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Bioavailability of polycyclic aromatic hydrocarbons in sediments : experiments and modelling

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Publication date
2009

[Link to publication](#)

Monte Carlo simulation of the energies of vaporization, hydration, solution and cavity formation of aromatic hydrocarbons

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Abstract

Electronic atomic charges for aromatic compounds and hydroxyl hydrogen bonded groups compatible with the Amber99a force field were derived by scaling PM3 charges to the experimental values of the energies of vaporization of benzene and water at 298.15 K. A switched summation cut off (9/5 Å outer/inner summation limits) was used. Energies of gas and liquid phases were calculated by Monte Carlo simulations in a canonical ensemble and were compared with Geometrical Optimization results. PM3 charges had to be scaled down or up by the factors of 0.9502 ± 0.0099 and 1.8737 ± 0.0093 for benzene and water, respectively. Geometrical Optimization results were different and could not describe differences between the gas and liquid with respect to contributions of degrees of freedom to vibrational energy.

Scaling factors led to a supercooled energy of vaporization of fluoranthene of 93.18 ± 0.17 kJ/mol, energies of hydration (-37.61 ± 23.22 and -57.99 ± 23.85 kJ/mol) and aqueous solution (-6.49 ± 23.22 and 35.19 ± 24.94 kJ/mol) of benzene and fluoranthene, respectively, all equal to their experimental values within error ranges. The energy of the solute in its aquatic environment could be calculated with substantial lower inaccuracy than the total energy of the solution.

The gas plus liquid benzene and fluoranthene phases and the water gas phase showed no or only minor deviations from harmonic behaviour of the atomic vibrations. The latter did not hold for the liquid water phase. Intermolecular energy of water molecules in the benzene- and fluoranthene-water system and in the pure liquid differed substantially as expressed into positive energies of cavity formation of 27.49 ± 24.27 and 82.68 ± 23.85 kJ/mol, respectively. It turned out that insignificant differences are present between the intramolecular vibrational energies in the liquid phases and only minor differences between liquid and gas.

Introduction

Molecular mechanics calculations of energies and free energies for equilibrium partitioning of organic compounds between gas and liquid phases require parameters for the intramolecular stretch-, bending- and torsional potential energy and for the nonbonded van der Waals and electrostatic interaction within and between molecules. The latter may include hydrogen bond energy and require separate derivation. Out of the many (nonelectrostatic) force fields available in the literature [1], the Amber99a force field [2] is a well established one. Several methods are available for finding electronic atomic charges, the main parameters for electrostatic interactions [2]. Quantum mechanical calculation may provide, easily as in the PM3 method [3], Mulliken atomic charges in isolated molecules. In any case, charges have to be scaled in order to obtain charges in condensed systems, which are compatible with the force field used and highly accurate in view of the calculation of energies and free energies of partitioning as we aim at. Moreover, a consistent method of summation cut off should be used for this purpose such as a switched summation cut off with sufficiently large range between the inner outer summation limits [4]. Accurately determined experimental values of the energy of vaporization are often used for the scaling required [5].

The calculation of free energies, and the partitioning constants directly connected to it, requires the statistical thermodynamics of Monte Carlo (MC), Molecular Dynamics (MD) or other methods [6]. In addition, energies may be calculated using Geometrical Optimization (GO). Calculation of energy may take place using a variety of ensembles, of which the canonical ensemble (at a constant number of particles N, volume V, and temperature T) is especially useful in combination with MC. The latter easily warrants constant T, although it requires the knowledge of V and a special treatment of the constancy of N in the method we will employ. GO does not give insight into temperature effects, but is carried out relatively easily.

Aromatic hydrocarbons are theoretically simple in view of their rigid structure, which suggest harmonic atomic vibrations to be of special interest and the presence of minor variation of intramolecular energy over different phases. In addition, they possess a low number of different atom types in the force field. The same holds for water having no torsional movement of atoms and no intramolecular nonbonded van der Waals and electrostatic interaction in the TIP3P model used. These compounds are of special relevance in environmental chemistry, thus requiring the knowledge of partitioning constants such as vapour pressure, aqueous solubility, Henry's law constants and sorption to dissolved organic matter [7]. The pertinent energies (enthalpies) are of importance in view of the temperature dependence of these properties.

Here electronic atomic charges for aromatic compounds and hydroxy (hydrogen bonded) groups compatible to the Amber99a force field and using a consistent summation cut off will be derived by scaling PM3 charges to the experimental values of the energies of vaporization of benzene and water at 298.15 K, which are accurately known. Energies of gas and liquid phases will be calculated by MC simulations in a canonical ensemble and will be compared with GO results. Results will be validated by the calculation of the supercooled energy of vaporization of

fluoranthene and of the energies of hydration, solution and cavity formation of benzene and fluoranthene, all at 298.15 K. Molecular and phase structural data such as radial distribution functions will not be employed here in view of the intended future use of the force field and charges for (free) energy calculations only.

Theory and method

Force field parameters

The potential energy E of a certain gaseous or liquid configuration [2, 8], see Eq. (1), includes contributions of intramolecular stretching of bonds r, bending of angles θ, torsion of (proper or improper) dihedral angles φ and intra- and intermolecular nonbonded interactions between atoms of the van der Waals and electrostatic type. r_o, θ_o, and φ_o are reference geometrical parameters for the unstrained structure. k_r, k_θ, and $V_n/2$ are vibrational force constants and n-fold torsional potential barriers, respectively. R refers to nonbonded distances and D to the dielectric constant. A and B are van der Waals repulsive and attractive parameters, respectively, and q are atomic point charges. The latter are also used for hydrogen-bonding in water. We applied a constant dielectric of $D = 1$ and scaling of close (1,4) intramolecular van der Waals and electrostatic nonbonded contributions by a factor of 0.5. Moreover, a switched summation cut off was employed with sufficiently large range between the inner (5 Å) and outer (9 Å) summation limits [4] in order to prevent artificial motion as found for smaller switch ranges in proteins.

