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EFFECTS OF METHODS AND BASIS SETS ON CALCULATION RESULTS USING VARIOUS SOLVATION MODELS

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Various quantum chemical approaches including *ab initio*, density functional theory (B3LYP, CAM-B3LYP, ω B97X-D, M06HF) and semiempirical (PM7) methods with different basis sets and various solvation models (SMD, IEFPCM, COSMO), as well as a supermolecular approach, and the basis set superposition error (BSSE) corrections, used to analyze the solvation effects are compared for polar (water, ethanol, dimethylsulfoxide, acetonitrile, acetone), weakly polar (chloroform) and nonpolar (benzene, n-hexane, carbon tetrachloride) solvents *per se* and interacting with unmodified and modified silicas. The DFT methods give smaller errors in the ΔG_s values than the PM7 method with various solvation models. For the molecular clusters with water alone or water with organics, the interaction energy decreases with enhanced amorphism of the systems. The supermolecular approach with PM7 gives worse results (in comparison to the experimental data) than those of SMD/PM7 or COSMO/PM7. An increase in the basis sets can give worse results than that at smaller ones because the parameters in the SMD model were calibrated using the experimental data and *ab initio* or DFT calculations of the same systems with relatively small basis sets.

Keywords: solvation effects, solvation models, quantum chemical methods, *ab initio* and DFT methods, semiempirical methods

INTRODUCTION

Energetic characteristics of solvation (e.g. Gibbs free energy of solvation, ΔG_s) of various solutes in aqueous or organic media are of importance because they determine the solubility of the compounds, the behavior upon co-adsorption with water, and these effects are especially interesting for organic solvents/solutes interacting with water [1–6]. There are different methods for theoretical analysis of the solvation effects and estimations of the ΔG_s values. Typically, *ab initio* (Hartree-Fock (HF) or HF with Møller-Plesset perturbation theory (MP/HF) improving HF by adding electron-correlation effects with Rayleigh–Schrödinger perturbation theory) or density functional theory (DFT) methods give the results with relatively small errors, which, however, depend on several factors such as method (HF, MP/HF, or DFT), MP order and DFT type, basis sets, and solvation methods [2, 4–11]. However, the application of the *ab initio* and DFT methods to large molecules is rather difficult due to clear computer restrictions [6, 12]. Therefore, the use of semiempirical methods (e.g. PM6, PM7, *etc.*) [12] could be preferable for large and complex systems. For example, the values of binding constant $K_a = \exp(-\Delta G/RT)$ (where ΔG is the

free energy of the complex formation, R is the gas constant, and T is the temperature) for doxorubicin molecules (12 molecules simultaneously bound to a hydrated molecule of human serum albumin (HSA) with a number of atoms ~ 11000) interacting with various sites of hydrated HSA molecule were calculated using the semiempirical method PM7 with COSMO (COnductor-likeScreeningMOdel) applied for aqueous media [13]. Clearly, the use of *ab initio* or DFT methods to study similar large systems is very difficult. The aim of this work is comparison of results of DFT and *ab initio* (HF with MP) methods to those of experimental data and semiempirical PM7 method for various solutes in aqueous and organic media using different models of solvation to search an optimal approach to analyze the solvation and intermolecular bonding effects for high-molecular weight compounds (e.g. proteins) interacting with water and low-molecular weight solutes or solvents and the interfacial effects for complex systems including two-three co-solvents, co-solutes or co-adsorbates at a silica surface initial and partially hydrophobized with trimethylsilyl groups. As a whole, this investigation direction is original and was stimulated by theoretical analyses of huge number of experimental investigations using ^1H

nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry, thermal stimulation depolarization current (TSDC), evaporation of free and adsorbed liquids, thermogravimetry (TG), cryoporometry, relaxometry, thermoporometry and other methods that were described in detail in monographs [4, 14, 15], reviews [16–22] and original papers [13, 23–25].

QUANTUM CHEMICAL METHODS

Quantum chemical calculations were carried out using *ab initio* (HF method with second-order MP (MP2)) and DFT methods with several hybrid functionals such as ω B97X-D, B3LYP, CAM-B3LYP, and M06HF [26] with the cc-pVDZ, aug-cc-pV6Z, 6-31G(d,p), and 6-311++G(3d,2p) basis sets [26–28] using the Gaussian 09 [26], GAMESS 2017 R1 [29, 30], and MOPAC 2016 [12] program suits. The solvation effects were analyzed using several solvation models such as a continuum solvation model based on the quantum mechanical charge density of a solute molecule interacting with a continuum description of the solvent (SMD) [10, 11] and Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) [26], COSMO [12, 31], and a supermolecular approach. Practically all calculations taking into account the solvation effects were performed with the parallel geometry optimization. Visualization of molecular structures was performed using the ChemCraft (version 1.8/523) [32] or GaussView 5.09 [33] programs.

Analysis of the solvation effects was started from a set of molecules and ions (water, organic solvents, *etc.*) alone calculated using several methods and compared to the experimental data to evaluate better approaches. Then various clusters of water (from 3 up to 5000 molecules), water with organic solvents (e.g. DMSO and acetonitrile), as well as initial and partly hydrophobized silica clusters, were calculated to analyze the effect of inter-cluster and outer-cluster interactions and to explain such effects as, e.g., better dissolution of organics in water than water in the same organics.

RESULTS AND DISCUSSION

For simplicity, small molecules and ions were studied using SMD/DFT and PM7 methods (Table 1). Much larger systems (up to 15000

atoms) were calculated using PM7 method (Table 2). Selected systems were also calculated using SMD/MP2/HF with the 6-31G(d,p) and 6-311++G(3d,2p) basis sets, PCM(IEFPCM)/ ω B97X-D/cc-pVDZ, and SMD/ ω B97X-D/aug-cc-pV6Z methods. The calculated values of the Gibbs free energy of solvation (ΔG_s) were compared to the experimental data collected from [10, 11].

