wide variety of ionic and neutral species [27-36]. This property is the basis of their broad practical applications in various areas of inorganic and organic chemistry, chemical fertilizers and pesticides, metallurgy, nuclear energy, biology, pharmacology and medicine [37,38].

Several thermodynamic studies of crown ethers solvation and complexation have recently appeared [3,26,39-44], investigation of solvation and association states of such important macrocycle ligands can help to

*Address correspondence to this author at the Modeling and Calculation Methods Laboratory, Taher Moulay University, B.P. 138, En-nasr Avenue, Mascara Road, 20002 Saida, Algeria; Tel/Fax: +21348471508; E-mail: berkane.ariche@univ-saida.dz

explain their high complexing abilities and selectivities in different media [39-44]. They dissolve exothermically in water and tetrachloromethane solvents, but the exothermicity is more important in water due to the formation of hydrogen-bond bridges between the adjacent oxygen atoms [26]. The contribution of hydrophobic hydration to enthalpy of hydration of ether moiety CH_2CH_2O may be estimated as slight [39], but solvation enthalpies correlate with neither electron-pair accepting nor electron-pair donating abilities of the solvents [3]. Moreover, Effects of hydrophobic hydration and hydrogen bonding are exhibited through the concentration dependence of the enthalpy of solution [26]. In spite of all the attention, it is generally agreed that a detailed picture of crown ethers solvation has yet to emerge.

None of the previous studies include solvation free energy estimations, as well as their electrostatic and non electrostatic contributions. The aim of this work is to determine accurate estimation of solvation free energy terms of crown ethers, using implicit solvation models. For each system, calculations were carried out in water and tetrachloromethane solutions. The outline of this paper is as follows: In Sec. 2, the different details of calculations used along this work are briefly described. The results are presented and discussed in Sec. 3. And the last section summarizes our conclusions.

2. CALCULATION DETAILS

Calculations were achieved for a series of cyclic polyethers $(CH2CH2O)_n$, containing two to six

(CH_2CH_2O) groups. Geometry optimizations, without imposing any symmetry constraints, were carried out using Hartree-Fock (HF) [45-47], second-order Møller-Plesset Method (MP2) [48,49] and DFT method with the hybrid functionals Becke's three-parameter exchange correlation functional and the correlation functional of Lee–Yang–Parr (B3LYP) [50-52] computational methods; the basis set used was 6-311G(d,p). The polarizable continuum models CPCM, IEFPCM and SMD were used in order to evaluate the solvation free energies components. The geometries in solution were fully optimized, starting from those obtained in the gas phase. Dielectric constants of 78.408 and 2.240 were utilized in order to simulate aqueous and tetrachloromethane environment respectively. Solvent excluded-surface SES cavities [35,54] were used to define the solute-solvent interface for the calculations of electrostatic and non-electrostatic terms. The calculations were performed with tesserae of $0.2Å^2$ average area. The numeral densities values of 0.033357 and 0.006202 were adopted for water and tetrachloromethane solvent respectively. All calculations in this work were performed using the GAUSSIAN09 suite of programs [55].

3. RESULTS AND DISCUSSION

Electrostatic contributions to solvation free energies of cyclic ethers $(CH_2CH_2O)_n$ in water and tetrachloromethane solvent are summarized in Table **1**. The results showed that all terms are negatives. Moreover, absolute values of electrostatic solvation

Table 1: Electrostatic Contributions to Solvation Free Energies (in kcal.mol^{-1}) of Cyclic Polyethers $(CH_2CH_2O)_n$ (n=2,6) in Aqueous and Tetrachloromethane Solutions