$$E = \Sigma_{\text{bonds},i}\, k_{r,i}\, (r_i - r_{o,i})^2 + \Sigma_{\text{angles},j}\, k_{\theta,j}\, (\theta_j - \theta_{o,j})^2 + \Sigma_{\text{(improper)dihedrals},k}\, (V_{n,k}/2)\, [1+\cos(n_{k.}\varphi - \varphi_{o,k})]$$
$$+ \Sigma_{\text{nonbonded atom types},m,m'}\, [A_{m,m'}/R_{m,m'}{}^{12} - B_{m,m'}/R_{m,m'}{}^{6}]$$
$$+ \Sigma_{\text{nonbonded atoms},n,n'}\, [q_n.q_{n'}/(D.R_{n,n'})] \tag{1}$$

Note that in this energy model no molecular or group rotations are included explicitly and that R^* and ε (the position and depth of the minimum in the potential curve between two similar atoms), are directly related to A and B via $A = \varepsilon R^{*12}$ and $B = 2\ \varepsilon R^{*6}$. R^* and ε for pairs of different atoms i, j were calculated from single atom types according to $R^*_{ij} = R^*_i + R^*_j$ and $\varepsilon_{ij} = (\varepsilon_i\ \varepsilon_j)^{1/2}$. Kinetic energy difference between condensed phases is supposed to be zero. The Amber99a force field parameters used are included in Table 1.

Table 1. Amber99a parameters [2, 9, 10].

Van der Waals nonbonded	R^* (Å)	ε (kJ/mol)	Model
C = Aromatic carbon	1.9080	0.3598	
HA = Aromatic hydrogen	1.4590	0.0628	
HW = Water hydrogen	0.0000	0.0000	
OW = Water oxygen	1.7683	0.6360	
Bond stretch	k_r (kJ/mol.Å^2)	r_o (Å)	
C-C	1962	1.400	
C-HA	1536	1.080	
OW-HW	2314	0.9572	TIP3P model
HW-HW	2314	1.5136	TIP3P model
Angle bending	k_θ (kJ/mol.rad^2)	θ_o (degree)	
C-C-C	264	120.00	
C-C-HA	146	120.00	
HW-OW-HW	418	104.52	TIP3P model
Angle torsion	$V_n/2$ (kJ/mol)	φ_o (degree)	n
-C-C-; ** = C or HA	60.70	180.0	2

PM3 electronic atomic charges and molecular geometries

After sketching of 2D models of water, benzene and fluoranthene 3D model building was applied. The geometries obtained were optimized in PM3 (restricted Hartree Fock, convergence limit = 0.00001, iteration limit = 50, accelerated convergence, Polak-Ribière optimization with a gradient criteria of 0.04 kJ/mol). The charges obtained are included in Table 2. Atomic numbers are depicted in Fig. 1.
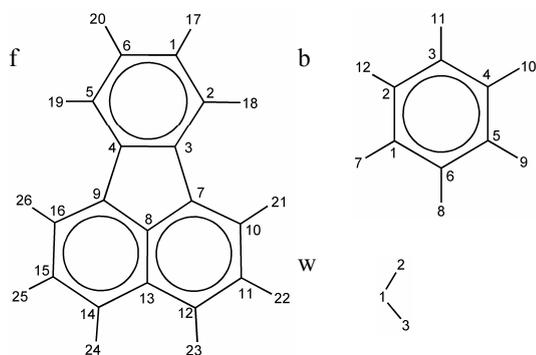

Figure 1. Atomic numbering in fluoranthene (f), benzene (b) and water (w).

Table 2. PM3 atomic charges of water, benzene and fluoranthene.

Atom no*	Water	Benzene	Fluoranthene	Atom no*	Fluoranthene
1	-0.3586	-0.1021	-0.1020	14	-0.0671
2	0.1793	-0.1021	-0.0751	15	-0.1108
3	0.1793	-0.1021	-0.0317	16	-0.0512
4		-0.1021	-0.0317	17	0.1020
5		-0.1021	-0.0751	18	0.1072
6		-0.1021	-0.1020	19	0.1072
7		0.1021	-0.0295	20	0.1020
8		0.1021	-0.0743	21	0.1061
9		0.1021	-0.0295	22	0.1011
10		0.1021	-0.0512	23	0.1037
11		0.1021	-0.1108	24	0.1038
12		0.1021	-0.0671	25	0.1011
13			-0.0311	26	0.1061

*See Fig. 1.

Experimental values of box volume and box contents

A canonical ensemble approach requires the constancy of volume V with a known value, in our method, leading to a known value of the edge a of the cubic box employed. This box will include a number of molecules N which corresponds to the density d of the liquid at 298.15 K. It was chosen such that a box edge of at least 18 Å was obtained in order to fulfil the requirement of two times the outer/inner 9/5 Å switched summation cut offs. In Table 3, the required data have been included.

Table 3. Experimental data of water, benzene and fluoranthene at 298.15 K.

Property	Water	Benzene	Fluoranthene
Molecular formula	H_2O	C_6H_6	$C_{16}H_{10}$
Molecular weight MW (g/mol)	18.01528	78.1134	202.26
Molar volume v (cm^3/mol)	18.0713 ± 0.0018^a	89.487 ± 0.010^b	172.43 ± 5.1^c
N	216	64	27
a (Å)^d	18.6451 ± 0.0006	21.1867 ± 0.0008	19.7732 ± 0.19
Z^e		5	10

^{a} Calculated from $d(25°C, l) = 0.9969 \pm 0.0001$ g/cm^3 [11] via $v = MW/d$;
^{b} Calculated from $d(25°C, l) = 0.8729 \pm 0.0001$ g/cm^3 [11] via $v = MW/d$;
^{c} Calculated from $d(2°C, s) = 1.252 \pm 0.0005$ g/cm^3 [11] via $v(T,s/l) = MW/d(T, s/l)$; $v(T°C, s) = v(25°C, s) [1 + 0.00025(T-25)]$ with $0.00025=$ thermal expansion coefficient solid (degree^{-1}); $v(25°C, l) = (13.051 \pm 2.654) + (0.98093 \pm 0.02697) v(25°C, s)$ [12];
^{d} Calculated via $a = (N.v/0.60221)^{1/3}$;
^{e} Via $Z =$ integer closest to v/v (water).

