Thermodynamic Modeling of the Aqueous Solubility of PAHs

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Polycyclic aromatic hydrocarbons (PAHs) are a family of compounds characterized by having two or more condensed aromatic rings. They are important environmental contaminants associated with oil spills and the incomplete combustion of organic materials. Different models are available in the literature for estimating the aqueous solubilities of organic compounds, but the most accurate are frequently based on the correlation of experimental data, which hampers their use as predictive tools. In this work, the cubic-plus-association equation of state (CPA EoS) is shown to be an accurate model for describing the aqueous solubilities of several solid PAHs in wide temperature and pressure ranges. The results obtained are in very close agreement with the literature data, even when the model is used in a totally predictive scheme. Following previous results on the aqueous solubilities of other organic pollutants, the use of the CPA EoS for describing the aqueous solubilities of organic pollutants such as polycyclic aromatic hydrocarbons is suggested.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are globally distributed environmental contaminants that have been a focus of great concern due to their known toxic and bioaccumulative effects. In humans, health risks associated with PAH exposure include cancer and DNA damage.

The major sources of PAHs in the environment are human activities. In the marine environment, these include oil spills from tankers, oil discharges by ships, and offshore oil and gas exploration.[1] PAHs can also be found associated with bitumen and asphalt production plants, paper mills, aluminum production plants, and industrial machinery manufacturing. There are however also sources of naturally occurring PAHs such as bush fires or forest fires, natural sources of coal, and hydrocarbon seepage and releases from active volcanoes.[1]

PAHs are often resistant to biological degradation and are not efficiently removed by conventional physicochemical methods such as coagulation, flocculation, sedimentation, filtration, and ozonation.[2] As a result, they are persistent in the environment and show a tendency to accumulate in soils and sediments, and are also highly dispersed by the atmosphere.

Because of their importance and toxic behavior, their solubilities in different solvents are of considerable interest, yet their aqueous solubilities are understandably the most important. Knowing their solubilities in water is fundamental for assessing the extent and rate of dissolution of these xenobiotics and their persistence in the environment.

Unfortunately, limited experimental solubility data for these compounds are available in literature. Hence, having a thermodynamic model able to accurately and consistently describe the thermodynamic properties for PAHs, in particular their aqueous solubilities, would be an essential step that would allow better monitoring of these xenobiotics.

A number of approaches to the description of the phase equilibria of these compounds have been attempted. For the aqueous solubility of PAHs, models that can correlate it with a specified property of the pollutant were successfully proposed by several authors. For example, Lu et al.[3] developed two quantum chemical descriptor models to describe the water solubilities of 32 PAHs. Zhao et al.[4] and Chu et al.[5] used simple linear equations establishing that the compound(s) under study must be characterized into a proper category of chemicals. Equations based on mobile order theory modified from Ruelle and Kesselring were also used to correlate water solubilities of 19 PAHs.[6] However, these models only consider the aqueous solubility at one temperature (25 °C) to calculate the descriptors or to establish the correlations between the solubility and, for instance, the partition coefficients. Only Paasivirta et al.[6] developed temperature-dependent relations but still within a limited temperature range (0–30 °C).

Thermodynamic models such as equations of state can also be used for evaluating the aqueous solubilities of PAHs. 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 the statistical associating fluid theory (SAFT)[7] and the cubic-plus-association (CPA).[8-10] The group contribution method for the SAFT pure compound parameters proposed by Tamouza et al.[11] was used for the calculation of vapor pressures and saturated liquid volumes of pure PAHs using three versions of SAFT: PC-SAFT,[12,13] SAFT-VR,[14] and a slightly modified version[15] of the original SAFT. Results for the vapor pressure and liquid saturation volume compared well with experimental data. The prediction of some binary mixtures with other PAHs, heptane, and toluene, were in agreement with the experimental data within a few percent.[16] This model has, however, never been used to describe the aqueous solubilities of PAHs.

The cubic-plus-association (CPA) equation of state (EoS) combines the Soave–Redlich–Kwong (SRK) cubic term for describing the physical interactions with Wertheim's first-order perturbation theory, which can be applied to different types of hydrogen bonding compounds.[9] The fact that the SAFT EoS and CPA EoS explicitly take into account the interactions encountered in mixtures of associating compounds makes them applicable to multicomponent, multiphase equilibria for systems

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containing associating components. The CPA EoS performs superiorly for aqueous systems, as shown by several authors,[9,10,17−23] and is also mathematically simpler, thus substantially simplifying and accelerating the phase equilibrium calculations when compared with the SAFT EoS. The CPA EoS was previously applied to the phase equilibrium of mixtures containing alcohols, glycols, water, amines, organic acids, and aromatic or olefin hydrocarbons.[9,10,17,18,21,22,24,25] This model has also been shown to be able to take into account the solvation phenomena occurring between water and aromatic hydrocarbons, olefinic hydrocarbons,[18] aromatic perfluorocarbons,[26] and esters.[23]

In this work, it will be shown that the CPA EoS can provide an accurate description of the aqueous solubilities of PAHs, using only a single, temperature-independent, association volume (solvating) parameter, β_{ij}.

