



Prediction of environmental parameters of polycyclic aromatic hydrocarbons with COSMO-RS

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ARTICLE INFO

Article history:

Received 16 December 2009

Received in revised form 24 February 2010

Accepted 26 February 2010

Available online 3 April 2010

Keywords:

Polycyclic aromatic hydrocarbons

Aqueous solubilities

Subcooled vapor pressures

Henry's law constant

Octanol–water partition coefficient

COSMO-RS

ABSTRACT

The methodology for the prediction of properties of environmental relevance of polycyclic aromatic hydrocarbons based on the conductor-like screening model for real solvents (COSMO-RS/COSMOtherm) is presented and evaluated, with a special focus on the aqueous solubility of polycyclic aromatic hydrocarbons and related aromatic hydrocarbons (PAHs).

It is shown that the solubility predictions as well as their temperature dependence obtained for a set of 12 polycyclic aromatic hydrocarbons and two related aromatic hydrocarbons are in good agreement with the experimental data. (Subcooled) Vapor pressures, Henry's law constants as well as octanol–water partition coefficients were also estimated and compared with experimental data showing the capability of the model to predict environmental related data with sufficient precision for practical purposes.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are globally distributed environmental contaminants with issues related to their known toxic and bioaccumulative characteristics (Menzie et al., 1992). In humans for instance, health risks associated with PAHs exposure include cancer and DNA damage.

Besides considerable sources of natural occurring PAHs, such as bushfires or forest fires, coal and hydrocarbon seepage and releases from active volcanoes (Nikolaou et al., 1984; Perez et al., 2008), the major sources of input of PAHs into the environment are of anthropogenic origin, via the combustion of organic fuel as a main route (Baek et al., 1991). In the marine environment, these sources include oil spills from tankers, oil discharges by ships, and offshore oil and gas exploration (Perez et al., 2008). PAHs are also found associated to several industrial processes. Recently, thin films of planar PAH molecules have gained interest due to their potential application in thin film electronic devices, like organic thin film transistors (OTFTs) and organic light-emitting diodes (OLEDs) (Klauk, 2006).

In general terms, organic substances released into the environment are subject to a variety of interconnected physical, chemical, and biological processes. Besides transformation processes, which

might occur due to structural changes in the substance, transport and mixing phenomena within given environmental compartments, as well as transfer processes between different phases and/or compartments, play a vital role in finally determining the overall fate of a substance in the environment. Knowledge of physico-chemical parameters describing these phenomena, like coefficients of substance partitioning between the liquid and gaseous phase, is therefore of crucial interest.

In the case of PAHs, fate-determining processes, like their incorporation into particulates, their distribution between gas and particulate phases as well as atmospheric phenomena involved in PAH deposition and transport, and furthermore possible chemical degradation reactions, were subject of a variety of studies (e.g., as reviewed by Baek et al. (1991)).

Atmospheric fallout for example, like wet and dry deposition of particles, was found to be an important route to remove gaseous and particle-associated PAHs from the atmosphere. PAHs are washed out from the atmosphere during precipitation events (Bidleman, 1988). Atmospheric fallout was proven to be a distinct pathway for the charging of many water bodies with PAHs (Andren and Strand, 1981; McVeety and Hites, 1988; Dickhut and Gustafson, 1995; Golomb et al., 1997).

PAHs are often resistant to biological degradation and are not efficiently removed by conventional separation techniques such as coagulation, flocculation, sedimentation, filtration or ozonation (Crisafulli et al., 2008). As a result, they are persistent in the envi-

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ronment and show a tendency to accumulate in soils and sediments, being also highly dispersed into the atmosphere. For instance, it can be assumed while PAH with two and three rings prevail in the air as vapor, in the subsoil there are dissolved in the ground- and seeping water. PAH with four and more rings occur in air and soil mainly bound to particles (Wild and Jones, 1995).

In 2003, the Aarhus Protocol on Persistent Organic Pollutants (1998), an addition to the 1979 Geneva Convention on Long-Range Transboundary Air Pollution, was ratified by several industrial states; in annex III, PAHs are listed as persistent organic pollutants (POP) (United Nations Economic Commission for Europe (UNECE), 2003).

Deducing from the importance of the interplay of physico-chemical properties and environmental conditions for the prediction of partitioning in multicompartiment systems, and therefore the evaluation of patterns of transport and distribution as well as long-range transport potential, accurate knowledge of vapor pressures and aqueous solubilities is fundamental (Mackay, 1991). While vapor pressures of solid and liquid phases of PAH have been extensively measured in the past (e.g., Mortimer and Murphy, 1923; Hoyer and Peperle, 1958), only limited experimental aqueous solubility data for these compounds are available in the literature, and, at times, the data are conflicting. For the related Henry's law constant and octanol–water partition coefficients, a large database on experimental values exists; unfortunately, with regard to the properties of the more hydrophobic compounds, due to the more challenging character of its experimental determination, the values are rather scattered (Mackay et al., 2006). Group-contribution based one- and multi-parameter linear free energy relationships (LFERs) for their estimation are widely applied (Schwarzenbach et al., 2003).