Building of phase structures and Molecular Mechanics procedures

I. Initial phase structures and GO

Where required, GO (Polak-Ribière optimization, convergence limit = 0.004 kJ/mol) using Amber99a force field parameters was carried out. After introduction of (scaled) PM3 charges, pure compound gas phases were built by GO applied to the (PM3) molecular geometries obtained before and by introduction of $N = 1$ molecule into a cubic box with the pure liquid edges a of Table 3. Pure liquid water was constructed by introduction of proper charges and $N = 216$ disordered molecules into the default box of the software [9] with an edge a of Table 3. For

benzene and fluoranthene liquids, gas phase molecules were placed into the box at equal distances and with orientations of their principal moments of inertia axes parallel to the box diagonals. N and a values were those of Table 3. This was followed by GO. The solution of benzene and fluoranthene in water was constructed via introduction of N-Z default water molecules around a gas phase solute molecule into a box with liquid water dimension, all molecules with charges obtained after scaling as described below. GO was applied to the structure obtained (first the water molecules only and then all molecules). Thus it was assumed that no substantial molar volume change of water and fluoranthene took place after mixing (the molar volume of the solute is around Z times that of water, see Table 3). Gas, pure liquid and solution phase GO structures obtained in this way were the initial structures used for further preoptimizing or final MD or MC runs.

II. MD
Short MD runs in threefold cyclic annealing were carried out with heating h, run r and cooling c times of 8/20/8 ps, respectively, a time step dt of 0.0008 ps, $T = 298.15$ K, $\Delta T = 30$ K and a Berendsen [13] temperature bath coupling constant τ of 3.2. The latter in order to restrict average temperature to $T = 298.15 \pm 1$ K. This was done starting with the GO structures described above. Each of the three short runs was treated with a final GO and the GO structure having the lowest potential energy was used as the input for a subsequent long MD or MC. In some liquid phase cases, cyclic annealing resulted into highly ordered structures with energies several hundreds of kJ/mol lower than expected. Then, the next higher result was adopted. A long single MD run employed the same conditions but with $h/r/c$ = 8/600/0 ps or longer run times.

III. MC
Gas phase Monte Carlo (MC) simulation employed $r = 5 \times 10^6$ steps, a step size of 0.05 Å leading to an acceptance ratio of around 0.5 and $T = 298.15$ K. Data were collected after periods of 100 steps leading to 50.000 data separated in 10 groups of 5.000 data. When mean group values of potential energies became constant within around 0.2 kJ/mol, which took place already in the first group, equilibrium was considered to be established. From this group on all potential energy data were separated into two large groups of which the mean values were calculated. The average of these two mean values and its standard deviation was considered as the final result of the MC run. Also after the long MC run a GO run took place.

A short ($r = 5.000$) MC run with the same settings was applied to some liquid phases as a preoptimization. Long MC runs for the liquid phase employed the same settings and $r \geq 120.000$ steps. At least 60.000 potential energy data were collected and grouped into at least 12 groups of 5.000 data. When mean group values of potential energies became constant within around 0.2 Z kJ/mol, which took place at the fifth group or earlier, equilibrium was considered to be established. Thereafter the final result was obtained in a way similar to that of the gas phase runs.

Scaling of charges

In order to find the scaling factor, $s = q/q_{PM3}$, of PM3 charges for water and benzene it was assumed that in the region of interest the energy of vaporization ΔE_{vap} is linearly dependent on s^2, see Eqs (2), (3) and (4). Thus it was assumed that all variation is caused by the electrostatic interactions of Eq. (1), both in the gas (*gas*) and the liquid (*liq*) phase.

$$E_{gas}(s) = B_{0,gas} + B_{1,gas}.s^2 \tag{2}$$
$$E_{liq}(s) = B_{0,liq} + B_{1,liq}.s^2 \tag{3}$$
$$\Delta E_{vap}(s) = \Delta B_0 + \Delta B_1.s^2 \tag{4}$$

We also applied a GO approach. Considering the *B*–parameters as independent of *s*, for several *s*-values the molar energies $E_{gas}(s)$, $E_{liq}(s)$ and $\Delta E_{vap}(s)$ were calculated and the *B*-parameters fitted. Once they were known the substitution of the experimental value of ΔE_{vap} in Eq. (4) led to the *s*-value wanted.

Validation of scaled charges and the energy of cavity formation

Using the *s* value for the *q*'s in Eq. (1) derived from benzene, the molar energies of the gas and liquid phases and their differences $\Delta E_{vap} = E_{gas} - E_{liq}$ of fluoranthene were calculated in the MC and GO approach. They were compared with experimental values as a validation of the usefulness of *s* for other aromatic hydrocarbons than benzene. Together with the *s* value derived from water, the energies of the solute (*i* = benzene or fluoranthene) gas phase $E_{i,gas}$, and of the solution in water (*w*) $E_{i,w}$, were calculated in the MC approach. From these and the energies of vaporization, the energies of hydration ΔE_{hyd} and of solution ΔE_{sol} were calculated according to Eqs (5), (6) and (7) and compared with experimental values of Table 7.

$$\Delta E_{vap} = E_{i,gas} - E_{i,liq} \tag{5}$$
$$\Delta E_{hyd} = E_{i,w} - E_{i,gas} - (216\text{-}Z).E_{w,liq} \tag{6}$$
$$\Delta E_{sol} = E_{i,w} - E_{i,liq} - (216\text{-}Z).E_{w,liq} = \Delta E_{vap} + \Delta E_{hyd} \tag{7}$$