One of the major advantages of an EoS-based model compared to G^E models or simple correlations is that it allows the prediction of the solubilities in wide ranges of pressures and temperatures. This is increasingly of importance as subcritical water has been increasingly used as a green extraction solvent to remove PAHs and pesticides from highly contaminated soils.[27−31] These processes rely on the decrease of water polarity with increasing temperature. Increasing the temperature with pressure to keep water in the liquid state has a dramatic effect on the solubilities of nonpolar compounds. Depending on the temperature, it can be very effective to selectively extract a variety of polar or nonpolar organic compounds from many different matrixes. The possibility to accurately describe aqueous PAH solubilities at high temperatures and pressures will help in better understanding the mechanisms of the pressurized hot water extraction of PAHs. The adequate representation of the solute + subcritical water phase behavior is important to select the optimum extraction conditions.

A good representation of the phase equilibria of water + PAH systems at high pressures is also important for other environmental purposes. As discussed previously, PAHs can be introduced in the marine environment during offshore oil and gas production and natural hydrocarbon seepage from reservoirs. Leaks during exploration of oils have hazardous consequences for profound sea overall biotic community structure, thereby affecting the health of the ecosystems exposed to these contaminants. Tracing the aqueous phase concentrations of PAHs in equilibrium allows simulation of mass transfer processes supporting response decisions in contamination scenarios and possible remediation strategies.[32]

Previous attempts to correlate these aqueous solubilities at elevated pressures were based only on straightforward relations for the temperature dependence of the solubilities, or on activity coefficient models such as UNIFAC.[28]

In this work it will be demonstrated that the CPA EoS can also be successfully used as a predictive tool for modeling the solubility of solid polycyclic aromatic hydrocarbons in pressurized hot water.

2. Model

The CPA EoS, proposed by Kontogeorgis and co-workers,[8−10] combines a physical contribution (from the Soave−Redlich−Kwong (SRK) or the Peng−Robinson (PR) equation of state) with an association contribution, originally proposed by Wertheim and used in other associating equations of state such as SAFT, accounting for intermolecular hydrogen bonding and solvation effects.[20,33,34] In terms of the compressibility factor the CPA EoS can be expressed as

$$Z = Z^{phys} + Z^{assoc} = \frac{1}{1 - b\rho} - \frac{a\rho}{RT(1 + b\rho)} - \frac{1}{2}\left(1 + \rho\frac{\partial \ln g}{\partial \rho}\right)\sum_i x_i \sum_{A_i}(1 - X_{A_i}) \quad (1)$$

where a is the energy parameter, b is the co-volume parameter, ρ is the molar density, g is a simplified radial distribution function,[19] X_{A_i} represents the mole fraction of component i not bonded at site A, and x_i is the mole fraction of component i.

The key element of the association term, X_{A_i}, is related to the association strength $\Delta^{A_iB_j}$ between two sites belonging to two different molecules, site A on molecule i and site B on molecule j, and is calculated by solving the following set of equations:

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j}\Delta^{A_iB_j}} \quad (2)$$

where $\Delta^{A_iB_j}$ is expressed as

$$\Delta^{A_iB_j} = g(\rho)\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right) - 1\right]b_{ij}\beta^{A_iB_j} \quad (3)$$

$\varepsilon^{A_iB_j}$ and $\beta^{A_iB_j}$ are the association energy and the association volume, respectively.

The simplified radial distribution function, $g(\rho)$ is given by[19]

$$g(\rho) = \frac{1}{1 - 1.9\eta}; \qquad \eta = \frac{1}{4}b\rho \quad \text{and} \quad b_{ij} = \frac{b_i + b_j}{2} \quad (4)$$

The pure component energy parameter of the CPA EoS is given by a Soave-type temperature dependency, while b is temperature independent:

$$a(T) = a_0[1 + c_1(1 - \sqrt{T_r})]^2 \quad (5)$$

where $T_r = T/T_c$; T_c is the critical temperature.

