

Solvation analysis of halogenated ethynyl benzenes

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Abstract

The quantum mechanical solvation analysis accounts for electric and electrostatic components of solvation by microscopic surface tension. Solvation analyses are performed for halogenated ethynyl benzene. Free energies, electrostatic interaction, dispersion energy, repulsion energy are calculated. The systematic comparison of the electrostatic contribution of the free energy of solvation is carried out from the self-consistent reaction field. The effects of cavities and the dipole moments are examined. The test set consists of sixteen solvents of various range of dielectric constant.

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1. Introduction

The quantum mechanical solvation model can predict the dependence of solvation free energy on conformation. It is important for modeling, partitioning and binding phenomena but only rarely it is available from experiments [1–3]. One of the simplest methods to perform solvation is the polarizable continuum model (PCSM). This is a more sophisticated method, which envisages a solute in a cavity formed by the union of spheres centered on each atom. The procedures are provided not only for the computation of the electrostatic interaction of the solute with the apparent surface charges, but also for the cavitation dispersion and repulsion contributions [4].

The PCSM is extended to halogen ethynyl benzenes such as 1-chloro-4-ethynyl benzene and 1-bromo-4-ethynyl benzene. These are used as starting materials for manufacturing monomers, used to form a precursor structure for application in opto electronics, micro electronics, photonic and micro electro chemical system devices. The poly carbosilanes and

amino carbene ligands are prepared by using halogenated ethynyl benzene [5].

2. Method of computation

The molecular structures are optimized by ab initio method [6]. The optimized geometries are solvated with solvent of various ranges of dielectric constants using STO-6-31G basis set. The computer program GAMESS [7] was used for this purpose.

3. Results and discussion

The standard state free energy of solvation describes the energy of interaction between molecule and solvent [8–10]. To illustrate the dependence on solute and solvent structure, the free energies of solvation calculated at STO-6-31G level of theory for a small group of solvents are classified as protic solvent, chlorinated solvent, hydrocarbons and other solvents. These solvents exhibit a broad range of dielectric constant (ϵ), index of refraction (η), macroscopic surface tension (γ), hydrogen bond acidity parameter (α) and hydrogen bond basicity parameter (β). These are listed for various solvents in Table 1.

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Table 1
Solvent descriptors

Solvent	ϵ	η	γ	α	β
<i>Protic solvents</i>					
H ₂ O	78.35	1.33	71.99	0.82	0.35
C ₂ H ₅ OH	24.85	1.36	31.62	0.37	0.48
CH ₃ OH	32.63	1.33	22.12	0.43	0.47
<i>Chlorinated solvents</i>					
CCl ₄	2.23	1.46	38.04	0.00	0.00
C ₆ H ₅ Cl	5.62	1.52	32.69	0.00	0.17
CH ₂ Cl ₂	8.93	1.37	27.33	0.10	0.05
C ₂ H ₄ Cl ₂	10.12	1.44	45.86	0.10	0.11
CHCl ₃	4.90	1.45	26.53	0.15	0.02
<i>Hydrocarbons</i>					
Heptane	1.91	1.38	28.28	0.00	0.00
C ₆ H ₆	2.27	1.50	40.62	0.00	0.14
C ₆ H ₅ CH ₃	2.37	1.50	40.20	0.00	0.14
<i>Other polar solvent</i>					
Aniline	6.89	1.59	60.62	0.26	0.41
THF	7.42	1.40	39.44	0.00	0.48
Acetone	20.49	1.36	33.77	0.04	0.49
CH ₃ NO ₂	36.56	1.38	52.58	0.06	0.31
DMSO	46.83	1.42	61.78	0.00	0.88

The electrostatic contribution to free energy of solvation depends on the dielectric constant of the solvent. By comparing the electrostatic contribution listed in Tables 2 and 3 with dielectric constants of the respective solvent. We observed that the electrostatic interaction increases with the increase of the dielectric constant.