System	model	H$_2$O			CCl$_4$		
		HF	MP2	B3LYP	HF	MP2	B3LYP
$(CH_2CH_2O)_2$	CPCM	-09,43	-08,87	-08,57	-04,96	-04,74	-04,58
	IEFPCM	-09,36	-08,80	-08,50	-03,91	-03,76	-03,83
	SMD	-10,05	-09,73	-09,88	-04,62	-03,93	-04,25
$(CH_2CH_2O)_3$	CPCM	-12,75	-12,34	-11,85	-06,92	-06,77	-06,42
	IEFPCM	-12,64	-12,24	-11,75	-05,17	-05,24	-05,10
	SMD	-13,07	-12,33	-12,85	-05,35	-04,53	-04,73
$(CH_2CH_2O)_4$	CPCM	-16,49	-16,01	-15,33	-08,77	-08,62	-06,01
	IEFPCM	-16,39	-16,05	-15,23	-06,44	-06,65	-06,44
	SMD	-15,52	-15,03	-15,39	-06,35	-05,31	-05,60
$(CH_2CH_2O)_5$	CPCM	-20,43	-19,77	-18,97	-10,59	-10,57	-09,96
	IEFPCM	-20,08	-19,61	-18,67	-07,75	-08,11	-07,77
	SMD	-17,96	-17,43	-17,71	-07,50	-06,18	-06,51
$(CH_2CH_2O)_6$	CPCM	-25,08	-23,91	-22,95	-12,37	-12,51	-11,69
	IEFPCM	-24,41	-23,66	-22,52	-08,98	-09,52	-09,07
	SMD	-20,67	-20,29	-20,68	-08,34	-07,22	-07,59

free energies estimated in tetrachloromethane solvent are always lower than those of water solvent. This may be due to the polar nature of water solvent. In addition, for both solvents and with all solvation models, calculated values increase linearly with molecular sizes. Qualitatively, we have previously observed the same behavior for straight-chain polyethers $CH_3O(CH_2CH_2O)_nCH_3(n=1,4)$ [56]. It is worth noting that the increase in electrostatic terms is more important in water solvent. According to Figures **1**, **2** and **3**, one can evaluate approximately the slope of straight lines which confirm the electrostatic free energies evolution in both solvents. It ranges from 2.53 for SMD/HF to 3.91 for CPCM/HF in water. While, in tetrachloromethane the slope ranges from 0.82 for SMD/MP2 to 1.94 for CPCM/MP2.
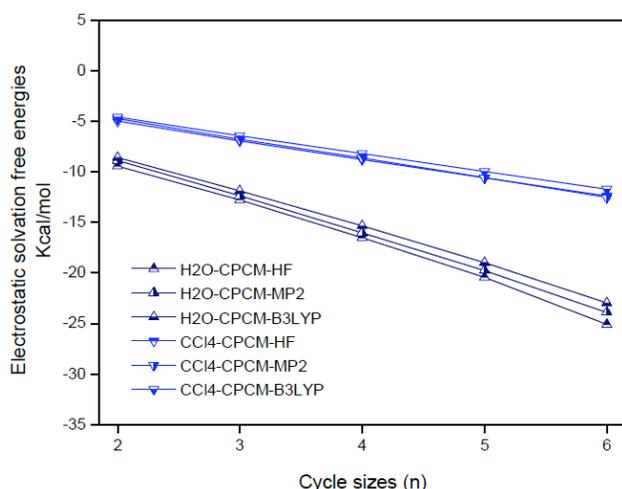

Figure 1: Electrostatic free energy components vs. cycle sizes for water (▲) and tetrachloromethane (▼). Using CPCM solvation model with HF, DFT/B3LYP and MP2 methods.
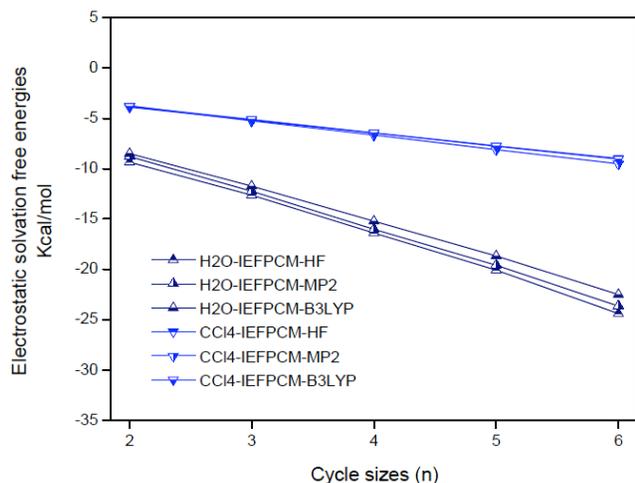