The experimental determination of aqueous solubilities of hydrophobic organic substances, as a function of temperature, is not an easy task; the obtained values may be often flawed due to intrinsic problems in the experimental setups, i.e., incomplete equilibration due to slow dissolution rates of the solid hydrocarbon or adsorption on the surface of glassware (Mackay and Shiu, 1977). Hence, having a thermodynamic model able to describe the thermodynamic properties for PAHs is an essential step forward to a more effective xenobiotic monitoring. A variety of different models for aqueous solubilities has been described to date. Empirical correlations apart, the more sound thermodynamic approach is based on the solid–liquid equilibrium equation (Eq. (1)), describing the liquid phase non-ideality by activity-coefficient models such as the Wilson equation (Wilson, 1964), non-random two liquid model (NRTL) (Renon and Prausnitz, 1968) or universal quasi-chemical activity-coefficient model (UNIQUAC) (Abrams and Prausnitz, 1975) and equation-of-state models (EoS) like statistical associating fluid theory (SAFT) or cubic-plus-association (CPA) (Chapman et al., 1990; Kontogeorgis et al., 1996). However, concerning new systems, these models have no predictive power. For that purpose, other approaches must be used such as solubility parameters (Hansen and Beerbower, 1971), or group contribution methods (GCMs), where estimates are obtained from molecular structure information only, requiring a strong data base on constituting groups, such as universal functional activity-coefficient model (UNIFAC) (Fredenslund et al., 1975). These methods have proved successful for many compounds, providing acceptable values for temperature dependent solubilities, but they fail for molecules with several functional groups or systems where the solute–solvent interactions are complex.

Based on the work of Pierotti et al. (1959), Tsonopoulos and Prausnitz (1971) presented an approximate group-contribution scheme with correlations of activity coefficients in “practically infinite dilute” aqueous solutions with molecular structure, at $T = 298.15$ K, for several aromatic solutes, including polycyclic

hydrocarbons. Lu et al. (2008) developed two Quantum Chemical Descriptors models to describe the water solubility of 32 PAHs. Chu and Chan (2000) and Zhao et al. (2005) used simple linear equations, provided that the compound(s) under study must be recognized as a proper category of chemicals. A GCM to estimate water solubilities of organics with a fragment scheme determined by multilinear regression, requiring many descriptors, was found working better for liquids than for solids (Kühne et al., 1995). Equations based on mobile order theory modified from Ruelle and Kesselring (1997) were also used to correlate water solubilities of 19 PAHs (Paasivirta et al., 1999). However, these models only consider the aqueous solubility at one temperature ($T = 298.15$ K) to calculate the descriptors or to establish the correlations between the solubility and, for instance, the air–water partition coefficients; only Paasivirta et al. (1999) developed temperature dependent relations but still within a limited temperature range (273.15–303.15 K).

EoS-type approaches to describe aqueous solubilities require equations of state that explicitly deal with hydrogen bonding and solvation effects. Two of the most successful equations of state of this type are SAFT (Chapman et al., 1990) and the CPA EoS (Kontogeorgis et al., 1996, 2006a,b). The group contribution method to calculate SAFT pure compound parameters proposed by Tamouza et al. (2004) was used for the vapor pressures and saturated liquid volumes of pure PAHs using three versions of SAFT: perturbed-chain statistical associating fluid theory (PC-SAFT) (Gross and Sadowski, 2000, 2001), variable range statistical associating fluid theory (SAFT-VR) (Gil-Villegas et al., 1997) and a slightly modified version (Benzaghou et al., 2001) of the original SAFT. The obtained results for these properties compared well with experimental data.

The CPA EoS performs superiorly for aqueous systems (Kontogeorgis et al., 1999, 2006a,b; Voutsas et al., 2000; Derawi et al., 2003a,b; Folas et al., 2006; Oliveira et al., 2007a) and it is also mathematically simpler, thus substantially simplifying and accelerating the phase equilibrium calculations when compared with SAFT. CPA was previously applied to the phase equilibrium of mixtures containing alcohols, glycols, water, amines, organic acids and aromatic or olefin hydrocarbons (Derawi et al., 2003a,b, 2004; Kaarsholm et al., 2005; Folas et al., 2006; Kontogeorgis et al., 2006a,b; Oliveira et al., 2007a). This model is also able to take into account the solvation phenomena occurring between water and aromatic hydrocarbons, olefinic hydrocarbons (Folas et al., 2006) as well as aromatic perfluorocarbons (Oliveira et al., 2007b). It has recently been shown that CPA EoS can provide an accurate description of the aqueous solubility of PAHs, using a single, temperature independent, association volume (solvating) parameter, β_{ij} (Oliveira et al., 2009), being able to account for high pressures, as well.

On the other hand, viable *a priori* predictive methods of (aqueous) solubilities of solid compounds have been long sought after. Over the last years, the quantum chemically based conductor-like screening model for realistic solvation (COSMO-RS), a novel approach for computing equilibrium thermodynamic properties, has proven to be a promising alternative when compared with group contribution methods, since it is based on a small number of adjustable parameters only, which are independent of molecular or structural information (Klamt, 2005). COSMO-RS is a surface interaction model and, contrary to group contribution methods, it considers molecular charge densities rather than the interaction of groups, which are obtained by molecular quantum chemical COSMO calculations. A key feature of COSMO-RS is the reduction of molecular properties to a probability distribution of screening charges for the molecule solvated in a perfect conductor, the so-called sigma profile of the molecule. The sigma profiles are used to estimate the exchange energies between the substrate and the solvent. The calculation of the sigma profiles of the components

is sensitive to the molecular configuration which is optimized in the ideal gas phase (Eckert and Klamt, 2002).

The goal of the present study was to evaluate the COSMO-RS/COSMOtherm potential for the prediction of environmentally important thermodynamic properties of 14 (polycyclic) aromatic hydrocarbons. While focused on temperature-dependent aqueous solubilities of solid PAHs, (subcooled) vapor pressures, air–water and octanol–water partition coefficients were predicted, as well, all at $T = 298.15$ K. The predicted values were compared with available literature data.