Tables 2 and 3 show how different characteristics of each solvent affect the free energy of solvation of the two selected

Table 2
Energies for 1-chloro-4-ethynyl benzene (kJ/mol)

Solvent	Electrostatic interaction	Dispersion energy	Repulsion energy	Free energy
<i>Protic solvent</i>				
H ₂ O	-9.58	-24.47	8.04	-2003108.24
C ₂ H ₅ OH	-19.99	-43.84	48.40	-2008756.47
CH ₃ OH	-20.05	-43.93	10.13	-2008797.18
<i>Chlorinated solvents</i>				
CCl ₄	-8.61	-43.97	15.77	-2008778.90
C ₆ H ₅ Cl	-15.28	-43.93	14.52	-2008775.59
CH ₂ Cl ₂	-17.29	-43.96	16.77	-2008788.11
C ₂ H ₄ Cl ₂	-17.94	-43.85	36.02	-2008762.24
CHCl ₃	-33.81	-28.88	-1304.11	-2001817.68
<i>Hydrocarbons</i>				
Heptane	-7.19	-43.97	12.38	-2008787.43
C ₆ H ₆	-8.71	-43.97	13.80	-2008775.55
C ₆ H ₅ CH ₃	-9.24	-43.93	26.94	-2008763.71
<i>Other polar solvent</i>				
Aniline	-16.27	-43.93	17.53	-2008744.04
THF	-16.65	-43.93	15.18	-2008575.72
Acetone	-19.62	-43.84	38.61	-2008768.39
CH ₃ NO ₂	-20.29	-43.89	18.15	-2008777.81
DMSO	-20.62	-43.84	39.91	-2008748.02

Table 3
Energies for 1-bromo-4-ethynyl benzene (kJ/mol)

Solvent	Electrostatic interaction	Dispersion energy	Repulsion energy	Free energy
<i>Protic solvent</i>				
H ₂ O	-21.34	-43.97	17.95	-7549371
C ₂ H ₅ OH	-20.18	-43.91	47.93	-7554413
CH ₃ OH	-20.22	-44.04	10.01	-7554453
<i>Chlorinated solvents</i>				
CCl ₄	-8.66	-44.04	15.57	-7554435
C ₆ H ₅ Cl	-15.36	-44.04	14.36	-7554431
CH ₂ Cl ₂	-17.41	-44.04	14.77	-7554444
C ₂ H ₄ Cl ₂	-18.12	-43.96	35.62	-7554418
CHCl ₃	-27.26	-28.68	-1112.01	-7546721
<i>Hydrocarbons</i>				
Heptane	-7.18	-44.04	12.31	-7554442
C ₆ H ₆	-8.71	-44.04	13.69	-7554431
C ₆ H ₅ CH ₃	-9.25	-44.04	13.77	-7554433
<i>Other polar solvent</i>				
Aniline	-16.41	-44.04	17.33	-7554399
THF	-16.78	-44.04	14.98	-7554225
Acetone	-19.84	-43.96	38.22	-7554425
CH ₃ NO ₂	-20.47	-44.00	17.96	-7554444
DMSO	-20.85	-43.96	39.48	-7554404

molecules, 1-chloro-4-ethynyl benzene and 1-bromo-4-ethynyl benzene. For example, the free energies in water, aniline and DMSO are unfavorable, since the macroscopic surface tensions of these solvents are high and it needs energy to make a surface in the solvent. Therefore these solvents with solute will have least free energy [11].

The free energies of chlorobenzene and benzene of similar range of refraction index and different dielectric constant are the same. This may be due to the hydrogen bond accepting ability of the solute and solvent interaction.

For THF, the refraction index is smaller than that of benzene. In addition, the hydrogen bond basicity parameter for THF is larger than that of benzene. The free energies of solvation of 1-chloro-4-ethynyl benzene and 1-bromo-4-ethynyl benzene in THF are less favorable than the corresponding free energy of solvation in benzene. The molecules afford more favorable electrostatic interactions in THF than in benzene, because of the high hydrogen bond basicity parameter. In 1,2-dichloroethane and acetone, the refraction index is similar but the free energy of molecules with 1,2-dichloroethane is more favorable than with acetone. But electrostatic interaction is high for molecules with acetone because the hydrogen bond basicity parameter of acetone is high. These results can be attributed to a balance between the more favorable solute–solvent dispersion interaction in solvents benzene and acetone and their hydrogen bond accepting ability. Tables 2 and 3 show that the free energy of solvation of molecules with chloroform is not as favorable as it is in benzene, for the same reason.

For water, the free energies of solvation of 1-chloro-4-ethynyl benzene and 1-bromo-4-ethynyl benzene are significantly different due to the hydrophobic effect. Therefore in water, the solvation free energy is least favorable out of the solvents listed.