Figure 2: Electrostatic free energy components vs. cycle sizes for water (▲) and tetrachloromethane (▼). Using IEFPCM solvation model with HF, DFT/B3LYP and MP2 methods.
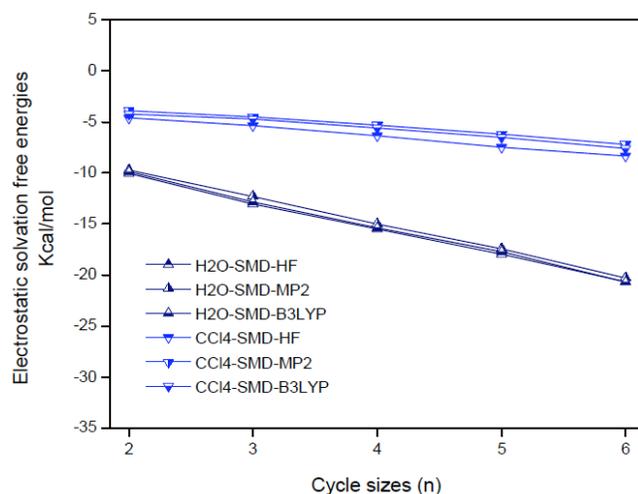

Figure 3: Electrostatic free energy components vs. cycle sizes for water (▲) and tetrachloromethane (▼). Using SMD solvation models with HF, DFT/B3LYP and MP2 methods.

In water solvent, the computed electrostatic contributions using CPCM and IEFPCM are very close, and they are slightly different to SMD values. With CPCM model, HF method provide high values of electrostatic contributions compared to those obtained at the MP2 and B3LYP level of theories. This overestimation of electrostatic terms is probably due to electron correlation effect [57-60], which is not considered in HF theory. Similar behavior was found for IEFPCM model. However, in this case MP2 values are slightly close to those calculated by HF method. Owing to our calculations, using SMD model all methods give similar values. This last consequence is due to the fact that SMD does not utilize partial atomic charges and, therefore, the applicability of the SMD model does not depend on the availability of reasonable charges for a given level of theory.

In the case of tetrachloromethane solvent, IEFPCM and SMD models give close values of electrostatic solvation free energies. However, CPCM seems slightly overestimates electrostatic terms. This unsatisfactory estimation is due to the fact that CPCM model is only asymptotically accurate in the case of large dielectric constant of solvent. Like water solvent, calculated electrostatic contributions in tetrachloromethane using CPCM model are large with HF method compared to MP2 and B3LYP; however, in this case HF results are very close to those of MP2.

With IEFPCM model, all values are almost similar; in contrast to the differences observed between results of the tree methods in CPCM model. It is apparent that the effect of theory level is negligible in this case. For

SMD estimations, B3LYP and MP2 values are similar and they are slightly low compared to HF values.

The non-electrostatic contributions to solvation free energies evaluated using CPCM and IEFPCM models (noted as $\Delta G_{n\text{-}ele}^{C/IEFCM}$, with their components: cavitation, repulsion and dispersion noted as ΔG_{cav}, ΔG_{rep} and ΔG_{dis} respectively) and SMD model (noted as $\Delta G_{n\text{-}ele}^{SMD}$) are presented in Table **2**. CPCM and IEFPCM models provide approximately similar values of non-electrostatic contributions. This is due to the fact that our systems are optimized using the same cavities type for all models, with the same cavity spheres and solvent radii. In comparison, values obtained using different levels of theory are slightly different. This is due to the differences between optimized structures of ether molecules.

Owing to our calculations, non-electrostatic contributions are linearly proportional to molecular size regardless of solvent and solvation model. As shown in Figure **4**, all non-electrostatic contributions evolve linearly with cycle sizes. However, they evolve differently for each solvation model. According to CPCM/IEFPCM models, $\Delta G_{n\text{-}ele}^{C/IEFCM}$ increase with molecular sizes, but calculated SMD values decrease when molecular size increases. In other hand, for each solvation model a similar evolution is observed in both solvent. Conforming to Figure **4**, the slopes of $\Delta G_{n\text{-}ele}^{C/IEFCM}$ range from 1.42 to 1.59 in water and from 0.65 to 0.88 in tetrachloromethane. With SMD model they range from -0.43 to -0.48 in water and around -0.80 to -0.82 in tetrachloromethane.