2. Methodology

2.1. Solid–liquid equilibrium thermodynamics of PAH

In a two-component solid–liquid equilibrium, the fugacity of the pure solid solute (defined as component 2) equals its fugacity in the solvent (defined as component 1), assuming complete immiscibility with the solvent in the solid state. Defining the standard-state fugacity as the fugacity of pure, subcooled liquid at a solution temperature T , an approximated expression for the activity of the solute, valid at low pressures, can be derived, and a single solid–solid-phase transition is assumed (Prausnitz et al., 1999):

$$\ln a_2 = \ln(\gamma_2 x_2) = \frac{\Delta_{fus}H(T_{fus})}{RT_{fus}} \left(\frac{T - T_{fus}}{T} \right) + \frac{\Delta_{trs}H(T_{trs})}{RT_{trs}} \left(\frac{T - T_{trs}}{T} \right) - \frac{\Delta_{fus}C_{p,m}(T_{fus})}{R} \left[\left(\frac{T - T_{fus}}{T} \right) + \ln \frac{T_{fus}}{T} \right] \quad (1)$$

with a_2 being the activity of the solute, γ_2 , as the activity coefficient of the solute, x_2 its mole fraction, $\Delta_{fus}H(T_{fus})$ as the molar enthalpy of fusion of the pure solute, at the fusion temperature T_{fus} , $\Delta_{trs}H(T_{trs})$ the molar solid–solid-phase transition enthalpy, at the transition temperature T_{trs} , and $\Delta_{fus}C_{p,m}(T_{fus})$ as the molar heat capacity change upon fusion, at fusion temperature T_{fus} , and R as the universal gas constant = $8.314472(15) \text{ J K}^{-1} \text{ mol}^{-1}$.

As a standard simplification throughout the chemical engineering literature the heat capacity change upon fusion is regarded as being independent of the temperature. The bracketed term multiplied with $\Delta_{fus}C_{p,m}$ is the balanced enthalpic and entropic thermal correction to 298.15 K included in Eq. (1) that is often considered as being small, as the opposite signs of the enthalpic and entropic correction lead to near cancellation (Coutinho et al., 1995; Coutinho and Daridon, 2001; Oliveira et al., 2009). Nevertheless, as Prausnitz et al. (1999) pointed out, the contribution of $\Delta_{fus}C_{p,m}$ may become large at temperatures far off the solute melting point. Neglecting this term might then introduce a considerable error into the solubility estimation (Tsonopoulos and Prausnitz, 1971).

2.2. COSMO-RS

COSMO-RS is a novel method for predicting thermodynamic properties of pure and mixed liquids on the basis of unimolecular quantum chemical calculations for the respective individual molecules. COSMO-RS combines the computational efficiency of the quantum chemical dielectric continuum solvation model COSMO with a statistical thermodynamics approach, based on the results of quantum chemical calculations (Klamt, 1995; Klamt and Eckert, 2000). The COSMO model is a variant of known dielectric continuum solvation methods. The solute molecules are assumed to be placed in a virtual conductor environment, where the solute induces a polarization charge density on the molecular surface, the interface between the molecule and the conductor. These charges act back on the solute and give rise to a more polarized electron density than in vacuum. During the

quantum chemical self-consistency cycle, the solute molecule is converged to its energetically optimal state in a conductor, with respect to electron density.

The standard procedure of COSMO-RS calculations consists of two main steps: quantum chemical COSMO calculations for the molecular species involved and COSMO-RS statistical calculations performed within the COSMOtherm program (Eckert, 2005; Eckert and Klamt, 2005). The COSMO-RS calculation with COSMOtherm (Version C2.1 Release 01.05) describes all interactions between molecules as contact interactions of the molecular surfaces, and these interactions can be related to the screening charge densities of the interacting surface parts. The COSMO output provides the total energy of a molecule in its conductor environment and the 3D polarization density distribution on the surface of each molecule – the sigma profile. This information acts as an input for the statistical thermodynamic calculations and is independent of the solvent dielectric constant and temperature. Furthermore, COSMO-RS performs statistical thermodynamic calculations and hence yields enthalpic and entropic information for each system. The COSMO-RS method depends only on a small number of general, element-specific adjustable parameters (predetermined from known properties of a small set of molecules), that are not specific for functional groups or types of molecules.

All statistical COSMO-RS thermodynamics calculations were done with COSMOtherm, using the parameter file BP-TZVP C21 0025. Prior to this step, DFT/COSMO (density functional theory/conductor-like screening model) calculations were performed using the Gaussian 03 suite of programs (Frisch et al., 2003), with the BP86 (Becke–Perdew) density functional (Perdew, 1986; Becke, 1988, 1993) and a TZVP (triple zeta valence polarized) basis set combination (Ahlrichs-TZVP) (Schäfer et al., 1994). The feasibility of COSMOtherm's ability to predict phase equilibria was successfully demonstrated, e.g., with the prediction of mutual solubilities of hydrocarbons and water (Klamt, 2003), aqueous solubility of chlorobenzenes (Oleszek-Kudlak et al., 2005), aqueous solubility of solid carboxylic acids (Schröder et al., 2010) and the prediction of liquid–liquid and vapor–liquid equilibria of water and ionic liquids binary systems (Freire et al., 2007, 2008a–c).

As COSMOtherm treats solids as subcooled melts, the Gibbs energies of fusion, $\Delta_{fus}G$, have to be known and provided in the input section (Eckert, 2005).