Note that Eqs (6) and (7) include a contribution of $(216\text{-}Z).E_{w,liq}$ and not of $216.E_{w,liq}$ required because of the loss of $Z = 5$ or 10 water molecules in the box on substitution of the solute molecule. The thermodynamic background of these equations makes use of the phase equilibrium condition of equality of the thermodynamical potential, $\mu_i = (\delta F/\delta n_i)_{V,T,N} = (\delta E/\delta n_i)_{V,T,N} - T(\delta S/\delta n_i)_{V,T,N}$, of a compound *i*, in both phases. It is a function of the derivative of free energy *F*, total energy *E*, and entropy *S* to the number of moles of compound *i* n_i, at constant volume *V*, temperature *T*, and total number of particles or moles *N* [14]. The partitioning properties of Eqs (5), (6), and (7) refer to differences between the energy part of reference thermodynamic potentials; for a solute in solution given in the Henry law convention [15]. Thus $(\delta E/\delta n_i)_{V,T,N}$ of a solution is approximated by the difference of the energy of a box

filled with one solute molecule plus 216-*Z* water molecules and (216-*Z*)/216 times the energy of the box filled with 216 water molecules only plus the energy of an isolated solute molecule.

When we know the molar energy of pure liquid water $E_{w,liq}$ we can also find the energy loss upon creation of a cavity for this substitution. Therefore we have to calculate the contributions to the total potential energy $E_{i,w}$ given in Eqs (8), (9), (10), (11) and (12).

$$E_{i,w} \quad = E_{i,\text{intra}} + (216\text{-}Z).E_{w,\text{intra}} + E_{w,w,\text{inter}} \quad + E_{i,w,\text{inter}} \tag{8}$$

$$E_{\underline{i},w} \quad = E_{i,\text{intra}} \qquad\qquad\qquad\qquad\qquad\quad + E_{i,w,\text{inter}} \tag{9}$$

$$E_{i,\underline{w}} \quad = \qquad\quad (216\text{-}Z).E_{w,\text{intra}} + E_{w,w,\text{inter}} \quad + E_{i,w,\text{inter}} \tag{10}$$

$$E_{w,w} \quad = \qquad\quad (216\text{-}Z).E_{w,\text{intra}} + E_{w,w,\text{inter}} \qquad\qquad = E_{i,w} - E_{\underline{i},w} \tag{11}$$

$$\Delta E_{\text{cav}} = E_{w,w} - E_{w,w,o} = E_{i,w} - E_{\underline{i},w} - (216\text{-}Z).E_{w,liq} \tag{12}$$

The contributions are: $E_{\underline{i},w}$ = intramolecular solute energy $E_{i,\text{intra}}$ plus the interaction of the solute with the surrounding solvent molecules $E_{i,w,\text{inter}}$; $E_{i,\underline{w}}$ = intramolecular energy of all solvent molecules (216-*Z*).$E_{w,\text{intra}}$ plus the interaction between the solvent molecules themselves $E_{w,w,\text{inter}}$ and again the interaction between all solvent molecules and the solute. $E_{w,w}$ = net intra plus intermolecular energy of the 216-*Z* solvent molecules in the solution. In the pure solvent 216-*Z* solvent molecules will have an energy of $E_{w,w,o} = (216\text{-}Z).E_{w,liq}$. The cavity formation energy ΔE_{cav} equals the difference between $E_{w,w}$ and $E_{w,w,o}$ in Eq. (12). It will be positive (a loss) because solvent molecules will be separated and will reorganize upon substitution of a solute molecule.

Hardware and software
All calculations were carried out on a PC with Pentium IV 3.2 GHz processor using Hyperchem 7 software [9]. This software also includes the complete Amber99a force field parameter lists, PM3 quantum mechanical options and references to the methods applied. In order to calculate energies connected to cavity formation a script was written to be used during snapshot play back runs of 6000 snapshots. Regression and other statistical parameters were calculated by S-Plus software [16].

Calculation and results

Scaling of PM3 atomic charges

I. Aromatic hydrocarbon atoms in benzene

Starting with the initial structure, found as described above, directly gas phase long MC runs were carried out at four values of the scaling factor s. The same was done for the liquid phase. Here, however, the $s = 1.0000$ long MC run was preceded by cyclic annealed short MD runs and a long MD run. The lowest energy GO structure obtained from this MD run was also used for the other s value MC runs. Results are included in Table 4 together with lowest GO energies and $E_{MC\text{-}GO}/\tfrac{1}{2}RT$, a measure of the deviation from harmonic vibration.

Table 4. MC and GO molar potential energies of gas (*gas*) phase and liquid (*liq*) phase benzene at 298.15 K and at several values of the scaling factor, s. At $s = 1.0000$, $q_{H,PM3} = 0.102113\ e = -q_{C,PM3}$. Energies in kJ/mol.

s^2	q_H	$E_{GO,gas}$	$E_{MC,gas}$	$E_{MC\text{-}GO,gas}/$ $\tfrac{1}{2}RT$	$E_{GO,liq}$	$E_{MC,liq}$	$E_{MC\text{-}GO,liq}/$ $\tfrac{1}{2}RT$
1.0000	0.1021	19.795	57.053 ± 0.017	30.06	-20.159	24.292 ± 0.063	35.87
0.8955	*0.0966*	*19.133*	*56.384 ± 0.017*	*30.06*	*-19.326*	*25.246 ± 0.008*	*35.97*
0.3999	0.0646	15.991	53.300 ± 0.008	30.10	-15.397	28.652 ± 0.013	35.54
0.3448	0.0600	15.644	52.936 ± 0.021	30.09	-15.071	29.167 ± 0.033	35.70

Using Eqs (2), (3) and (4) in the MC approach and the experimental value of $\Delta E_{vap,exp} = 31.355 \pm 0.071$ kJ/mol (see Table 7) the following results were derived from these energies (R = correlation coefficient and SER = standard error of regression).