All the absolute values of non-electrostatic terms (ΔG_{cav}, ΔG_{rep} and ΔG_{dis}) calculated with CPCM/IEFPCM are greater in water solvent. Thus, the resulting $\Delta G_{n\text{-}ele}^{C/IEFCM}$ is more favorable in tetrachloromethane solvent. It is worth noting that this last conclusion is

Table 2: Non-Electrostatic Contributions to Solvation Free Energies (in kcal.mol^{-1}) of Cyclic Polyethers $(CH_2CH_2O)_n$ (n=2,6) in Aqueous and Tetrachloromethane Solutions

| System	Contribution	H$_2$O			CCl$_4$		
		HF	MP2	B3LYP	HF	MP2	B3LYP
$(CH_2CH_2O)_2$	ΔG_{cav}	+12,45	+12,65	+12,56	+08,94	+09,18	+09,10
	ΔG_{rep}	+05,23	+05,46	+05,44	+02,61	+02,69	+02,68
	ΔG_{dis}	-18,13	-18,19	-18,20	-12,98	-12,99	-13,01
	$\Delta G_{n\text{-}ele}^{C/IEFCM}$	-00,45	-00,07	-00,20	-01,43	-01,11	-01,22
	$\Delta G_{n\text{-}ele}^{SMD}$	+01,78	+02,22	+01,98	-02,46	-02,85	-02,27
$(CH_2CH_2O)_3$	ΔG_{cav}	+18,28	+18,77	+18,50	+13,25	+13,67	+13,42
	ΔG_{rep}	+06,87	+07,10	+07,10	+03,35	+03,42	+03,43
	ΔG_{dis}	-24,26	-24,29	-24,34	-17,36	-17,32	-17,37
	$\Delta G_{n\text{-}ele}^{C/IEFCM}$	+00,89	+1,59	+01,26	-00,76	-00,23	-00,53
	$\Delta G_{n\text{-}ele}^{SMD}$	+01,43	+01,87	+01,63	-03,23	-03,61	-03,06
$(CH_2CH_2O)_4$	ΔG_{cav}	+23,72	+24,59	+23,96	+17,22	+17,87	+17,46
	ΔG_{rep}	+08,29	+08,67	+08,49	+04,00	+04,13	+04,08
	ΔG_{dis}	-29,82	-30,02	-29,77	-21,26	-21,32	-21,26
	$\Delta G_{n\text{-}ele}^{C/IEFCM}$	+02,18	+03,25	+02,68	-00,05	+00,67	+00,28
	$\Delta G_{n\text{-}ele}^{SMD}$	+00,80	+01,36	+01,05	-04,04	-04,41	-03,83
$(CH_2CH_2O)_5$	ΔG_{cav}	+29,18	+29,80	+29,66	+21,19	+21,63	+21,60
	ΔG_{rep}	+10,65	+10,23	+11,11	+04,97	+04,81	+05,13
	ΔG_{dis}	-36,44	-35,17	-36,61	-25,56	-24,87	-25,65
	$\Delta G_{n\text{-}ele}^{C/IEFCM}$	+03,40	+04,86	+04,16	+00,60	+01,57	+01,08
	$\Delta G_{n\text{-}ele}^{SMD}$	+00,29	+00,84	+00,54	-04,81	-05,14	-04,58
$(CH_2CH_2O)_6$	ΔG_{cav}	+35,23	+35,84	+35,83	+25,42	+26,07	+25,91
	ΔG_{rep}	+12,83	+12,02	+13,51	+05,98	+05,58	+06,18
	ΔG_{dis}	-43,39	-41,55	-43,85	-30,22	-29,21	-30,32
	$\Delta G_{n\text{-}ele}^{C/IEFCM}$	+04,67	+06,32	+05,49	+01,18	+02,45	+01,77
	$\Delta G_{n\text{-}ele}^{SMD}$	-00,15	+00,47	+00,18	-05,77	-06,10	-05,47
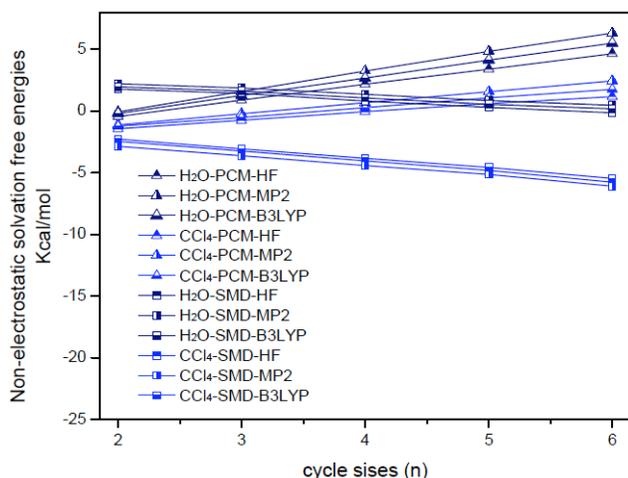
Figure 4: Non-electrostatic free energies components vs. cycle sizes for water and tetrachloromethane using CCPCM/IEFPCM (▲) and SMD (■) solvation models.