These $\varepsilon^{A_iB_j}$ and $\beta^{A_iB_j}$ parameters, characteristic of associating components, and the three additional parameters of the SRK term (a_0, b, c_1) are the five pure compound parameters (a_0, c_1, b, ε, β) of the model. They are obtained for each component, by fitting experimental vapor pressure and liquid density data. For non-associating components, such as hydrocarbons, only the three parameters of the SRK term are required, which can either be obtained from vapor pressures and liquid densities or be calculated in the conventional manner (from critical data and the acentric factor).

When fitting the pure component parameters, the objective function used is

$$OF = \sum_i^{NP}\left(\frac{P_i^{exp} - P_i^{calc}}{P_i^{exp}}\right)^2 + \sum_i^{NP}\left(\frac{\rho_i^{exp} - \rho_i^{calc}}{\rho_i^{exp}}\right)^2 \quad (6)$$

When the CPA EoS is extended to mixtures, the energy and co-volume parameters of the physical term are calculated employing the conventional van der Waals one-fluid mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij}; \qquad a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \quad (7)$$

where k_{ij} is a binary interaction parameter fitted from binary equilibrium data and

$$b = \sum_i x_i b_i \quad (8)$$

Although aromatic hydrocarbons are themselves non-self-associating, it is well-known that aromatic compounds are able to cross-associate (solvate) with water.[35,36] For extending the CPA EoS to mixtures containing cross-associating molecules, combining rules for the cross-association energy ($\varepsilon^{A_iB_j}$) and cross-volume parameters ($\beta^{A_iB_j}$) are required.[37] Different sets of combining rules have been proposed by several authors,[37−40] including not solely for $\varepsilon^{A_iB_j}$ and $\beta^{A_iB_j}$ but also for the cross-association strength, $\Delta^{A_iB_j}$.

For systems of aromatic(s) + water, as is the case of the systems studied in this work, only water is a self-associating molecule; thus, a different procedure is required. Folas et al.[18] proposed a methodology for dealing with these solvating phenomena. The cross-association energy between aromatic hydrocarbons and water is taken as half the water association energy, and the cross-association volume ($\beta^{A_iB_j}$) is used as an adjustable parameter, fitted to equilibrium data. This methodology has been successfully applied to mixtures with water or glycols and aromatic or olefinic hydrocarbons.[17,18]

For estimating the $\beta^{A_iB_j}$ parameter, the following objective function was employed:

$$\text{OF} = \sum_i^{\text{NP}} \left(\frac{x_i^{\text{calc}} - x_i^{\text{exp}}}{x_i^{\text{exp}}} \right)^2 \tag{9}$$

where single phase or all phase data can be selected during the parameter optimization.

Following previous suggestions, for water a four-site (4C) association scheme is adopted, considering that hydrogen bonding occurs between the two hydrogen atoms and the two lone pairs of electrons in the oxygen of the water molecule.[10] For aromatics a single association site is considered, cross-associating with water, as suggested by theoretical and experimental evidence.[35,36]

The thermodynamics of the solid−liquid equilibrium (SLE) is well established in the literature.[41] The solubility of a solute s can be calculated from the following generalized expression that relates the reference state fugacities:

$$\ln \frac{f_s^{\text{liq}}(T,P)}{f_s^{\text{sol}}(T,P)} = \frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right) - \frac{\Delta C_p}{R}\left[\frac{T_m}{T} - \ln\left(\frac{T_m}{T}\right) - 1\right] \tag{10}$$

where $\Delta_{\text{fus}}H$ is the solute enthalpy of fusion, T is the absolute temperature, T_m is the solute melting temperature, ΔC_p is the difference of the liquid and solid molar heat capacities, and R is the gas constant. In this expression the formation of a pure solid phase is considered, there are no solid−solid phase transitions, the solute ΔC_p term is constant in the temperature range $[T - T_m]$, and the Poynting term correction is neglected; as well, the effect of pressure on T_m, ΔC_p and $\Delta_{\text{fus}}H$ is considered. For solid−liquid equilibria, pressure changes usually do not have important effects on equilibria unless the pressure changes are very large (10−100 MPa).[41]

It was observed that the heat capacity contribution can be neglected with respect to the enthalpic term, and consequently the following expression for the solubility is obtained, while using an equation of state:

$$x_s = \frac{\varphi_s^{L0}}{\varphi_s^L} \exp\left[-\frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \tag{11}$$

where φ is the fugacity coefficient and subscript "0" refers to a pure component.

3. Results and Discussion

The PAHs studied in this work are all non-self-associating. The CPA parameters for these pure compounds are thus only three parameters required for the physical part of the EoS.