2.2.1. Aqueous solubilities

The mole fractions of the respective solute were refined using the iterative automatic solubility calculation option of COSMOtherm:

$$\log_{10} \left(x_2^{SO(i+1)} \right) = \left[\mu_2^{(P)} - \mu_2^{(1)} \left(x_2^{SO(i)} \right) + \min(0, \Delta_{fus}G) \right] / (RT \ln 10) \quad (2)$$

where x_2^{SO} is the mole fraction of solid 2 dissolved in the solvent phase 1 at saturation, $\mu_2^{(P)}$ is the chemical potential of pure compound 2, $\mu_2^{(1)}$ is the chemical potential of compound 2 at infinite dilution in the solvent compound 1, and i represents the iteration count.

The chemical potential of compound X_i in system S is obtained from integration of the σ -potential over the surface of X_i

$$\mu_{C,S}^{X_i} = \mu_{C,S}^{X_i} + \int p^{X_i}(\sigma) \mu_S(\sigma) d\sigma \quad (3)$$

with $\mu_{C,S}^{X_i}$ as the combinatorial contribution to the chemical potential, derived from the combinatorial free energy expression:

$$\mu_{C,S}^{X_i} = \frac{\partial G_{C,S}}{\partial x_i} = RT \left[\lambda_0 \ln r_i + \lambda_1 \left(1 - \frac{r_i}{\bar{r}} - \ln \bar{r} \right) + \lambda_2 \left(1 - \frac{q_i}{\bar{q}} - \ln \bar{q} \right) \right] \quad (4)$$

with three adjustable parameters λ_0 , λ_1 , and λ_2 , as well as r_i the molecular volume, q_i the molecular area of compound i , \bar{r} the total volume and \bar{q} the total area of all compounds in the mixture, with

$$\bar{r} = \sum_i x_i r_i \quad (5)$$

$$\bar{q} = \sum_i x_i q_i \quad (6)$$

Optionally, the combinatorial term can be switched off.

2.2.2. Henry's law constant

Combining aqueous solubility with vapor pressure data, one obtains the respective air–water partition coefficient (Henry's constant or Henry's law coefficient), a fundamental physico-chemical property which is important for the prediction of the partition of PAH between air and aqueous phases, a key parameter to evaluate their tendency to stay in the gas and aqueous phase, and hence, their fate in the environment. This procedure fails for solutes which have appreciable solubility in water, calling then for its experimental determination (Shiu and Mackay, 1997). For estimating Henry's law constant, one needs the vapor pressure of the solid substance (p_S) or the (subcooled) liquid (p_L), as well as the aqueous solubility of the solid or the (subcooled) liquid (Paasivirta et al., 1999). If the compound is solid, its vapor pressure p_S will be lower than that of the subcooled liquid p_L by the factor of the fugacity ratio $\frac{p_S}{p_L}(T) = \exp\left(-\frac{\Delta_{fus}G(T)}{RT}\right)$ (Mackay et al., 1982; Van Noort, 2004).

In COSMOtherm's temperature/mixture input, an automatic Henry's law coefficient calculation can be calculated. Below the melting point, COSMOtherm treats the PAHs as hypothetical (subcooled) liquid. The respective Henry's law coefficient at infinite dilution in water, $k_{H,2}$, is obtained applying Henry's law (Eq. (7)) (Bhatia and Sandler, 1995):

$$k_{H,2} = \gamma_2^\infty(T, p, x_2) p_2(T) \quad (7)$$

with γ_2^∞ as the infinite dilution activity coefficient.

The pure compound vapor pressure at temperature T , $p_2(T)$, is predicted via

$$p_2(T) = \exp\left\{-\left(\mu_2^{gas} - \mu_2^2\right)/RT\right\} \quad (8)$$

with μ_2^{gas} as the chemical potential of the pure compound in the gas phase and μ_2^2 as the chemical potential of the pure compound in itself. Introducing the Gibbs free energy of fusion at temperature T

into term μ_2^2 , the vapor pressures of the solid PAH at this temperature T is also accessible.

Besides the importance of the air–water partition information at a given temperature, the temperature dependence of Henry's law constant, which also can be predicted via COSMOtherm, is directly linked to molar free enthalpies of hydration, which allows to access molar enthalpies and entropies of the hydration process.

2.2.3. Octanol–water partition coefficient

Another important measure in modelling transport and fate as well as in assessing environmental risks is the octanol–water partition coefficient, which describes a compound's distribution between the solvents 1-octanol and water. It is used as an indicator, quantifying a substance's potential for bioaccumulation.

In COSMOtherm, the partition coefficient $\log K_{OW}$ is predicted via computation of the chemical potentials of substance x in the respective solvent, at infinite dilution (Eq. (9)):

$$\log K_{OW} = \log_{10} \left[\exp \left\{ \left(\mu_W^x - \mu_O^x \right) / RT \right\} \frac{V_{W,m}}{V_{O,m}} \right] \quad (9)$$

with μ_W^x as the chemical potential of pure compound x in water and μ_O^x as the chemical potential of pure compound x in 1-octanol. The quotient of molar volumes, $V_{W,m}/V_{O,m}$, can be set in the input section. Besides of the density difference of the solvents, their mutual solubility has to be taken into account.

2.3. Compounds and literature data

Table 1 lists the polycyclic aromatic hydrocarbons chosen, as well as their respective melting properties literature data. With biphenyl and m-terphenyl, two aromatic hydrocarbons with connected phenyl rings were also included. They are significantly different from condensed polycyclic aromatic hydrocarbons with an equal number of rings in two things: their molecules are bigger and their interactions with water are weaker (Tsonopoulos and Prausnitz, 1971).