$$E_{gas,MC}\ (s) = (50.785 \pm 0.017) + (6.2601 \pm 0.0222).s^2 \tag{13}$$
$$R = 1.0000;\ SER = 0.013$$
$$E_{liq,MC}\ (s) = (31.6156 \pm 0.1431) - (7.2366 \pm 0.1983).s^2 \tag{14}$$
$$R = -0.9992;\ SER = 0.117$$
$$\Delta E_{vap,MC}\ (s) = (19.1698 \pm 0.1439) + (13.4967 \pm 0.1996).s^2 \tag{15}$$
$$SER = 0.13$$
$$s_{MC} = 0.9502 \pm 0.0099;\ q_{H,MC} = 0.0967 \pm 0.0007$$

With $s^2 = 0.8955$ a $\Delta E_{vap,MC}$ of $56.384 - 25.246 = 31.137$ kJ/mol was calculated according to the italics line of Table 4. This is only 0.218 kJ/mol lower than the experimental value of 31.355 kJ/mol, and close to the latter in view of the calculation error of method (0.13 kJ/mol). Thus the results of the italics line include an internal validation of the method.

The benzene molecule contains 12 atoms, leading to 36 degrees of freedom. In a harmonic approach of the vibrations each degree of freedom would contribute $\tfrac{1}{2}RT$ (1.2393 kJ/mol at 298.15 K) in the MC approach in addition to the vibrationless GO energy. From Table 4 it can be seen that in the liquid phase almost all 36 (35.54 – 35.97) degrees are used for the vibrations, whereas in the gas phase 30 (30.06 – 30.10) are used. In the latter phase six degrees are used for

the translation and rotation of the molecule as a whole, leading to a contribution to the kinetic energy.

Employing the GO values of Table 4 would have given a quite different scaling factor of s^2 ≈ 0.3999 leading to $\Delta E_{vap,GO}$ of 15.991 – (-15.397) = 31.388 kJ/mol. However, the GO approach does not include the atomic vibration in the gas nor in the liquid phase and, as a consequence, cannot describe the difference in degrees of freedom between gas and liquid phase. Using the MC derived scaling factor for the GO values of the italics line results into a quite erroneous value of $\Delta E_{vap,GO}$ of 19.133 – (-19.326) = 38.459 kJ/mol.

II. Hydrogen bonded hydroxy atoms in water

The water molecule contains three atoms. In the TIP3P model only bond stretch and bending is included and no torsions and nonbonded van der Waals and electrostatic energies. Six out of the nine degrees of freedom will be used for the rotation and translation of the molecule as a whole in the gas phase. Thus an exact value of $3\times\frac{1}{2}RT$ = 3.7179 kJ/mol should be the value of MC approach. This was confirmed by a subsequent long run MC calculation, leading to 3.7062 ± 0.0218 kJ/mol. We used the theoretical value of 3.7179 kJ/mol, independent of charge, for further calculations. The GO value, having no strain energy, was 0.000 kJ/mol. Starting with the initial structure, found as described before, for the liquid phase short MC runs at values of $q_O = -2q_H = -0.834$ e and lower lead to a trial value of $q_O = -2q_H = -0.706$ e. This GO structure became the starting point of four subsequent long MC runs with varying $s^2 = (q_O/q_{O,PM3})^2$ and two additional runs at $s^2 = 3.5145$. Results are included in Table 5. Also lowest GO energies are included again with $E_{MC-GO}/\frac{1}{2}RT$, a measure of the deviation from harmonic vibration.

Table 5. MC and GO molar potential energies of gas (*gas*) phase and liquid (*liq*) phase water at 298.15 K and at several values of q_O and s^2. At s =1.0000, $q_{O,PM3}$ = 0.358573 e = - $2q_{H,PM3}$. Energies in kJ/mol.

s^2	q_O	$E_{GO,gas}$	$E_{MC,gas}$	$E_{MC-GO,gas}/$ $\frac{1}{2}RT$	$E_{GO,liq}$	$E_{MC,liq}$ ±	$E_{MC-GO,liq}/$ $\frac{1}{2}RT$
3.2860	-0.6500	0.000	3.7179	3.00	-47.409	-34.095 ± 0.042	10.74
3.5145	*-0.6722*	*0.000*	*3.7179*	*3.00*	*-51.388*	*-37.756 ± 0.000*	*11.00*
3.5145	-0.6722	0.000	3.7179	3.00	-51.388	-37.961 ± 0.192	10.83
3.5145	-0.6722	0.000	3.7179	3.00	-51.388	-37.706 ± 0.142	11.04
3.5379	-0.6744	0.000	3.7179	3.00	-51.476	-38.233 ± 0.004	10.69
3.8760	-0.7060	0.000	3.7179	3.00	-56.877	-43.965 ± 0.025	10.42

Using Eqs (2), (3) and (4) in the MC approach and the experimental value of $\Delta E_{vap,exp} = 41.514 \pm 0.071$ kJ/mol of Table 7 the following results were derived from Table 5. Of the $s^2 = 3.5145$ runs only the italics value run was employed.

$$E_{gas,MC}\,(s^2) = 3.7179 \tag{16}$$
$$E_{liq,MC}\,(s^2) = (21.0857 \pm 0.7895) - (16.7711 \pm 0.2218).s^2 \tag{17}$$
$$R = 0.9998;\ SER = 0.092$$
$$\Delta E_{vap,MC}\,(s^2) = (-17.3678 \pm 0.7895) + (16.7711 \pm 0.2218).s^2 \tag{18}$$
$$SER = 0.092$$
$$s_{MC} = 1.8737 \pm 0.0093;\ q_{O,MC} = -0.6719 \pm 0.0033$$

From Table 5 at $s^2 = 3.5145$ and $q_O = -0.6722$ (italics values) a $\Delta E_{vap,MC} = 3.7179 - (-37.756) = 41.476$ kJ/mol was calculated, which is - within calculation and experimental errors - equal to $\Delta E_{vap,exp} = 41.514$ kJ/mol. Using the average of the three $s^2 = 3.5145$ runs leads to a $\Delta E_{vap,MC} = 3.7179 - (-37.807) = 41.526$ kJ/mol even closer to the experimental value. The three $s^2 = 3.5145$ runs together demonstrate that intra and inter liquid phase run variation results in errors of up to 0.192 kJ/mol and of 0.109 kJ/mol on the average. This corresponds with the SER = 0.092 kJ/mol of s^2 derivation (*i.e.* for runs at varying s).