Typically, an overestimation (by the modulus) of the values of ΔG_s (Table 1) was smaller (from -0.7 to -2.61 kcal/mol) than the underestimation (from $+1.8$ to $+12.4$ kcal/mol). This is especially characteristic for the PM7 results, which were obtained in direct calculations of a molecule or ion surrounded by a water cluster with 100 H₂O. An increase in the basis set could result in decreased or increased errors (Table 1). For example, for solvated anion OH⁻, which was calculated using SMD/B3LYP/6-31G(d,p), the error is smaller than that of SMD/CAM-B3LYP/6-311++G(3d,2p), or $\Delta G_s = -107.3$ kcal/mol (SMD/MP2/6-31G(d,p)) and -99.0 kcal/mol (SMD/MP2/6-311++G(3d,2p)), and -92.7 kcal/mol (SMD/ ω B97X-D/aug-cc-pV6Z), which are worse than that by SMD/ ω B97X-D/cc-pVDZ. Typically, SMD gives better results (i.e. smaller errors with respect to the experimental data) than PCM(IEFPCM), since for H₃O⁺ $\Delta G_s = -77.9$ kcal/mol (PCM/ ω B97X-D/cc-pVDZ) is worse than that by SMD/ ω B97X-D/cc-pVDZ (see Table 1). From these comparisons, it is possible to recommend such models/methods for calculations of the solvation effects for simple molecules as SMD with ω B97X-D/cc-pVDZ, B3LYP/6-31G(d,p), or MP2/HF/6-31G(d,p), i.e., there is no need to use large basis sets for calculations of the solvation effects. Additionally, for simpler semiempirical approaches, calculations of the molecules and ions surrounded by the 100 H₂O shell using the PM7 method give worse results than those with the COSMO or SMD methods (see errors in Table 1). Among DTF calculations the worse results (larger errors in Table 1) were obtained with M06HF/6-311++G(3d,2p) despite a large basis set. The errors depend also on the solute types, e.g., it is larger for H₃O⁺ than for OH⁻ or NH₄⁺ (Table 1).

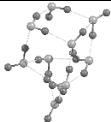
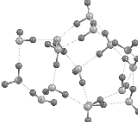
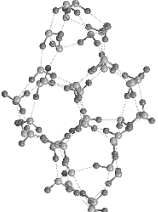
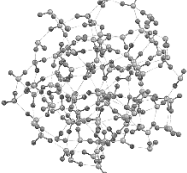
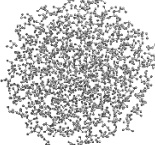
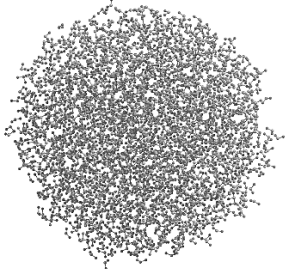
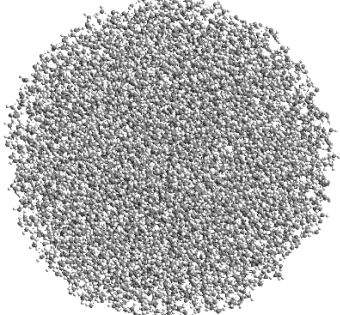
In the case of semiempirical methods, there are several possibilities to analyze the solvation

Table 1. Calculations of ΔG_s (kcal/mol) for molecules and ions solvated in aqueous solution using the SMD/DFT method with various functionals and basis sets or SMD/PM7, and E_{sol} (kcal/mol) for a molecule solvated in a cluster with 100H₂O (PM7) or PM7/COSMO for individual molecules/ions

Solute	B3LYP 6-31G(d,p)	CAM-B3LYP 6-311++G(3d,2p)	ω B97X-D cc-pVDZ	M06HF 6-311++G(3d,2p)	PM7 100H ₂ O	PM7/COSMO	PM7/SMD	Experimental [10, 11]
H ₂ O	-7.8	-7.5	-7.1	-8.0	-3.4	-7.41	-8.07	-6.31
OH ⁻	-105.4	-94.7	-106.4	-98.3	-80.3	-100.51	-114.39	-106.0
H ₃ O ⁺	-96.4	-96.5	-96.2	-96.3	-77.1	-93.56	-97.50	-104.0
CH ₃ CH ₂ OH	-4.2	-4.6	-3.7	-5.3	-4.7	-5.96	-5.48	-5.01
C ₆ H ₅ OH	-5.3	-5.3	-5.2	-7.7	-8.5	-5.93	-4.14	-6.62
C ₆ H ₆	-0.66	-0.85	-0.93	-3.0	0.9	-1.99	0.22	-0.87
CHCl ₃	-1.4	-1.3	-1.16	-1.5		-3.11	-1.83	-1.07
CH ₃ CN	-3.4	-4.4	-3.3	-4.4	-3.4	-7.31	-3.07	-3.89
NH ₄ ⁺	-82.0	-82.3	-81.6	-82.4	-50.0	-83.12	-80.67	-79.0
Average errors	-1.6 / +1.8	-1.3 / +4.1	-0.7 / +2.8	-1.4 / +7.7	-2.1 / +12.4	-2.13 / +5.54	-2.61 / +2.70	

Note. E_{sol} was calculated as the difference in the total energy of a molecule surrounded by a water cluster with 100 H₂O and that for the cluster with no solute molecule or ions

Table 2. Average interaction energy per a water molecule in water clusters from 10 to 5000 molecules (PM7)

Structure	ΔE_t (kJ/mol)
 10H ₂ O	-14.2
 16H ₂ O	-15.1
 44H ₂ O	-14.4
 100H ₂ O	-14.2
 692H ₂ O	-14.1
 2000H ₂ O	-13.4
 5000H ₂ O	-14.5

effects. First, the use of the SMD (implemented in Gaussian and GAMESS) or other (e.g. COSMO in MOPAC 2016) solvation methods with no a real solvation shell of a molecule. Second, it is possible to construct a real solvation shell surrounding a solute molecule using various water clusters (Table 2). Note that the interaction energy (per a molecule) in the water clusters depends weakly on their size (Table 2, clusters with 10–5000 water molecules), but it becomes greater if a structure is closer to that of ice (Ih), but it is lower than the experimental value (Table 1). In other words, enhanced amorphism of the water clusters leads to diminution of the average interaction energy. A similar effect is observed for the ^1H NMR spectra of water and ice, since the values of δ_{H} are greater for ice (~7 ppm) than for bulk liquid water possessing amorphous structure (~4–5 ppm) [4].