Experimental data for the heat capacity change upon fusion are difficult to access. The heat capacity changes upon fusion considered here were derived from a group contribution method (Chickos et al., 1993, 2002) and assumed as constant. In general, these values are larger than $\Delta_{fus}C_{p,m}$ values derived from experimental heat capacity data for the solid and liquid state, as described by Allen et al. (1999), at $T = 298.15$ K. The aforementioned group additivity estimates for

Table 1
Polycyclic aromatic hydrocarbon melting property literature data (Roux et al., 2008, if not stated otherwise) ($\Delta_{fus}H(T_{fus})$) – enthalpies of fusion at fusion temperature, T_{fus} – fusion temperature and $\Delta_{fus}C_{p,m}$ – heat capacity change upon fusion).

Polycyclic aromatic hydrocarbons	CAS registry number	$\Delta_{fus}H(T_{fus})$ (kJ mol ⁻¹)	T_{fus} (K)	$\Delta_{fus}C_{p,m}$ (J K ⁻¹ mol ⁻¹)
Naphthalene	91-20-3	19.06 ± 0.08	353.4	48.0
Biphenyl	92-52-4	18.57 ± 0.004	342.1	56.6
m-Terphenyl	92-06-8	31.0 ± 0.4	361.2	87.4
Fluoranthene, Benzo[j,k]fluorine	206-44-0	18.73 ± 0.02	383.3	83.9
Acenaphthene, 1,8-ethylenenaphthalene	83-32-9	21.46 ± 0.02	366.6	63.1
9,10-Dihydroanthracene	613-31-0	23.84 ^a	382.18 ^a	72.0
9,10-Dihydrophenanthrene	776-35-2	12.79 ^b	306.52 ^b	72.0
Fluorene, 9H-Fluorene	86-73-7	19.58 ± 0.06	387.9	66.6
Anthracene	120-12-7	29.4 ± 0.1	488.9	70.2
Pyrene, Benzo[d,e,f]phenanthrene	129-00-0	17.36 ± 0.04	423.8	84.0
Chrysene ^A , Benzo[a]phenanthrene	218-01-9	26.2 ± 0.2 ^c	531.4	92.4
Phenanthrene ^B	85-01-8	16.46 ± 0.04 ^d	372.4	70.2
Benzo[a]anthracene	56-55-3	21.4 ± 0.3	434.3	92.4
Triphenylene, Benzo[l]phenanthrene	217-59-4	24.74 ± 0.01	471.0	92.4

^{A/B} $\Delta_{tpce}^l H_m(T_{fus})$ – total phase change enthalpy at fusion temperature, includes phase transitions prior to melting).

^a Chirico et al. (1987a,b).

^b Lee-Bechtold et al. (1979).

^c $\Delta_{trans} H_m(T_{trans}) = 3.22 \pm 0.4$, $T_{trans} = 512$ K.

^d $\Delta_{trans} H_m(T_{trans}) = 0.22$, $T_{trans} = 347.5$ K.

Table 2

The correlation of experimental aqueous solubility data, as a function of temperature, of the PAHs studied, in the respective temperature interval, with $\ln x_2 = AT^{-1} + B$.

PAH	$-A$ (K)	B	R^2	(T) (K)	References
Naphthalene	4026.38	1.75	0.982	294.85–348.15	Rössling and Franck (1983); Wang and Wong (2005); Karásek et al. (2006, 2007, 2008a)
Biphenyl	4776.98	1.95	0.988	297.75–337.65	Wauchope and Getzen (1972)
m-Terphenyl	5165.38	-2.51	0.9975	278.00–323.13	Reza et al. (2002)
Fluoranthene	4541.10	-2.47	0.756	286.35–303.05	Rössling and Franck (1983); Wang and Wong (2005); Karásek et al. (2006, 2007, 2008a)
Acenaphthene	4899.82	1.79	0.994	295.35–347.85	Rössling and Franck (1983); Wang and Wong (2005); Karásek et al. (2006, 2007, 2008a,b)
9,10-Dihydroanthracene	4581.78	-0.47	0.998	278.12–313.17	Reza and Trejo (2004)
9,10-Dihydrophenanthrene	2253.83	-7.09	0.983	277.96–298.16	Reza et al. (2002)
Fluorene	5253.34	2.12	0.996	297.75–346.55	Wauchope and Getzen (1972)
Anthracene	6698.70	3.34	0.990	287.15–347.25	Rössling and Franck (1983); Wang and Wong (2005); Karásek et al. (2006, 2007, 2008a,b)
Pyrene	5712.29	0.89	0.998	285.35–347.85	Rössling and Franck (1983); Wang and Wong (2005); Karásek et al. (2006, 2007, 2008a,b)
Chrysene	4821.67	-6.52	0.930	284.15–302.15	Rössling and Franck (1983); Wang and Wong (2005); Karásek et al. (2006, 2007, 2008a)
Phenanthrene	5277.2	1.72	0.991	284.25–346.55	Rössling and Franck (1983); Wang and Wong (2005); Karásek et al. (2006, 2007, 2008a, b); NIST Chemistry Webbook
Benz[a]anthracene	5364.52	-3.06	0.991	280.05–302.85	May et al. (1983)
Triphenylene	5347.09	-3.44	0.996	285.15–301.35	May et al. (1983)

heat capacities of solid and liquid PAHs are based on group values for tertiary and (internal) quaternary aromatic sp^2 carbon atoms derived from mostly (alkylated) aromatic compounds with 6–14 carbon atoms, which might give rise to larger derived heat capacity changes upon fusion than the ones observed experimentally. Next to the benzenoid PAH, five- and six-membered rings have to be taken into account with a different treatment, while considering larger molecules, since five-membered rings introduce strain and curvature into a molecule (Yu et al., 2004).