Through a simultaneous regression of vapor pressure and liquid density data, collected from the DIPPR database[42] covering the range of reduced temperatures from 0.45 to 0.85, the three parameters of the physical part (a_0, b, c_1) of the CPA EoS were estimated.

The pure compound parameters for 25 polycyclic aromatic hydrocarbons (and water) are reported in Table 1. A good description of vapor pressures and liquid densities of PAHs is achieved with the CPA EoS, with a global average deviation of 1.1% for vapor pressures and 1.4% for liquid densities.

Having estimated the pure compound parameters, it is possible to describe aqueous solubilities. An extensive literature search to collect experimental solubility data of PAHs in water, as a function of temperature, was carried out, and it was possible to collect data for the solubilities of 11 PAHs: fluorene, biphenyl, triphenylene, benz[a]anthracene, naphthalene, anthracene, pyrene, fluoranthene, chrysene, acenaphthene, and phenanthrene. Data for these systems at ambient pressure were available in the temperature range 273.15−348.15 K.[43−52] Thermophysical properties for the studied PAHs are reported in Table 1.

The data available at ambient pressure present considerable scatter, and strong discrepancies among the various authors can easily be found. For instance, for pyrene at 298.15 K, the deviation that can be found between the experimental values collected from literature can be as high as 35%.

In order to reduce the deviations due to this data scattering, the choice of the most adequate data was done by producing the van't Hoff plots of the solubility, $\ln(x)$ vs $1/T$, and rejecting the data that deviate significantly from linearity. Correlations of the aqueous solubility thus obtained for each compound are reported in Table 2, and from this point forward all the data that were used for modeling purposes were obtained from these correlations. Moreover, a number of compounds showed solubility data going through a minimum at temperatures lower than the ambient temperature. These data were also discarded as the CPA EoS, like other thermodynamic models and linear relations, is not able to adequately describe this region.

For fluorene, benz[a]anthracene, and triphenylene no liquid density data were available, so their pure compound parameters were considered to be equal to the ones of the PAH with the same number of aromatic rings: biphenyl for fluorene and chrysene for benz[a]anthracene and for triphenylene. Also for these two last compounds no critical temperature data were available, and estimates were thus generated from the group contribution model proposed by Marrero and Pardillo.[53]

The first approach to the modeling of the aqueous solubility of PAHs with the CPA EoS was carried out in a completely predictive manner, using k_{ij} (eq 7) and the solvation parameter β_{ij} (eq 3) equal to zero. The deviations thus obtained between the CPA predictions and the experimental data are reported in Table 3. A global average deviation of 59% was obtained. These results are quite impressive as we should note that these compounds present mole fraction aqueous solubilities on the order of 10^{-5} or even smaller, suggesting that an excellent description could be achieved by further taking into account the cross-association between PAHs and water.

In order to consider this water−aromatic ring cross-association, solvation parameters for each binary PAH + water were regressed from the experimental solubility data. The results for the β_{ij} parameter and CPA deviations are presented in Table 4.

Table 1. Pure Component CPA Parameters, Deviations in the Description of Saturation Pressures and Liquid Densities, and Values of Critical Temperature (T_c), Normal Melting Temperature (T_m), and Enthalpy of Fusion[42,52,61]