Table 4
Cavitation enthalpies for 1-chloro-4-ethynyl benzene (kJ/mol)

Solvent	Pierotti	Sinanglu
<i>Protic solvent</i>		
H ₂ O	64.69	69.12
C ₂ H ₅ OH	44.72	24.46
CH ₃ OH	44.59	24.86
<i>Chlorinated solvents</i>		
CCl ₄	44.29	18.82
C ₆ H ₅ Cl	52.25	10.69
CH ₂ Cl ₂	44.76	14.53
C ₂ H ₅ Cl ₂	48.01	14.11
CHCl ₃	42.96	43.52
<i>Hydrocarbons</i>		
Heptane	38.33	13.68
C ₆ H ₆	48.69	20.52
C ₆ H ₅ CH ₃	47.42	20.35
<i>Other polar solvent</i>		
Aniline	76.09	38.75
THF	224.99	7.55
Acetone	42.46	11.19
CH ₃ NO ₂	72.53	31.17
DMSO	58.08	19.98

The cavitation enthalpies in Tables 4 and 5 obtained in the present calculations are expected to have reasonable accuracy from the formulas given by Sinanglu and Pierotti [12,13]. The cavitation enthalpies calculated by two methods give two different results. This is because the calculation based on the macroscopic surface formula is not compatible with the value obtained by Ben Naim [8,14]. The trend is similar. Among all the solvents, THF provides the highest positive values for both molecules. Thus the solvation of halo ethynyl benzene in THF

Table 5
Cavitation enthalpies for 1-bromo-4-ethynyl benzene (kJ/mol)

Solvent	Pierotti	Sinanglu
<i>Protic solvent</i>		
H ₂ O	66.95	71.73
C ₂ H ₅ OH	46.22	25.24
CH ₃ OH	46.09	25.67
<i>Chlorinated solvents</i>		
CCl ₄	45.76	19.76
C ₆ H ₅ Cl	53.97	11.86
CH ₂ Cl ₂	46.25	15.54
C ₂ H ₄ Cl ₂	49.61	15.23
CHCl ₃	44.36	13.08
<i>Hydrocarbons</i>		
Heptane	39.56	14.36
C ₆ H ₆	50.30	21.54
C ₆ H ₅ CH ₃	49.02	21.35
<i>Other polar solvent</i>		
ANILINE	18.81	9.62
THF	233.20	8.49
ACETONE	10.48	2.86
CH ₃ NO ₂	54.47	32.48
DMSO	60.08	21.52

is more endothermic than in other solvents in the present study. In the case of protic solvent, this value is more positive in aqueous solution than in methanol and ethanol, because of weaker interaction in aqueous solution than in other polar solvents.

Dipole moments are more sensitive to details of the model, because the non-electrostatic effects are not treated self consistently [15]. The dipole moments are calculated based on the wave function. The changes in the dipole moments are based on the dielectric behaviour of the solvent. The value of the dipole moments increases with the increase in dielectric constant of both molecules. But in the case of protic solvent, there is zigzag trend in dipole moment with dielectric constant. This may be due to the hydrogen bonding nature of the solvents. However, the solvation effect leads to a systematic increase in the dipole moment similar to empirical and semi-empirical calculations of other similar types of organic compounds [16,17] (Table 6).

4. Conclusion

We have presented the PCSM solvation analysis for 1-chloro-4-ethynyl benzene and 1-bromo-4-ethynyl benzene to balance the electrostatic and solvation effect in a systematic manner. The macroscopic surface tension systematically accounts for deviations between electrostatic contributions and free energies of solvation. The PCSM model for halogenated ethynyl benzene with organic solvents lends itself to specific parameterization for more complicated condensed phases. We anticipate that several of these latter features will make useful tools in polymer preparation and its development.

Table 6
Induced dipole moments for 1-chloro-4-ethynyl benzene and 1-bromo-4-ethynyl benzene (Debye)

Solvent	1-chloro-4-ethynyl benzene	1-bromo-4-ethynyl benzene
<i>Protic solvent</i>		
H ₂ O	2.15	2.50
C ₂ H ₅ OH	2.45	2.49
CH ₃ OH	2.46	2.47
<i>Chlorinated solvents</i>		
CCl ₄	2.18	2.09
C ₆ H ₅ Cl	2.35	2.33
CH ₂ Cl ₂	2.39	2.39
C ₂ H ₅ Cl ₂	2.41	2.42
CHCl ₃	3.20	2.11
<i>Hydrocarbons</i>		
Heptane	2.14	2.03
C ₆ H ₆	2.18	2.09
C ₆ H ₅ CH ₃	2.20	2.11
<i>Other polar solvent</i>		
Aniline	2.37	2.36
THF	2.38	2.37
Acetone	2.45	2.47
CH ₃ NO ₂	2.46	2.48
DMSO	2.47	2.50

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