Table 2 lists the coefficients of the correlation used for the compiled experimental aqueous solubility literature data with temperature as a function of temperature, $\ln x_2 = A \cdot T^{-1} + B$, and the respective temperature interval.

3. Results and discussion

3.1. Aqueous solubilities

The temperature dependence of the aqueous solubilities of the 12 polycyclic aromatic and two related aromatic hydrocarbons was predicted with COSMOtherm and compared with available literature data. For all solutes, melting properties data are found in the literature. Experimental aqueous solubilities of polycyclic aromatic and related hydrocarbons are remarkably well reproduced with COSMOtherm, as shown in the deviation plot of Fig. 1a, considering that within the chosen test set of compounds, a span of five orders of magnitude (in decadic logarithms of mole fraction solubilities) is covered. The model works particularly well for small fused rings (naphthalene) and the aromatic hydrocarbons where the rings are not annealed (solid lines). The aqueous solubilities of non-alternant PAHs and PAHs with hydrogenated rings are slightly overestimated (dashed lines), with a more pronounced effect for the solubilities of the remaining fully aromatic, larger systems (dash-dotted lines), coinciding with their higher fusion temperatures. This indicates problems in the description of the liquid state expressed via the solid state when far from the melting point, with the simple assumptions made here. On the other hand, the larger fully aromatic PAHs show aqueous solubilities beyond $\log x_2 = -8$, at ambient temperature, rendering their accurate experimental determination a challenging task.

If the combinatorial contribution in COSMOtherm is not used (Fig. 1b), the predicted aqueous solubilities decrease leading there-

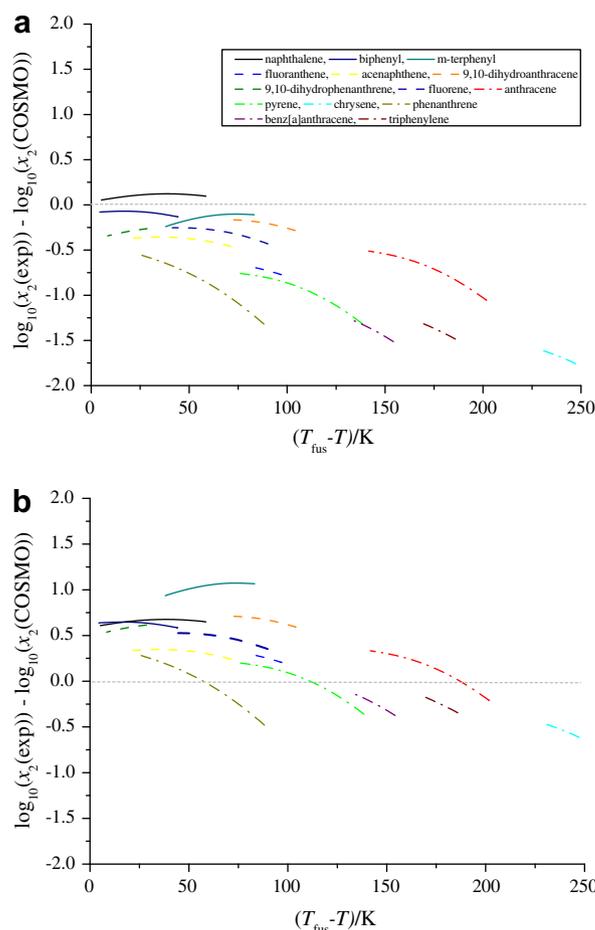


Fig. 1. Plots of the solubility difference between literature aqueous solubility data and the solubility obtained with COSMOtherm, as a function of $(T_{fus} - T)$, with the combinatorial term switched on (a), and off (b).

fore to an upward shift of all temperature dependent logarithmic mole fraction solubilities. The extent of each molecule's shift depends mainly on its size, in terms of molecular volume and molec-

Table 3
Henry's law constants, at infinite dilution in water, at $T = 298.15$ K. Overview of the spread of experimental literature data and selected values (Mackay et al., 2006), and COSMOtherm results.

PAH	$k_{H,2}$ (exp.; 298.15 K) (bar)	$k_{H,2}$ (selected; 298.15 K) (bar)	$k_{H,2}$ (COSMO; 298.15 K) (bar)
Naphthalene	23.575–41.118	23.796	36.969
Biphenyl	6.392–22.878	15.849	12.355
m-Terphenyl	–	–	0.479
Fluoranthene	0.609–1.085	0.553	1.212
Acenaphthene	3.569–13.514	6.752	18.785
9,10-Dihydroanthracene	–	–	3.695
9,10-Dihydrophenanthrene	–	–	6.163
Fluorene	3.569–6.558	4.355	6.141
Anthracene	1.085–4.804	2.214	3.779
Pyrene	0.274–1.107	0.509	1.551
Chrysene	0.059–0.293	0.036	0.278
Phenanthrene	1.317–3.071	1.771	3.231
Benz[a]anthracene	0.056–0.450	0.322	0.342
Triphenylene	–	0.012	0.064

ular surface area (Eq. (4)). This procedure is leading to very good solubility predictions for the larger fused rings. On the other hand, aqueous solubilities of non-alternant PAHs and PAHs with hydrogenated rings are now slightly underestimated, with naphthalene, biphenyl and m-terphenyl showing the largest effect. Fig. 1b shows the respective deviations on solubility when plotted versus ($T_{fus} - T$), when the combinatorial term is switched off.

3.2. Henry's law constants and subcooled vapor pressures

Henry's law constants were calculated for all compounds at $T = 298.15$ K and they are listed in Table 3, together with available experimental data.