also valid for SMD solvation model. As shown in Figure **8**, cavitation and repulsion contributions have positive signs. Moreover, cavitation terms are the highest terms in both solvents and for all calculation methods. According to our data the ratio repulsion/cavitation is almost constant with all methods; it ranges from 0.30 to 0.40 in water solvent and from 0.20 to 0.30 in tetrachloromethane solvent.

Table **3** presents the solvation free energies computed for water and tetrachloromethane using CPCM, IEFPCM and SMD solvation models and HF, MP2 as well as B3LYP levels of theory. Overall, it can be seen from Table **3** that estimated values are close

for each molecular system. This estimation seems to be more accurate for water solvent. All calculated solvation free energies presented in this paper are negative. This provides favorable solvation of all systems in both solvents. Moreover, obtained terms are larger in water solvent, and it can be concluded that solvation of cyclic ethers $(CH_2CH_2O)_n$ (n=2,6) is more favorable in the polar solvent.

Owing to our calculations, all solvation models provide consistent solvation free energy values in water, excepting those obtained with B3LYP and MP2 for largest molecular systems. The differences range from 1.79 to 3.47 Kcal.mol^{-1} for the first method and from 1.84 to 2.48 Kcal.mol^{-1} for the second one. These divergences could be due essentially to the variation of optimized molecular structures obtained by selected calculation methods; it is worth noting that when molecular geometry changes the cavity changes and consequently all free energy contributions change.

The obtained solvation free energies values using HF seem to be overestimated in comparison with those of MP2 and B3LYP methods; the differences range from 1.10 to 2.95 Kcal.mol^{-1}. This overestimation is due to the correlation effect errors [57-60], in addition to differences of optimized molecular structures. The calculated values using SMD are slightly different to those evaluated with CPCM and IEFPCM models; particularly when MP2 method is utilized, the differences can attain up to 2.50 Kcal.mol^{-1}.

Table 3: Solvation Free Energies (in kcal.mol^{-1}) of Cyclic Polyethers $(CH_2CH_2O)_n$ (n=2,6) in Aqueous and Tetrachloromethane Solutions

System	Model	H$_2$O			CCl$_4$		
		HF	MP2	B3LYP	HF	MP2	B3LYP
$(CH_2CH_2O)_2$	CPCM	-09,88	-08,94	-08,77	-06,39	-05,85	-05,80
	IEFPCM	-09,81	-08,87	-08,70	-05,34	-04,87	-05,05
	SMD	-08,27	-07,51	-07,90	-07,08	-06,78	-06,52
$(CH_2CH_2O)_3$	CPCM	-11,87	-10,76	-10,59	-07,68	-07,00	-06,95
	IEFPCM	-11,76	-10,66	-10,49	-05,93	-05,46	-05,63
	SMD	-11,64	-10,46	-11,22	-08,58	-08,14	-07,79
$(CH_2CH_2O)_4$	CPCM	-14,31	-12,77	-12,65	-08,82	-07,95	-07,89
	IEFPCM	-14,20	-12,80	-12,55	-06,48	-05,97	-06,16
	SMD	-14,72	-13,67	-14,34	-10,39	-09,72	-09,43
$(CH_2CH_2O)_5$	CPCM	-17,04	-14,91	-14,82	-09,99	-09,00	-08,89
	IEFPCM	-16,69	-14,75	-14,52	-07,15	-06,54	-06,69
	SMD	-17,67	-16,59	-17,17	-12,31	-11,32	-11,09
$(CH_2CH_2O)_6$	CPCM	-20,41	-17,59	-17,46	-11,19	-10,07	-09,92
	IEFPCM	-19,74	-17,34	-17,03	-07,80	-07,08	-07,30
	SMD	-20,82	-19,82	-20,50	-14,11	-13,32	-13,06