Interaction of water molecules with a silica surface is similar (slightly stronger) to that for water *per se* [4]. Therefore, the value of ΔG_s per a silanol (Table 3) is close to that for 100 H_2O (Table 1) or other water clusters (Table 2). Partial hydrophobization (especially with small values of $\Theta_{\text{TMS}} \approx 0.041\text{--}0.125$ determined a relative value of substituted silanols by trimethylsilyl (TMS) groups) weakly affects the hydration energy of silica clusters (Table 3, Fig. 1). The solvation energy *vs.* a number of TMS groups in clusters $\text{Si}_8\text{O}_{12}(\text{OH})_n(\text{OSi}(\text{CH}_3)_3)_{8-n}$ ($n = 8, 7, 6, \dots, 0$) calculated using SMD/ ω B97X-D/cc-pVDZ//cc-pVDZ for water, ethanol, and *n*-hexane as solvents (Fig. 1) shows that an increase in the degree of hydrophobization leads to stronger solvation of the functionalized silica clusters only in *n*-hexane, but the solvation effects decrease not only in water but also in ethanol. The latter is due to weaker van-der-Waals interactions for nonpolar fragments/groups than the hydrogen bonds of the O-H...O type between polar fragments/groups. Adsorbed water molecules onto a silica cluster with a TMS group slightly enhance the hydration energy (Table 3) due to an increase in electrostatic contributions into solvation energy. Some ions or polar molecules can be adsorbed close or between TMS groups at a surface of partially hydrophobized silicas. In such places, the hydration shells cannot be formed as that at a hydrophilic surface that can lead to adsorption of

ions or small polar molecules (e.g. amino acids) onto the partially hydrophobized silicas in contrast to the absence of the adsorption onto initial hydrophilic nanosilica. These features of hydrophilic, partially and completely hydrophobized nanosilicas can lead to changes in the organization of the nanoparticles in aqueous, water-ethanol or other dispersion media [4, 24].

Water molecule or clusters are better solvated (*i.e.*, ΔG_s is lower or larger by the modulus) in water than in other solvents (both polar (ethanol, DMSO, acetonitrile, acetone) and nonpolar (benzene, hexane) or weakly polar (chloroform) ones) independent of the water cluster size (Table 4). However, this difference decreases with increasing size of the clusters. This explain why water and nonpolar liquids tend to reduce the contact area. However, for water molecules in aqueous media, the values of non-electrostatic contributions into the Gibbs free energy of solvation are positive (*i.e.* destabilizing) and maximal (see the SMD-CDS values in Table 4). This is due to strong interaction between water molecules *per se* that causes great energy spent on the formation of a cavity for a solute in the aqueous media. Note that all properties of water are unusual [5], and the main reason of that is strong hydrogen bonds in water, in which all atoms take part since each O atom forms two hydrogen bonds and each H atom form one hydrogen bond. However, this is true for the water molecules located in the typical structures with the hydrogen bonds in contrast to interstitial water molecules [5] located between the molecules with the typical hydrogen bonds. The presence of interstitial water in liquid water results in several effects. For example, the average coordination number of water molecules (*i.e.* the number of the molecules in the first coordination sphere) can be about 4.5 in contrast to 4 for ice Ih; therefore, the density of ice Ih is lower than that of liquid water. The solvation parameters of water in ethanol are close to those for water in water (because the hydrogen bonds O-H...O are similar for both systems) that can explain good mixing of water with ethanol [5, 10, 11].

The difference in the values of the Gibbs free energy of solvation without and with the basis set superposition error (BSSE) corrections decreases with increasing size of solvated water clusters due to a decrease in a number of contacts of solvated molecules with surroundings

Table 3. Total solvation energy (kJ/mol) (in brackets, the values per a silanol group are shown) of a silica cluster with silanols and a TMS group