Using the pertinent MC scaling factor a $\Delta E_{vap,GO} = 0.000 - (-51.388) = 51.388$ kJ/mol, an erroneous value, results for the GO procedure. Vice versa, using the GO data of Table 5 a quite lower scaling factor would have been the result. From Table 5 it can be seen that in the liquid phase more than nine degrees of freedom $(10.42 - 11.04)$ are used for the vibrations. Nine degrees would have meant complete harmonic behaviour without rotations and translation of the molecule as a whole in the liquid phase. Again the GO approach will not reflect the difference in degrees of freedom between the gas and the liquid.

External validation of scaled charges

I. Energy of vaporization of fluoranthene

Starting with the initial structures of fluoranthene, found as described above, directly a gas phase long MC run was carried out applying the scaling factor of benzene, $s = 0.9463$ (within the error equal to 0.9502 derived according to Eqs (13), (14) and (15)), to the PM3 charges of Table 2. The same was done for the liquid phase. Here, however, the long MC run was preceded by cyclic annealed short MD runs and a long MD run. Also lowest GO energies were calculated. Results are included in Table 6 together with $E_{MC-GO}/\frac{1}{2}RT$, a measure of the deviation from harmonic vibration in the MC approach.

Table 6. MC and GO molar potential energies of gas and liquid phase fluoranthene at 298.15 K and at a scaling factor of $s = 0.9463$. Energies in kJ/mol.

Compound	Phase	E_{GO}	E_{MC}	$E_{MC\text{-}GO}/\frac{1}{2}RT$
Fluoranthene	Gas	126.223	215.844 ± 0.033	72.32
	Liquid	25.941	122.662 ± 0.176	78.05
	ΔE_{vap}	100.29	93.18 ± 0.18	-5.73

From Table 6 it can be seen that the energy of vaporization of fluoranthene in the MC approach (93.18 ± 0.18 kJ/mol) is identical only to the higher one of the experimental values given in Table 7. The GO result is even more than 7 kJ/mol higher than the MC result.

With respect to the liquid phase, the MC results for fluoranthene are close to a harmonic vibration behaviour without rotations and translations of the molecules as a whole. Exact harmonic behaviour would imply contributions of 78 degrees of freedom not far from the calculated result of 78.05. With respect to the gas phase the MC result show the same lack of around six (5.73) degrees of freedom as in the benzene case, which cannot be treated in the GO approach.

II. Energies of hydration and solution of benzene and fluoranthene in water

Starting with the initial structures of benzene and fluoranthene in water, found as described before and using the MC scaling factors of benzene ($s = 0.9463$) and water ($s = 1.8747$) for the solute and the solvent, respectively, threefold cyclic annealing with short MD runs took place. The lowest GO structure was used for a long MC run. In this way $E_{i,w}$ of Eqs (5), (6) and (7) was found. $E_{w,liq}$ was already obtained during the scaling of pure water. We used the average value at $s^2 = 3.5145$ from Table 5 of -37.807 ± 0.109 kJ/mol. Note that we need the energies of the complete box $E_{i,w}$ and $(216\text{-}Z).E_{w,liq}$ - including their relatively large errors - and not the molar energies per molecule, in order to calculate the energies of hydration ΔE_{hyd} and solution ΔE_{sol}. The results of E_{gas} and E_{liq} (already found, see Table 4, 5 and 6) lead to ΔE_{vap} also summarized in Table 7.

Table 7. Energies of vaporization, hydration and solution of benzene and fluoranthene and of benzene and fluoranthene in water at 298.15 K using MC scaling factors derived from benzene and water. Energies in kJ/mol.

Energy	Water ($Z=0$)	Benzene ($Z=5$)	Fluoranthene ($Z=10$)
$E_{i,w}$		-7958.43 ± 3.51	-7630.32 ± 8.08
(216-Z) $E_{w,liq}$	-8166.25 ± 23.51	-7977.21 ± 22.97	-7788.18 ± 22.43
ΔE_{hyd} (calc)	41.526 ± 0.109	31.137 ± 0.021	93.18 ± 0.18
(exp)	41.514 ± 0.071[a]	31.355 ± 0.071[a]	85.73 ± 1.84[b]
			or 93.39 ± 5.56[b]
ΔE_{hyd} (calc)		-37.61 ± 23.22	-57.99 ± 23.85
(exp)		-29.25 ± 0.21[c]	-54.73 ± 6.44
			or -62.76 ± 8.33[d]
(QM)[e]		-15.98	-31.00
ΔE_{sol} (calc)		-6.49 ± 23.22	35.19 ± 24.89
(exp)		2.09 ± 0.25[f]	31.00 ± 6.19[g]

[a] From ΔH_{vap}(25ºC) = 43.99 ± 0.07 kJ/mol (water) and ΔH_{vap}(25ºC) = 33.83 ± 0.07 kJ/mol (benzene) [17] and ΔE_{vap}(25ºC) = ΔH_{vap}(25ºC) – RT;

[b] Calculated from ΔH_{vap} = 67.513 kJ/mol (T = 563.5 K; [18]), 77.358 kJ/mol (T = 398.15 K; [19]) and 79.291 kJ/mol (T = 398.15 K; [20]) using $\Delta C_{P,vap}$ = -87.03 J/mol.K (Estimated according to $C_{P,G}$ and $C_{P,L}$ methods given by [21] and [17]), averaging and subtraction of RT. Using $\Delta C_{P,vap}$ = -136.31 J/mol.K (T = 298.15 K; [22]) leads to 93.39 ± 5.56 kJ/mol;