Inspection of Table **3** reveals that in tetrachloromethane solvent obtained values with each solvation model are coherent; they evolve linearly with molecular sizes. However, each solvation model produces a different evolution in comparison with other models. Solvation free energies estimated by IEFPCM change weakly with molecular sizes. Using CPCM they grow significantly but with SMD the increase is more important. The slopes of straight lines evaluated from Figures **6**, **7** and **8** clearly illustrate these evolutions. For IEFPCM the slope values are -0.62, -0.56 and -0.56, for CPCM they are -1.20, -1.06 and -1.03. However, for SMD they attain -1.76, -1.63 and -1.64 for HF, MP2 and B3LYP levels of theory respectively. The computed solvation free energies using IEFPCM model are the smallest for all computational methods and all systems, they are followed by terms calculated by
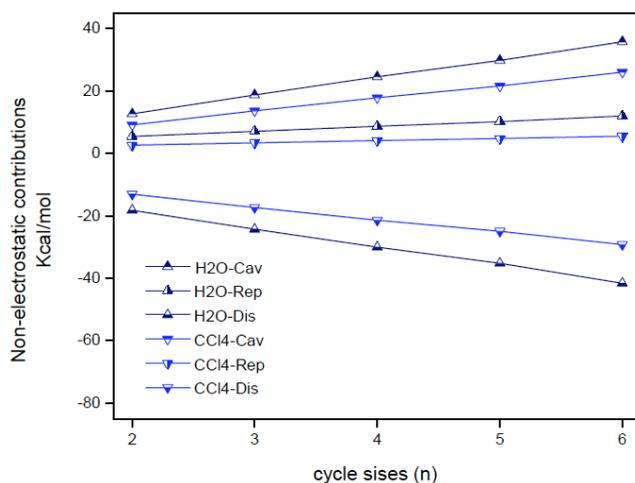

Figure 5: Non-electrostatic contributions to solvation free energies vs. cycle sizes for water (▲) and tetrachloromethane (▼) using SMD solvation model.
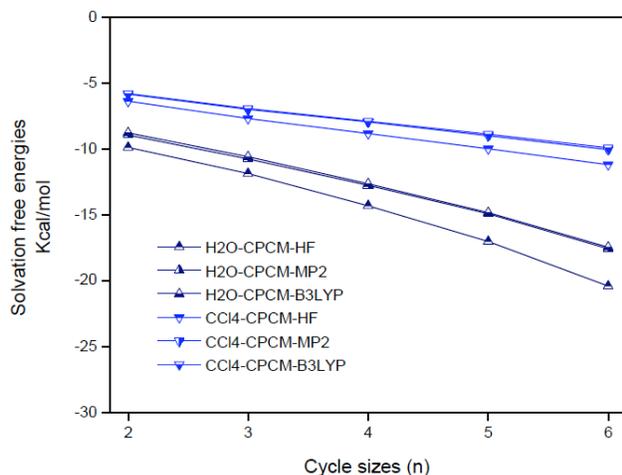

Figure 6: Solvation free energies vs. cycle sizes for water (▲) and tetrachloromethane (▼) using CPCM solvation model.