Considering that in some cases considerable discrepancies among compiled experimental values of different authors exist, which are the result of known difficulties in performing the respective measurements, COSMO-RS/COSMOtherm is a good tool to estimate the order of magnitude of the Henry's law constants of the selected compounds. Relative to the selected values of Mackay et al. (2006), the predicted Henry's law constants are overestimated, with a root mean square (rms) deviation of 0.30 log-units, compared to the rms-deviation of 0.38 log-units reported occurring in a COSMO-RS validation set of 150 compounds (Eckert and Klamt, 2002), and a maximum deviation of 0.89 log($k_{H,2}$) units, found for chrysene (versus 0.75 log-units of forementioned validation set). Table 4 lists calculated COSMOtherm subcooled vapor pressure data of PAHs, in comparison with typical experimental data, given in decadic logarithmic units of pressure in Pascal, at $T = 298.15$ K.

No literature data on subcooled vapor pressures were encountered for m-terphenyl as well as 9,10-dihydroanthracene and 9,10-dihydrophenanthrene, hence no data for the Henry's law constants are given. Experimental subcooled vapor pressures are mostly obtained with a retention time method based on gas chromatography or derived from solid vapor pressures using approximations. Given this, for PAH, COSMOtherm delivers satisfactory data on the magnitude to be expected, within a deviation comparable to the one recently found between experimental and COSMO-RS values in biphenyl and selected polychlorinated biphenyl (PCB) congeners at 298 K (Nakajoh et al., 2009), although their value for biphenyl itself is slightly higher (0.134 log-units) than the one presented here, most probable caused by using density functional theory (DFT) with B3-LYP functional and 6–31 + G(d,p) basis set in the quantum chemical COSMO calculations and geometry optimizations. As in the case of PCB congeners (Nakajoh et al., 2009), COSMO-RS slightly overestimates the subcooled vapor pressures for PAH as well, with a highest absolute deviation of 1.27 log-units in the case of chrysene.

By combination of the Gibbs free energy of fusion with Eq. (8), an estimation of solid vapor pressures can be obtained with COSMO-RS, as well. Naphthalene and biphenyl were chosen for demonstration as they are the only substances under study with solid vapor pressures above 1 Pa, at ambient temperature. For naphthalene, at $T = 298.15$ K, $\log_{10} p_S$ (COSMO) = 1.346, while a typical experimental value reads $\log_{10} p_S$ (experimental) = 1.045 (Monte et al., 2006); for biphenyl, $\log_{10} p_S$ (COSMO) = 0.1165 versus $\log_{10} p_S$ (experimental) = 0.075 (Burkhard et al., 1984; all vapor pressures in Pascal). For the respective fugacity ratios p_S/p_L , 0.328 (naphthalene) and

Table 4
Subcooled vapor pressures, at $T = 298.15$ K, experimental literature data, and COSMOtherm results.

PAH	$\log_{10} p_L$ (experiment; 298.15 K)	$\log_{10} p_L$ (COSMO; 298.15 K)	Deviation (exp.–COSMO)
Naphthalene	1.568 ^a	1.841	–0.273
Biphenyl	0.560 ^a	0.500	0.060
m-Terphenyl	–	–2.966	–
Fluoranthene	–2.223 ^a	–1.326	–0.897
Acenaphthene	0.182 ^a	0.993	–0.811
9,10-Dihydroanthracene	–	–0.334	–
9,10-Dihydrophenanthrene	–	–0.176	–
Fluorene	–0.279 ^a	0.153	–0.432
Anthracene	–1.140 ^a	–0.365	–0.775
Pyrene	–1.821 ^b	–1.03	–0.791
Chrysene	–3.770 ^a	–2.504	–1.266
Phenanthrene	–1.097 ^a	–0.359	–0.738
Benz[a]anthracene	–3.265 ^b	–2.524	–0.741
Triphenylene	–3.622 ^a	–2.840	–0.782

^a Lei et al. (2002).

^b Hinckley et al. (1990).

Table 5

1-Octanol–water partition coefficients, at $T = 298.15$ K. Overview of the spread of experimental literature data and selected values (Mackay et al., 2006, except ^a), and COSMOtherm results, both from partition coefficient calculations ($\log K_{OW}$ (COSMO)) and from the QSPR-approach, using implemented Abraham's linear free energy relationships, as well as the respective deviations from the reported literature values.

PAH	$\log K_{OW}$ (exp; 298.15 K)	$\log K_{OW}$ (selected; 298.15 K)	$\log K_{OW}$ (COSMO)	Deviation (exp–COSMO)	$\log K_{OW}$ (COSMO-Abraham)	Deviation (exp–COSMO-Abraham)
Naphthalene	3.10–3.77	3.37	3.07	0.30	3.20	0.17
Biphenyl	3.16–4.29	3.90	3.74	0.16	3.84	0.06
m-Terphenyl	–	5.52 ^a	5.42	0.10	5.59	–0.07
Fluoranthene	4.47–5.23	5.22	4.43	0.79	4.74	0.48
Acenaphthene	3.92–4.49	3.92	3.64	0.28	3.69	0.23
9,10-Dihydroanthracene	–	–	4.07	–	4.12	–
9,10-Dihydrophenanthrene	–	–	4.18	–	4.27	–
Fluorene	3.68–4.32	4.18	3.82	0.36	3.92	0.26
Anthracene	3.45–5.34	4.54	4.05	0.49	4.29	0.25
Pyrene	4.50–5.52	5.18	4.30	0.88	4.61	0.57
Chrysene	5.50–5.91	5.60	4.85	0.75	5.24	0.36
Phenanthrene	4.28–4.67	4.57	3.96	0.61	4.22	0.35
Benz[a]anthracene	5.33–5.91	5.91	4.95	0.96	5.31	0.60
Triphenylene	4.83–6.27	5.49	4.73	0.76	5.20	0.29

^a Yaws (1999).