[c] Calculated from ΔH_{hyd}(25ºC,l) = -31.7 ± 0.2 kJ/mol [23] = ΔE_{hyd}(25ºC,l) – RT;

[d] Calculated from ΔE_{hyd}(25ºC,l) = - ΔE_{vap}(25ºC)[b] + ΔE_{sol}(25ºC,l)[g];

[e] Ref. [24];

[f] Calculated from ΔE_{sol}(25ºC,l) = ΔE_{hyd}(25ºC,l)[c] + ΔE_{vap}(25ºC)[a];

[g] Calculated from ΔH_{sol}(25ºC,s) = 45.0 ± 6.0 kJ/mol [25] and ΔH_{fus}(25ºC) = 14.0 ± 1.6 kJ/mol [17] via ΔE_{sol}(25ºC,l) = ΔH_{sol}(25ºC,l) = ΔH_{sol}(25ºC,s) - ΔH_{fus}(25ºC).

From Table 7 it follows that calculated energies of solution are identical to their experimental values within the (large) error ranges. The same holds for the energies of hydration. The hydration (solvation) energies of benzene and fluoranthene in water (-15.98 and -31.00 kJ/mol, respectively) have also been determined by Kubicki [24] employing a quantum mechanical MP2/6-31G(d) method and the Dielectric Continuum Solvation Model IEFPCM. These results are in reasonable accordance with our values, taking into consideration the large differences in methods used and calculational errors. Note that solvation energies calculated by us are closer to experimental values than those calculated by this author.

Energy of cavity formation and intramolecular energies

During the long MC runs of $E_{i,w}$ and $E_{w,liq}$ snapshot files containing 6000 structures were created. After play-back of the files, data were obtained concerning the energies defined in Eqs (8), (9), (10), (11) and (12). From these were calculated the energy of cavity formation ΔE_{cav} [Eq. (12)], the energy of a solute molecule in its aqueous environment [$E_{i,w}$, Eq. (9)] and the intramolecular energies of the solutes and water E_{intra} in various phases. Results are given in Table 8.

Table 8. Energies of cavity formation and intramolecular energies. Energies in kJ/mol.

Energy	Water	Benzene	Fluoranthene
ΔE_{cav} (calc)		27.49 ± 24.27	82.68 ± 23.85
(QM)[a]		59.0	112.1
$E_{i,w}$		-8.95 ± 5.19	75.19 ± 0.75
E_{intra}[b] (*gas*)	3.7179	56.384 ± 0.017	215.844 ± 0.033
(*liq*)	4.393 ± 0.004		214.97 ± 0.54
(*sol*,b)	4.406 ± 0.000	56.27 ± 0.13	
(*sol*,f)	4.414 ± 0.000		215.35 ± 0.29

[a] Ref. [24];
[b] *gas* = gas phase; *liq* = pure liquid; *sol*,b = benzene in water; *sol*,f = fluoranthene in water

From Table 8 it follows that positive energies of cavity formation were calculated amounting to 27.49 ± 24.27 and 82.68 ± 23.85 kJ per mol substituted benzene and fluoranthene, respectively. The cavity formation energies of benzene and fluoranthene in water (59.0 and 112.1 kJ/mol, respectively) have also been determined [24] employing a quantum mechanical model mentioned above. These results are again in reasonable accordance with our values, taking into consideration the large differences in methods used and calculational errors.

The energy of a benzene or fluoranthene molecule in an aqueous environment amounts to -8.95 or 75.19 kJ/mol and can be calculated with an inaccuracy of 5.19 or 0.75 kJ being much lower than the inaccuracies of the energy of a complete liquid box (around ± 25 kJ, see Table 7). This is important when the solute partitions over two aqueous phases, *e.g.* pure water and water plus dissolved organic carbon and when it can be assumed that the energies of cavity formation are equal. It follows from Eqs (8), (9), (10), (11) and (12) that the difference between the $E_{i,w}$ values will be equal to the difference in $E_{i,w}$ values of the two phases in those cases.

In addition it is shown that there is a statistically not significant difference of around 0.38 kJ/mol in intramolecular energy of a fluoranthene molecule in solution and pure liquid. Both are around 0.67 kJ/mol lower than the energy of gaseous fluoranthene. The same holds for a water molecule in the solutions and pure water. Here, these energies are, however, around 0.67 kJ/mol higher than in gaseous water. Also the intramolecular energies of benzene in solution and gas phase differ by less than 0.13 kJ/mol. It can be concluded that the energy of cavity formation is dominated completely by intermolecular van der Waals and electrostatic interactions.

Discussion and conclusions

Atomic charges

Atomic charges have been derived with inaccuracies of around 0.6% as given by Eqs (15) and (18), leading to the reproduction of the energies of vaporization of both benzene and water within the experimental errors. In an external validation the energy of vaporization of fluoranthene was calculated by MC using the PM3 charge scaled values of benzene. Again calculated and experimental values were reasonably close in view of the range of experimental values of around 8 kJ/mol. It is concluded that the benzene scaling factor can be used safely for other aromatic hydrocarbons as well. In an external validation using both the scaling factor of benzene and that of water the values of the energies of hydration and solution of benzene and fluoranthene in water were calculated by MC. The results were identical to experimental values within the relatively large calculational (up to 23.85 kJ/mol) and experimental (up to 8 kJ/mol, see Table 7) error ranges. It is concluded that the scaled PM3 charges of water can be used for the calculation of the hydration and solution properties of other aromatic solutes in water as well.