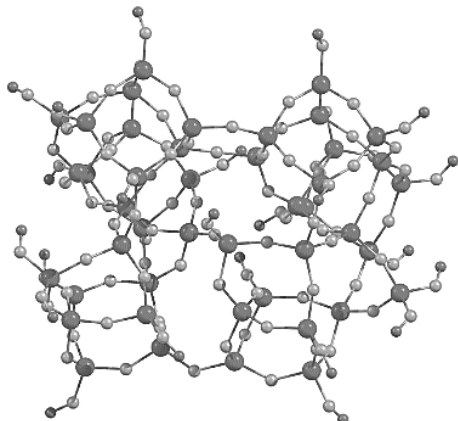
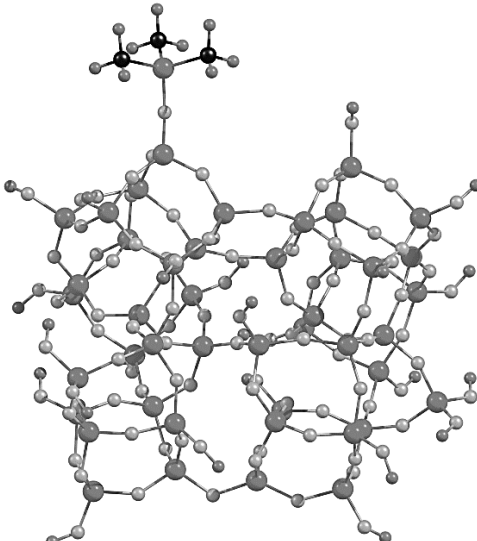
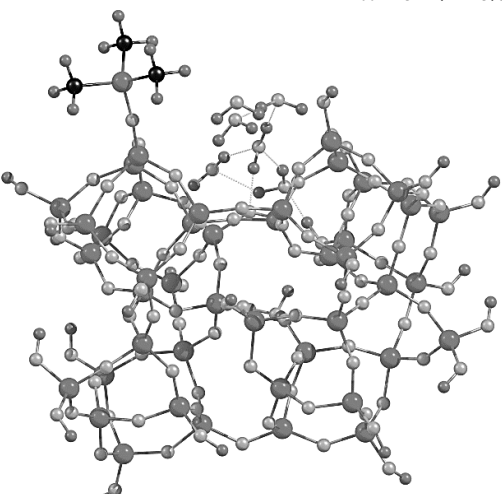
Structure	PM7/COSMO
 <p style="text-align: center;">$\text{Si}_{44}\text{O}_{100}\text{H}_{24}$</p>	-375.1 (-15.6) -474.6 (PM7/SMD) (-19.8)
 <p style="text-align: center;">$\text{Si}_{44}\text{O}_{100}\text{H}_{23}\text{Si}(\text{CH}_3)_3$</p>	-368.2 (-16.0)
 <p style="text-align: center;">$\text{Si}_{44}\text{O}_{100}\text{H}_{23}\text{Si}(\text{CH}_3)_3@7\text{H}_2\text{O}$</p>	-384.7

Table 4. Calculations of water molecule and clusters ($n = 3, 8, 16$, and $44 \text{ H}_2\text{O}$) solvated in different solvents with SMD/ ω B97X-D/cc-pVDZ (Gaussian 09)

n	Parameter	Acetone	Acetonitrile	Benzene	Chloroform	DMSO	Ethanol	Hexane	Water	Vacuum
1	E_t	-	-76.4067057642	-76.4034656956	-76.4055208029	-76.4053815837	-76.4104665884	-76.4026484632	-76.4109902370	-76.3996333120
	SMD-CDS	76.4067987024	-1.6	-3.8	0.1	-3.0	3.1	-2.9	6.1	-
	ΔE	-18.8	-18.6	-10.1	-15.5	-15.1	-28.5	-7.9	-29.8	-
3	E_t	-	-229.252371577	-229.247520706	-229.250253141	-229.250381731	-229.259381031	-229.246063591	-229.260851903	-229.240840218
	SMD-CDS	229.252872388	-3.3	-8.0	0.3	-6.4	7.1	-6.1	12.0	-
	ΔE	-7.9	-	-	-	-	-	-	-	-
8	G_{et}	-229.207464	-229.206760	-229.201675	-229.204964	-229.204804	-229.214728	-229.200108	-229.216783	-229.194610
	ΔE (ΔG_{et})	-31.6(-33.7)	-30.3(-31.9)	-17.5(-18.6)	-24.7(-27.2)	-25.1(-26.8)	-48.7(-52.8)	-13.7(-14.4)	-52.6(-58.2)	-110.2
	$\Delta G_{et}/n$	-11.3	-10.6	-6.2	-9.1	-8.9	-17.6	-4.8	-19.4	-36.7
16	E_t	-	-611.401184009	-611.391462089	-611.396167655	-611.397720432	-611.412242149	-611.388472129	-611.414946313	-611.377594883
	SMD-CDS	611.402303907	-6.6	-15.6	0.5	-12.4	13.5	-11.8	21.7	-
	ΔE	-15.2	-61.9	-36.4	-48.8	-52.9	-91.0	-28.6	-98.1	-474.2
44	E_t	-	-1222.81229300	-1222.79347305	-1222.79726527	-1222.80662414	-1222.83635435	-1222.78890744	-1222.84693628	-1222.77316703
	SMD-CDS	1222.81434599	-11.4	-28.7	1.8	-22.0	25.9	-21.8	32.6	-
	ΔE	-26.9	-102.7	-53.3	-63.3	-87.9	-166.0	-41.3	-193.8	-995.6
44	E_t	-	-3362.82176998	-3362.77376045	-3362.79020943	-3362.80781650	-3362.86812137	-3362.76013145	-3362.87946428	-3362.70846500
	SMD-CDS	3362.82777181	-32.2	-73.8	1.8	-60.4	63.1	-55.9	97.7	-
	ΔE	-73.4	-297.5	-171.4	-214.6	-260.8	-419.2	-135.7	-449.1	-2953.8
44	$\Delta E/n$	-7.1	-6.8	-3.9	-4.9	-5.9	-9.5	-3.1	-10.2	-67.1

Note. The values of G_{et} and ΔG_{et} (shown in brackets) were calculated with BSSE corrections; CDS = cavity-dispersion-solvent, *i.e.* non-electrostatic terms. E_t in Ha, others in kJ/mol