0.409 (biphenyl) are obtained, which compare with the ones derived from experiment (0.31 for naphthalene (Van Noort, 2004) and 0.361 for biphenyl, with the Gibbs free energy of fusion expression derived from experimental heat capacities, as described in Allen et al. (1999), considering experimental heat capacity data for the liquid state (Chirico et al., 1987a,b) and the solid state (O'Rourke and Mraw, 1983). Provided that information about the Gibbs free energy of fusion is available, COSMOtherm facilitates a good estimation of a compound's volatility in its solid state.

3.3. Octanol–water partition coefficient

At $T = 298.15$ K, a quotient of molar volumes $V_{w,m}/V_{o,m}$ of 0.1142 was considered in the octanol–water partition coefficient predictions, corresponding to a water phase and a wet 1-octanol phase, with “wet 1-octanol” standing for a content of 0.24 mol fractions of water. The trans- and gauche-conformers of 1-octanol were taken into account (Palombo et al., 2006). The results are listed in Table 5, together with compiled values of Mackay et al. (2006).

Additionally, the COSMOtherm σ -moments correlate with a variety of properties, including octanol–water partition coefficients, which is applied in COSMOtherm's automatic QSPR calculation section. The current COSMOtherm release includes an octanol–water partition coefficient property file parameterized on the Turbomole BP-SVP-AM1 COSMO level only, as well as a number of QSPR property files holding QSPR coefficients for the five Abraham parameters (Abraham, 1993), based on group contributions, and the definition of thermodynamic partition properties via the six Abraham coefficients, for both computational COSMO levels BP-SVP-AM1 and BP-TZVP (Zissimos et al., 2002). For comparison, Table 5 lists the results of the latter method, as well.

COSMOtherm's automatic partition coefficient calculations yield somewhat lower octanol–water partition coefficients than reported in the literature, with a deviation of 0.639 log-units (rms) and the largest deviation for benz[a]anthracene (0.96 log-units), which compares to the reported parameterization data set deviations (0.471 (rms) and 0.723 (max) $\log K_{OW}$) (Eckert and Klamt, 2002). The QSPR-approach gives $\log K_{OW}$ -values more close to the reported ones, with a deviation of 0.395 log-units (rms) and the largest deviation for benz[a]anthracene (0.60 log-units).

4. Conclusions

The predictive capability of the conductor-like screening model for real solvents (COSMO-RS) method, in its COSMOtherm imple-

mentation, along with DFT/COSMO calculations at the BP86 density functional and the TZVP-basis set, was tested on a set of 12 polycyclic aromatic hydrocarbons and two related aromatic hydrocarbons, with the aim to obtain physico-chemical properties of environmental relevance. Accurate quantitative knowledge of parameters describing partition phenomena, like coefficients of substance partitioning between the liquid and gaseous phase, are fundamental in interpretation and modelling of environmental fate. (Subcooled) Vapor pressures, Henry's law constants as well as the octanol–water partition coefficients of the selected substances were estimated, though the main focus of the work was on predictions of temperature-dependent aqueous solubilities.

With the chosen approach, one is able to predict the temperature dependence of the aqueous solubilities of polycyclic aromatic hydrocarbons and related aromatic hydrocarbons studied here with accuracy acceptable for many purposes. In comparison with other predictive methods, aqueous solubility data are obtained without any additional adjustable parameter. Of high importance for the prediction of aqueous solubilities is the availability of accurate thermodynamic melting point data. The model works particularly well for small fused rings, as well as for aromatic hydrocarbons where the rings are not annealed.

Given the background of scattered literature data caused by known difficulties in experimental determinations, satisfactory results were obtained in the prediction of Henry's law constants as well as for 1-octanol–water partition coefficients. Vapor pressures of the subcooled liquid, which are frequently inaccessible with direct experimental methods and which are applied in Henry's law constant estimations, are reasonably well predicted by COSMO-RS/COSMOtherm. The predicted Henry's law constants are overestimated, relative to the selected values of Mackay et al. (2006), with a root mean square (rms) deviation of 0.30 log-units, compared to the rms-deviation of 0.38 log-units reported occurring in a COSMO-RS validation set of 150 compounds (Eckert and Klamt, 2002), and a maximum deviation of 0.89 $\log(k_{H,2})$ units, found for chrysene (versus 0.75 log-units of forementioned validation set).

The estimation of octanol–water partition coefficient yield slightly lower values than found in the literature, with a deviation of 0.639 log-units (rms).

To obtain more accurate predictions of physico-chemical properties from statistical COSMO-RS thermodynamics, quantum chemical calculation at a higher-level of theory and a larger basis set might be an imperative in future advancements of the method. Even though, in summary it can be said, that COSMO-RS represents an interesting alternative and possible auxiliary to existing prediction methods.

Acknowledgments

Mariana B. Oliveira acknowledges Fundação para a Ciência e a Tecnologia (FCT) through her PhD (SFRH/BD/29062/2006) scholarship. Marisa A.A. Rocha appreciates financial support of FCT for project PTDC/EQU-FTT/65252/2006. Bernd Schröder is grateful to FCT and the European Social Fund (ESF) under the 3rd Community Support Framework (CSF), for the award of a Post-Doc scholarship SFRH/BPD/38637/2007.

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