CPCM model and SMD gives the largest values. Finally, like predicted values in water solvent, in tetrachloromethane solvent HF method seems overestimate solvation free energies.
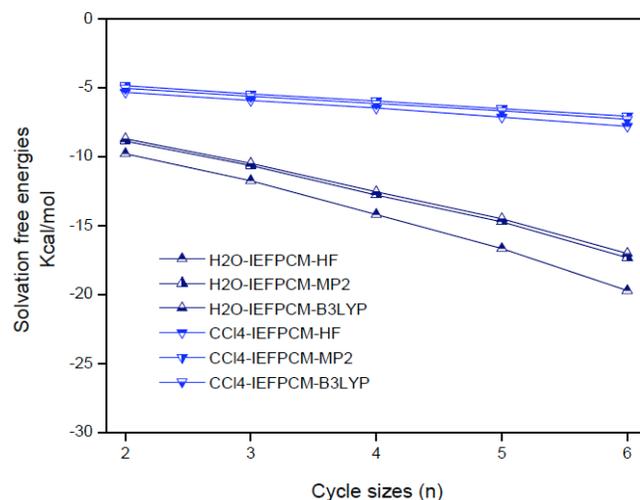

Figure 7: Solvation free energies vs. cycle sizes for water (▲) and tetrachloromethane (▼) using IEFPCM solvation model.
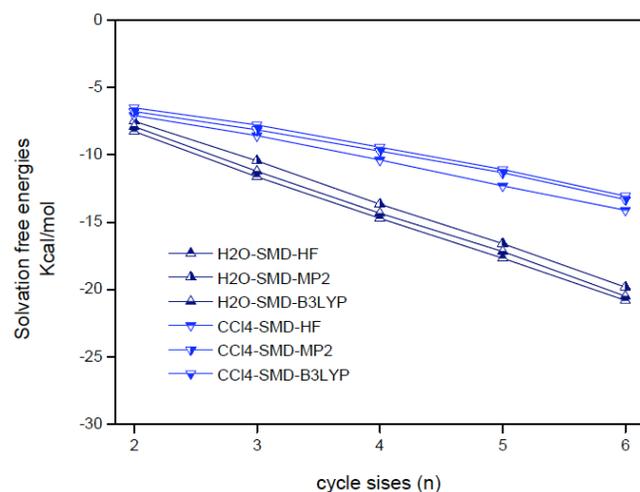

Figure 8: Solvation free energies vs. cycle sizes for water (▲) and tetrachloromethane (▼) using SMD solvation model.

4. CONCLUSIONS

The solvation free energies of cyclic polyethers $(CH_2CH_2O)_n$ (n=1,6) have been studied computationally in water and tetrachloromethane using CPCM, IEFPCM and SMD solvation models at HF, MP2 and B3LYP/6-311G(d,p) levels of theory. On the basis of the obtained results, calculated terms of solvation free energies as well as their electrostatic and non-electrostatic contributions evolve linearly with molecular sizes. The absolute values of electrostatic contributions calculated in tetrachloromethane are always lower than those of water. The non-electrostatic contributions to the

solvation free energies estimated by SMD are remarkably different to those given by CPCM and IEFPCM models. Concerning the overall solvation free energies, it was found that all calculated values are negative, which provide favorable solvation of all systems in both solvents. Furthermore, it can be concluded that solvation of cyclic ethers is more favorable in water solvent.

ACKNOWLEDGEMENTS

ABBREVIATIONS

HF	=	Hartree-Fock method
MP2	=	Second-order Møller-Plesset Method
B3LYP	=	DFT method with the hybrid functionals Becke's three-parameter exchange correlation functional and the correlation functional of Lee–Yang–Parr
CPCM	=	Conductor-like polarizable continuum model
IEFPCM	=	Integral equation formalism polarizable continuum model
SMD	=	Universal solvation model based on solute electron density
ΔG^{sol}_{tot}	=	Solvation free energy
ΔG^{sol}_{ele}	=	Electrostatic contributions to the solvation free energies
ΔG^{sol}_{n-ele}	=	Non-electrostatic contributions to the solvation free energies
$\Delta G_{n-ele}^{C/IEFCM}$	=	Non-electrostatic contributions to solvation free energies evaluated using CPCM and IEFPCM
ΔG_{cav}	=	Cavitation contribution
ΔG_{rep}	=	Repulsion contribution
ΔG_{dis}	=	Dispersion contribution
ΔG_{n-ele}^{SMD}	=	Non-electrostatic contributions to solvation free energies evaluated using SMD

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