Table 5. Calculations of water molecule and clusters ($n = 3, 8, 16$, and $44 \text{ H}_2\text{O}$) solvated in different solvents with SMD/ ω B97X-D/cc-pVDZ (GAMESS 17.1), G_t in Ha, others in kJ/mol (values in brackets are with BSSE corrections)

n	Parameter	Acetone	Acetonitrile	Benzene	Chloroform	DMSO	Ethanol	Hexane	Water
1	G_t	-76.4069457090	-76.4069425959	-76.4040424000	-76.4057072508	-76.4066204669	-76.4099431361	-76.4032052729	-76.4068719206
	ΔG_s	-19.2 (-11.3)	-19.2 (-11.3)	-11.6 (-3.6)	-15.9 (-8.0)	-18.4 (-10.4)	-27.1 (-19.2)	-9.4 (-1.5)	-19.1 (-11.1)
3	G_t	-229.2530586097	-229.2526726555	-229.2484352517	-229.2503845520	-229.2526502872	-229.2565568480	-229.2469400063	-229.2522484648
	ΔG_s	-32.8 (-24.8)	-31.8 (-23.9)	-20.0 (-12.1)	-25.4 (-17.5)	-31.4 (-23.5)	-43.7 (-35.8)	-16.1 (-8.1)	-34.8 (-26.8)
	$\Delta G_s/n$	-10.9 (-8.3)	-10.6 (-8.0)	-6.7 (-4.0)	-8.5 (-5.8)	-10.5 (-7.8)	-14.6 (-11.9)	-5.4 (-2.7)	-11.6 (-8.9)
8	G_t	-611.4025666578	-611.4015753704	-611.3930199932	-611.3962392322	-611.4022774502	-611.4069658678	-611.3899736169	-611.4004958141
	ΔG_s	-68.9 (-61.0)	-66.9 (-59.0)	-41.0 (-33.1)	-51.4 (-43.5)	-67.2 (-59.2)	-86.2 (-78.2)	-32.8 (-24.9)	-75.1 (-67.2)
	$\Delta G_s/n$	-8.6 (-7.6)	-8.4 (-7.4)	-5.1 (-4.1)	-6.4 (-5.4)	-8.4 (-7.4)	-10.8 (-9.8)	-4.1 (-3.1)	-9.4 (-8.4)
16	G_t	-1222.8147009780	-1222.8124112936	-1222.7955710054	-1222.7966458993	-1222.8147906571	-1222.8133102832	-1222.7909403400	-1222.8017129681
	ΔG_s	-110.4 (-102.5)	-105.6 (-97.7)	-59.4 (-51.5)	-64.7 (-56.8)	-108.3 (-100.4)	-129.5 (-121.6)	-47.0 (-39.0)	-119.7 (-111.8)
	$\Delta G_s/n$	-6.9 (-6.4)	-6.6 (-6.1)	-3.7 (-3.2)	-4.0 (-3.6)	-6.8 (-6.3)	-8.1 (-7.6)	-2.9 (-2.4)	-7.5 (-7.0)
44	G_t	-3362.8274584472	-3362.8200698435	-3362.7803373487	-3362.7890706662	-3362.8284524725	-3362.8295881173	-3362.7664450295	-3362.8141232195
	ΔG_s	-318.9 (-311.0)	-304.7 (-296.8)	-186.2 (-178.3)	-220.8 (-212.9)	-314.3 (-306.4)	-352.3 (-344.4)	-147.2 (-139.2)	-342.5 (-334.6)
	$\Delta G_s/n$	-7.2 (-7.1)	-6.9 (-6.7)	-4.2 (-4.1)	-5.0 (-4.8)	-7.1 (-7.0)	-8.0 (-7.8)	-3.3 (-3.2)	-7.8 (-7.6)

Table 6. Calculations of molecules solvated in own solution with SMD/ ω B97X-D/cc-pVDZ (Gaussian 09)

Solvent	μ (D)	E_{HOMO} (Ha)	E_{LUMO} (Ha)	q_{H}	q_{XH}	$q_{\text{O(N,C)}}$	$q_{\text{C(S,C)}}$
Acetone	3.54	-0.32181	0.07413			-0.263	-0.007
	2.93 (g)*						
Acetonitrile	4.89	-0.41113	0.11720			-0.207	-0.123
	3.92 (g)*						
Benzene	0.0	-0.32812	0.06567	0.016	-0.016	0.066	-0.264
	0.0	-0.40365	0.00995				
Chloroform	1.47	-0.39342	0.03971	0.197	-0.148	-0.016	
	1.08 (g)*						
DMSO	5.15	-0.29276	0.13180			-0.626	0.477
	3.96 (g)*						
Ethanol	1.98	-0.34555	0.15355	0.185	-0.350		
	1.69 (g)*						
n -Hexane	0.05	-0.38189	0.14546	0.037	-0.051		
	2.36	-0.38301	0.16252	0.184	-0.369		
Water	1.85 (g)*						
	2.9 \pm 0.6 (l)*						

Note. *Experimental data for (g) gas and (l) liquid phases; μ is the dipolar moment, E_{HOMO} and E_{LUMO} are the energies of the highest occupied and lowest unoccupied molecular orbitals (i.e. boundary orbitals); q are the atomic (Mulliken) charges

Table 7. Calculations of molecules solvated in own solution with SMD/ ω B97X-D/cc-pVDZ (GAMESS 17.1) (ΔG_s values in brackets are with BSSE corrections)

Solvent	ΔG_s (kJ/mol) (BSSE)	μ (D)	E_{HOMO} (Ha)	E_{LUMO} (Ha)	q_{H}	$q_{\text{x(H)}}$	$q_{\text{O(N,C)}}$	$q_{\text{C(S,C)}}$
Acetone	-21.9 (-14.0)	3.49	-0.3239	0.0718			-0.261	-0.008
Acetonitrile	-23.1 (-15.1)	4.86	-0.4126	0.1153			-0.204	-0.122
Benzene	-21.8 (-14.0)	0.0	-0.3294	0.0645	0.018	-0.018		
CCl ₄	-17.0 (-9.1)	0.0	-0.4034	0.0072			0.071	-0.284
Chloroform	-20.1 (-12.2)	1.46	-0.3936	0.0360	0.199	-0.165	-0.012	
DMSO	-27.4 (-19.5)	5.04	-0.2970	0.1263			-0.620	0.486
Ethanol	-18.8 (-10.8)	1.92	-0.3474	0.1506	0.177	-0.343		
<i>n</i> -Hexane	-16.4 (-8.5)	0.05	-0.3823	0.1451	0.038 (0.024)	-0.101 (-0.050)		
Water	-19.1 (-11.1)	2.15	-0.3726	0.1573	0.159	-0.317		