The Amber99a force field parameters of Table 1 were also used for the calculation of the properties of water and benzene by others. However, they employed different methods and found charges different from ours. The TIP3P water force field parameters [10] employed a $q_O = $ -0.834 e = -$2q_H$ value originally based on a fit to the structural and energetic properties of gas phase complexes of water and alcohols and for liquid water after which further refinement took place. Applied to liquid water this model reproduced the experimental value of the heat of vaporization within 0.25 kJ/mol. This was done in an *NPT* ensemble classical MC calculation at 298.15 K and 1 atm using 125 rigid water monomers, neglecting the gas phase energy, and spherical cut offs of 7.5 Å. Both the neglect of the gas phase energy (not done by us) and the cut off being lower than 9 Å (our value) can explain the lower value of $q_O = $ -0.6719 ± 0.0033 e we found. The van der Waals parameters of the Amber99a force field were derived employing an MC fit (not specified further) to the experimental liquid density and enthalpy of vaporization of benzene [2] and 6-31G* standard (R)ESP charges ($q_C = $ -$q_H = $ -0.145 e). Similar high charge values were found for carbon and hydrogen in the nonburied aromatic parts of peptide fragments. The details of the calculation of the heat of vaporization of benzene were not given. One could infer that an unspecified gas phase energy was included, but summation cut offs could have been lower than 9 Å. The latter would contribute to the higher charge value than found by us ($q_C = $ -$q_H = $ 0.0967 ± 0.0007 e).

Harmonic behaviour and whole molecule kinetics

Kinetic energy is the sum of the mean kinetic energies of the atoms, $\frac{1}{2}\Sigma_{i=1-N_{at}}$ m_i $(v_{ix}^2 + v_{iy}^2 + v_{iz}^2)$, where m_i are the masses of the N_{at} atoms i and $v_{ix,iy,iz}$ are the vectorial components of their velocities. This sum is often equalled to $3N_{at}RT/2$ in order to calculate temperature [9,26]. When the atoms have velocity components that are equal or otherwise related this will lead to translations or rotations of the molecules as a whole. In that case $6RT/2$ (= 7.4358 kJ/mol at 298.15 K) of kinetic energy is spent to these movements and cannot contribute to the vibrational potential energy of the atoms. It is reasonable to assume that these movements occur in the gas phase for our type of molecules at 298.15 K. The (vibrational) potential energy of the atoms includes a constant part (the minimum GO energy) and a temperature dependent part. The latter should reflect the loss of energy because of whole molecule movement in the gas phase. In a liquid phase there should be no or much smaller loss because of restricted whole molecule movement.

In the case of an (almost) harmonic force field Eq. (1) with only square terms, each atomic degree of freedom will contribute $RT/2$ to the temperature dependent part of the vibrational potential energy [27]. Deviations from harmonic behaviour should be expected when the contributions of energy terms in Eq. (1) are not harmonic and are large. This is especially pertaining to the nonbonded van der Waals energy in an atomic distance $R_{m,m'}$ region far from the potential minimum and for the electrostatic potentials, having no minimum at all. In the gas phase these contributions are small (aromatics) or zero (water) and small or zero deviation will result. In liquid phases still the net result of all summed contributions could be more less harmonic as a consequence of compensation of positive and negative deviations.

The gas phase MC results ($E_{MC-GO}/\frac{1}{2}RT$) for benzene (Table 4), water (Table 5) and fluoranthene (Table 6) clearly show that the vibrational potential energy is close to $6RT/2$ kJ/mol lower than a value connected to a vibrational energy based on all $3N_{at}$ degrees of freedom of the atoms. This is in accordance with the expected loss to whole molecule movement and with a literature value of gaseous water of 3.85 ± 0.17 kJ/mol [28] obtained by an MD method. The MC results of liquid fluoranthene (Table 6) and liquid benzene (Table 4) correctly point at the absence of whole molecule movement and a complete use of atomic degrees of freedom for harmonic atomic vibrational potential energy. Apparently, deviation causing contributions of nonbonded van der Waals and electrostatic interactions are low and/or compensating compared to the harmonic bond stretch-, bending- and torsional interactions. The strong electrostatic interaction compared to stretch and bending contributions in liquid water, however, clearly leads to a moderately high deviation from harmonicity of around $[(10.42-11.04) -9]$ $RT/2 \approx 2.13$ kJ/mol (see Table 5).

NVT ensemble

Total, potential plus kinetic, energy is the state property to be considered in the calculation of the energy difference between the gas and the liquid phase or between liquid phases. In our approach and that of others [29], only potential energy is taken into consideration. This is allowed when the kinetic energies of the two pertinent phases are equal. This condition is in accordance with Eqs (5), (6) and (7). The hydration Eq. (6) can be viewed as a difference between the system of the solution and of the unmixed components. In our case, in both systems one solute and 216-Z water molecules are present and kinetic energy, expressed as $\frac{1}{2}\Sigma_{i=1\text{-}Nat}\ m_i$ $(v_{ix}^2 + v_{iy}^2 + v_{iz}^2)$, will cancel. Simultaneously, the *NVT* ensemble condition of constant N is fulfilled.

With respect to the condition of constant V our method is not suited to calculate V but requires the a priori knowledge of it. For pure liquids at 298.15 K several simple estimation methods are available [30, 12] when experimental data are missing. For solutions we assume that the partial molar volumes are equal to the specific volumes of the pure components. For benzene in water an experimental value of 82.6 cm³/mol is available [23] leading to $Z = 5$, the same value we found and included in Table 3. Another possibility would have been to cram the solute and 216 water molecules into a box with volume identical to that of pure liquid water. In this way the condition of constant N and V would have been fulfilled without the $Z/216$ correction of Eqs (5), (6) and (7). However, in preliminary calculations (not shown here) we met difficulties to obtain a sufficiently fast establishment of equilibrium, which will be an even larger problem for solutes larger than fluoranthene. In addition, also in this method unrealistic partial molar volumes would have been used. Finally, we did not use the Particle Insertion (Widow) method, because we expected our system to be too dense and too less simple to fulfil the requirements of this method [6].

Acknowledgement

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