Table 8. Calculations of molecules solvated in aqueous solution with SMD/ ω B97X-D/cc-pVDZ (GAMESS 17.1) (ΔG_s values in brackets are with BSSE corrections)

Solvent	ΔG_s (kJ/mol) (BSSE)	μ (D)	E_{HOMO} (Ha)	E_{LUMO} (Ha)	q_{H}	$q_{\text{x(H)}}$	$q_{\text{O(N,C)}}$	$q_{\text{C(S,C)}}$
Acetone	-28.8 (-20.9)	3.57	-0.3231	0.0711			-0.267	-0.011
Acetonitrile	-31.7 (-23.8)	4.88	-0.4120	0.1148			-0.208	-0.121
Benzene	-32.6 (-24.7)	0.0	-0.3302	0.0633	0.028	-0.028		
CCl ₄	-21.5 (-13.6)	0.0	-0.4039	0.0073			0.071	-0.286
Chloroform	-26.4 (-18.4)	1.56	-0.3931	0.0371	0.208	-0.162	-0.015	
DMSO	-38.0 (-30.1)	5.12	-0.2964	0.1258			-0.629	0.484
Ethanol	-21.0 (-13.1)	1.83	-0.3407	0.1517	0.165	-0.319		
<i>n</i> -Hexane	-24.6 (-16.7)	0.04	-0.3849	0.1422	0.041 (0.023)	-0.103 (-0.053)		

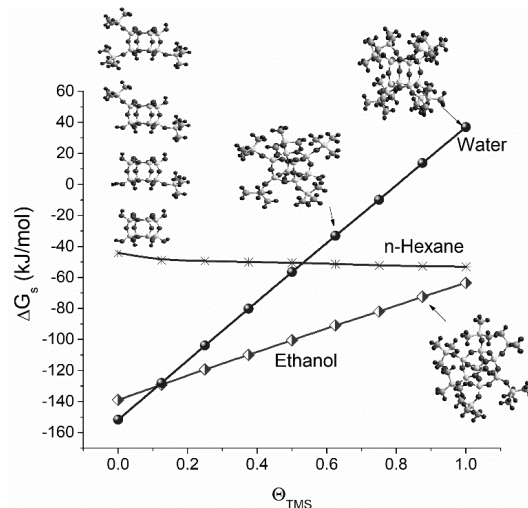
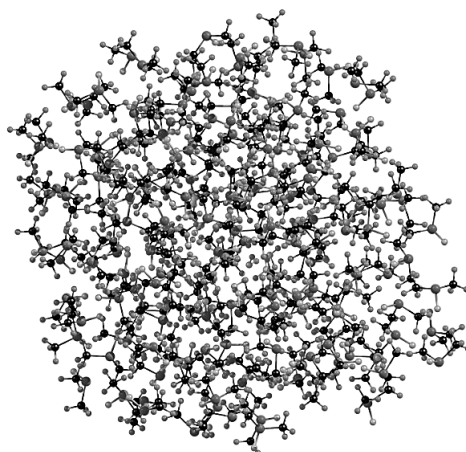
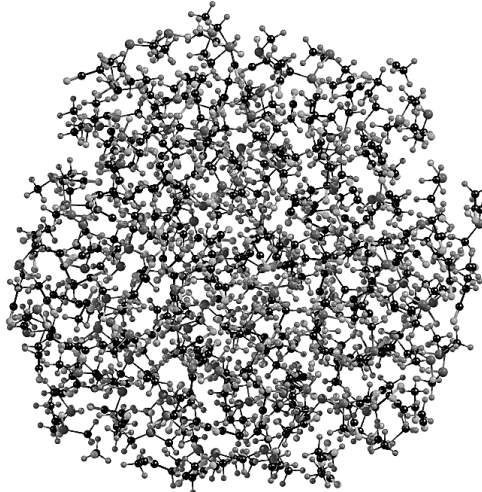


Fig. 1. Gibbs free energy of solvation vs. a number of TMS groups in clusters $\text{Si}_8\text{O}_{12}(\text{OH})_n(\text{OSi}(\text{CH}_3)_3)_{8-n}$ ($n = 8, 7, 6, \dots, 0$) calculated using SMD/ ω B97X-D/cc-pVDZ//cc-pVDZ for water, ethanol, and *n*-hexane as solvents



a – $171(\text{CH}_3)_2\text{SO}@16\text{H}_2\text{O}$
at $\Delta E_t = -9.1$ kcal/mol per a molecule



b – $132(\text{CH}_3)_2\text{SO}@172\text{CH}_3\text{CN}@44\text{H}_2\text{O}$
at $\Delta E_t = -2.0$ kcal/mol per a molecule

Fig. 2. Water clusters in surrounding with (a) DMSO and (b) DMSO and acetonitrile (PM7)

per a molecule (Tables 4 and 5). For $3\text{H}_2\text{O}$ (Table 4), the BSSE correction leads to stronger solvation results. It should be noted that Gaussian 09 and GAMESS 17 R1 give slightly different results upon using the same DFT (with SMD) and basis sets, but observed relative changes in the values are practically the same (Tables 6–8). Therefore, upon analysis of the solvation effects (or other theoretical results) it is better to use only one program suit.

For molecules with strongly polar groups, e.g., S=O in dimethylsulfoxide (DMSO), causing a maximal dipolar moment (Tables 6–8, μ), the solvation effects are strong for both own and aqueous solutions, since $|\Delta G_s|$ is maximal. Great atomic charges on these polar bonds, especially for O in DMSO, lead to high location of the highest occupied molecular orbitals (E_{HOMO}) and lower location of the lowest unoccupied MO (E_{LUMO}) that correspond to enhanced polarizability of the bond. It is higher (HOMO) in aqueous solution than in own one due to stronger polarization effects caused by water molecules. Strong interactions between DMSO and water give a relatively large value of ΔE_i per a molecule of a complex cluster (Fig. 2 a). However, addition of acetonitrile molecules to the DMSO/water cluster results in diminution of the interaction energy per a molecule in the cluster (Fig. 2 b). This result can be explained by enhanced amorphism of the cluster with the molecules of three types. In the experiments, this leads, e.g., to complex ^1H NMR spectra of DMSO/acetonitrile/water solutions bound to a surface of any adsorbent [4]. Additionally, bound water (i.e., water being under confined space effects) possesses lower activity as a solvent, i.e., it can dissolve smaller amounts of any solute than bulk free water. Therefore, the value of chemical shift of the proton resonance (δ_{H}) of water/acid bound to an adsorbent is characterized by smaller values (by several ppm) than that for free bulk solution of the same acid at the same concentration [5].

There are interesting features of solvation of organics in water that gives lower values of ΔG_s (i.e. better solution) than that in own solution (Tables 7 and 8). This seems as a contradiction to the experimental data, since hexane, benzene, carbon tetrachloride, and chloroform are poorly water-soluble, i.e., they are practically immiscible with water [4, 5, 10, 11]. However,

the solubility of water in these solvents are much worse than the solubility of nonpolar organics in the aqueous media [10, 11]. One could conclude that nonpolar organics are poorly soluble in the aqueous media due to more negative effects for water upon dissolution in the organic solvents (i.e., ΔG_s is less negative for water molecules dissolved in the organics), but not for these organics are dissolved in water since the value of ΔG_s for an organic molecule in water could be lower than that for own solution. Therefore, the solubility of benzene in water is approximately three times greater than that of water in benzene [34, 35]. Thus, theoretical results can well explain some unexpected experimental data.

CONCLUSIONS

Comparison of the theoretical results on solvation of molecules and ions of various solvents with experimental data shows that DFT methods give smaller errors in the ΔG_s values than the PM7 method with various solvation models. For the molecular clusters with water alone or water with organics, the interaction energy decreases with enhanced amorphism of the systems, e.g., transformation of ice-like structures to amorphous one. The supermolecular approach with PM7 gives worse results (in comparison to the experimental data) than those of SMD/PM7 or COSMO/PM7. The SMD/PM7 or COSMO/PM7 could be recommended for applications to large systems, which cannot be calculated using *ab initio* or DFT methods. For relatively accurate calculations of the solvation effects, the DFT methods such as B3LYP (with the 6-31G(d,p) basis set) or ω B97X-D (with the cc-pVDZ basis set) with the SMD method could be applied. An increase in the basis sets can give worse results than that at smaller ones because the parameters in the SMD model were calibrated using the experimental data and *ab initio* or DFT calculations of the same systems with relatively small basis sets. Typically, the SMD results are better (i.e. close to the experimental values for molecules and ions) than that of PCM (IEFPCM). Therefore, the SMD model with B3LYP/6-31G(d,p) or ω B97X-D/cc-pVDZ for relatively small systems (up to several hundreds of atoms) of PM7/SMD or PM7/COSMO (up to several tens of thousands of atoms) could be recommended to analyze the solvation effects.

Вплив методів та базисних наборів на результати розрахунків з використанням різних моделей сольватації

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Різні квантово-хімічні методи включно з *ab initio*, ТФГ та напівемпіричним наближенням з різними базисними наборами та моделями сольватації і супермолекулярним наближенням було використано для аналізу ефектів сольватації для полярних, слабо полярних та неполярних розчинників.

Ключові слова: ефекти сольватації, моделі сольватації, квантово-хімічні методи, *ab initio* та ТФГ методи, напівемпіричні методи

Влияние методов и базисных наборов на результаты расчетов с использованием разных моделей сольватации

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Разные квантово-химические методы, включая *ab initio*, ТФГ и полуэмпирические приближения с разными базисными наборами и моделями сольватации и супермолекулярным приближением были использованы для анализа эффектов сольватации для полярных, слабо полярных и неполярных растворителей.

Ключевые слова: эффекты сольватации, модели сольватации, квантово-химические методы, *ab initio* и ТФГ методы, полуэмпирические методы

REFERENCES

1. Tapia O., Bertrán J. *Solvent Effects and Chemical Reactivity*. (New York: Kluwer Academic Publishers, 2000).
2. Canuto S. *Solvation Effects on Molecules and Biomolecules. Computational Methods and Applications*. (Dordrecht: Springer, 2008).
3. Yaws C.L. *Thermophysical Properties of Chemicals and Hydrocarbons*. (New York: Norwich, William Andrew Inc., 2008).
4. Gun'ko V.M., Turov V.V. *Nuclear Magnetic Resonance Studies of Interfacial Phenomena*. (Boca Raton: CRC Press, 2013).
5. Chaplin M. *Water structure and science*. <http://www.lsbu.ac.uk/water/>.
6. Schleyer P.v.R. *Encyclopedia of Computational Chemistry*. (New York: John Wiley & Sons, 1998).
7. Cramer C.J. *Essentials of computational chemistry: theories and models*. (Chichester, UK: John Wiley & Sons, Ltd, 2008).
8. Dziejdz J., Helal H.H., Skylaris C.-K., Mostofi A.A., Payne M.C. Minimal parameter implicit solvent model for *ab initio* electronic-structure calculations. *EPL*. 2011. **95**(4): 43001.
9. Cramer C.J., Truhlar D.G. Implicit solvation models: Equilibria, structure, spectra, and dynamics. *Chem. Rev.* 1999. **99**(8): 2161.
10. Marenich A.V., Cramer C.J., Truhlar D.G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B*. 2009. **113**(18): 6378.

11. Marenich A.V., Cramer C.J., Truhlar D.G. Performance of SM6, SM8, and SMD on the SAMPL1 test set for the prediction of small-molecule solvation free energies. *J. Phys. Chem. B*. 2009. **113**(14): 4538.
12. Stewart J.J.P. MOPAC 2016, Colorado Springs, CO: Stewart Computational Chemistry, USA, 2017. <http://openmopac.net/>.
13. Gun'ko V.M., Turov V.V., Krupska T.V., Tsapko M.D. Interactions of human serum albumin with doxorubicin in different media. *Chem. Phys.* 2017. **483–484**: 26.
14. Gun'ko V.M., Turov V.V., Gorbik P.P. *Water at the Interfaces*. (Kyiv: Naukova Dumka, 2009).
15. Turov V.V., Gun'ko V.M. *Clustered Water and Ways of its Applications*. (Kyiv: Naukova Dumka, 2011).
16. Gun'ko V.M., Turov V.V., Bogatyrev V.M., Zarko V.I., Leboda R., Goncharuk E.V., Novza A.A., Turov A.V., Chuiko A.A. Unusual properties of water at hydrophilic/hydrophobic interfaces. *Adv. Colloid Interface Sci.* 2005. **118**(1–3): 125.
17. Gun'ko V.M., Zarko V.I., Goncharuk E.V., Andriyko L.S., Turov V.V., Nychiporuk Y.M., Leboda R., Skubiszewska-Zięba J., Gabchak A.L., Osovskii V.D., Ptushinskii Y.G., Yurchenko G.R., Mishchuk O.A., Gorbik P.P., Pissis P., Blitz J.P. TSDC spectroscopy of relaxational and interfacial phenomena. *Adv. Colloid Interface Sci.* 2007. **131**(1–2): 1.
18. Gun'ko V.M., Savina I.N., Mikhalovsky S.V. Cryogels: Morphological, structural and adsorption characterization. *Adv. Colloid Interface Sci.* 2013. **187–188**: 1.
19. Gun'ko V.M., Turov V.V., Zarko V.I., Goncharuk O.V., Pakhlov E.M., Skubiszewska-Zięba J., Blitz J.P. Interfacial phenomena at a surface of individual and complex fumed nanooxides. *Adv. Colloid Interface Sci.* 2016. **235**: 108.
20. Gun'ko V.M. Interfacial phenomena: effects of confined space and structure of adsorbents on the behavior of polar and nonpolar adsorbates at low temperatures. *Current Physical Chemistry*. 2015. **5**(2): 137.
21. Gun'ko V.M. Modeling of interfacial behavior of water and organics. *J. Theor. Comput. Chem.* 2013. **12**(07): 1350059.
22. Blitz J.P., Gun'ko V.M. Kinetics and mechanism of chemical reactions at silica surfaces. *Encyclopedia of Surface and Colloid Science*. Third Edition. (Boca Raton: Taylor & Francis, CRC Press, 2015). P. 3491.
23. Gun'ko V.M., Nasiri R., Sazhin S.S. Effects of the surroundings and conformerisation of n-dodecane molecules on evaporation/condensation processes. *J. Chem. Phys.* 2015. **142**(3): 034502.
24. Gun'ko V.M., Pakhlov E.M., Goncharuk O.V., Andriyko L.S., Marynin A.I., Ukrainets A.I., Charnas B., Skubiszewska-Zięba J., Blitz J.P. Influence of hydrophobization of fumed oxides on interactions with polar and nonpolar adsorbates. *Appl. Surf. Sci.* 2017. **423**: 855.
25. Gun'ko V.M., Turov V.V., Schur D.V., Zarko V.I., Prykhod'ko G.P., Krupska T.V., Golovan A.P., Skubiszewska-Zięba J., Charnas B., Kartel M.T. Unusual interfacial phenomena at a surface of fullerite and carbon nanotubes. *Chem. Phys.* 2015. **459**: 172.
26. Frisch M.J., Trucks G.W., Schlegel H.B. Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2013.
27. Chai J.-D., Head-Gordon M. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. *Phys. Chem. Chem. Phys.* 2008. **10**(44): 6615.
28. Yang, K. Zheng J., Zhao Y., Truhlar D.G. Tests of the RPBE, revPBE, τ -HCTHhyb, ω B97X-D, and MOHLYP density functional approximations and 29 others against representative databases for diverse bond energies and barrier heights in catalysis. *J. Chem. Phys.* 2010. **132**(16): 164117.
29. Schmidt M.W., Baldridge K.K., Boatz J.A., Elbert S.T., Gordon M.S., Jensen J.H., Koseki Sh., Matsunaga N., Nguyen K.A., Su Sh., Windus T.L., Dupuis M., Montgomery J.A. General Atomic and Molecular Electronic Structure System. *J. Comput. Chem.* 1993. **14**(11): 1347.
30. Gordon M.S., Schmidt M.W. *Theory and Applications of Computational Chemistry, the First Forty Years*. (Amsterdam: Elsevier, 2005) P. 1167.
31. Klamt A., Schüürmann G. COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. *J. Chem. Soc. Perkin Trans.* 1993. **0**: 799.
32. Zhurko G.A., Zhurko D.A. Chemcraft (version 1.8, build 523, 2017). <http://www.chemcraftprog.com>.
33. Dennington R., Keith T., Millam J. GaussView, Version 5.09, Semicem Inc., Shawnee Mission KS, 2013.
34. Kirchnerova J., Cave G.C.B. The solubility of water in low-dielectric solvents. *Can. J. Chem.* 1976. **54**(24): 3909.
35. Graziano G. Benzene solubility in water: A reassessment. *Chem. Phys. Lett.* 2006. **429**(1–3): 114.

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