										AAD, %	
compound	T_c (K)	T_m (K)	$\Delta_{fus}H$ (kJ mol^{-1})	a_0 (Pa m^6 mol^{-2})	c_1	b ($\times 10^4$ m^{3}mol^{-1})	V_{vdw} (m^3 kmol^{-1})	ε (J mol^{-1})	β	P^σ	ρ_{liq}
1-ethylnaphthalene	775.36	259.22	16.3	4.92	1.00	1.47	0.10			1.56	0.58
1,2,3,4-tetrahydronaphthalene	719.16	237.39	12.5	3.87	0.91	1.25	0.08			0.97	0.51
1-butylnaphthalene	792.00		25.1	6.25	1.13	1.83	0.12			1.07	1.06
1-nonylnaphthalene	848.50	281.90	−	10.63	1.21	2.79	0.17			0.52	2.66
1-decylnaphthalene	858.50	288.30	−	11.55	1.24	3.00	0.18			0.50	2.87
1-propylnaphthalene	781.58	263.88	17.6	5.71	0.99	1.65	0.11			2.02	1.15
n-hexylnaphthalene	812.73	255.15	24.1	7.79	1.24	2.21	0.14			0.92	1.66
2,6-dimethylnaphthalene	776.29	383.94	23.3	5.14	1.00	1.53	0.10			0.84	1.59
2,7-dimethylnaphthalene	776.63	369.62	23.4	5.16	1.00	1.53	0.10			1.97	1.95
2,6-diethylnaphthalene	807.00	322.15	20.3	6.43	1.06	1.78	0.12			1.37	1.72
1-phenylnaphthalene	849.00	318.15	−	6.95	1.19	2.01	0.12			0.61	1.76
1-n-hexyl-1,2,3, 4-tetrahydronaphthalene	776.00	−	−	8.06	1.21	2.33	0.14			0.95	2.02
1-n-pentylnaphthalene	807.00	318.81	23.4	6.95	1.19	2.01	0.13			1.10	1.17
1-methylnaphthalene	773.52	332.18	9.7	4.37	0.93	1.32	0.09			0.58	0.74
naphthalene	748.49	353.42	19	3.75	0.86	1.17	0.07			0.75	0.46
2-methylnaphthalene	761.05	330.64	17.5	4.50	0.90	1.34	0.09			3.14	0.88
2-ethylnaphthalene	772.25	341.11	14.7	5.07	0.94	1.49	0.10			0.85	0.75
anthracene	875.46	488.78	29.4	6.50	0.88	1.58	0.10			0.48	0.36
pyrene	937.08	423.50	17.4	7.86	0.93	1.77	0.11			0.72	2.87
fluoranthene	915.33	386.54	18.7	7.92	0.88	1.81	0.11			2.56	3.05
acenaphthalene	795.67	531.15	6.9	5.34	1.07	1.61	0.08			0.93	0.63
chrysene	982.38	366.56	26.2	9.19	1.15	2.04	0.13			0.61	2.08
acenaphthene	808.58	372.44	21.5	4.90	0.93	1.37	0.09			0.36	1.10
phenanthrene	871.14	423.38	16.8	6.26	0.93	1.56	0.10			0.48	1.01
biphenyl	773.00	342.20	18.6	4.73	1.01	1.42	0.09			1.01	1.42
benz[a]anthracene	892.29	432.00	22.3								
triphenylene	999.39	473.60	24.2								
fluorene	870.00	387.46	19.6								
water	647.29	273.15	6.00	0.12	0.67	0.145		16655	0.069	1.32	0.59
global AAD, %										1.07	1.39

Table 2. Correlations of Experimental Solubility Data for the PAHs Studied in This Work

compound	correlation	R^2	ref
fluorene	$\ln(x) = -5253.34(1/T) + 2.12$	0.996	50
triphenylene	$\ln(x) = -5347.09(1/T) - 3.44$	0.996	51
benz[a]anthracene	$\ln(x) = -5364.52(1/T) - 3.06$	0.991	51
biphenyl	$\ln(x) = -4776.98(1/T) + 1.95$	0.988	50
naphthalene	$\ln(x) = -4026.38(1/T) + 1.75$	0.982	55, 57−60
anthracene	$\ln(x) = -6698.70(1/T) + 3.34$	0.990	55−60
pyrene	$\ln(x) = -5712.29(1/T) + 0.89$	0.998	55−60
fluoranthene	$\ln(x) = -4541.10(1/T) - 2.47$	0.756	55, 57−60
chrysene	$\ln(x) = -4821.67(1/T) - 6.52$	0.930	55, 57−60
acenaphthene	$\ln(x) = -4899.82(1/T) + 1.79$	0.994	55−60
phenanthrene	$\ln(x) = -5277.20(1/T) + 1.72$	0.991	55−61

Table 3. Deviations between CPA Predictions and Experimental Aqueous Solubility Data for PAHs Using $k_{ij} = \beta_{ij} = 0$

no. of aromatic rings	compound	AAD, %
2	fluorene	35.0
4	triphenylene	81.1
4	benz[a]anthracene	74.9
2	biphenyl	68.0
2	naphthalene	41.9
3	anthracene	60.4
4	pyrene	60.3
3	fluoranthene	84.6
4	chrysene	74.8
2	acenaphthene	32.6
3	phenanthrene	38.8
global AAD, %		59.3

Table 4. Regressed β_{ij} Values and CPA Modeling Results for PAH Aqueous Solubilities

no. of aromatic rings	compound	β_{ij}	AAD, %
2	fluorene	0.0185	2.2
4	triphenylene	0.0985	6.9
4	benz[a]anthracene	0.0693	6.1
2	biphenyl	0.0717	4.6
2	naphthalene	0.0269	5.6
3	anthracene	0.0455	2.6
4	pyrene	0.0403	2.9
3	fluoranthene	0.1425	6.4
4	chrysene	0.0749	11.8
2	acenaphthene	0.0193	9.2
3	phenanthrene	0.0186	4.2
global AAD, %			5.7

deviations of 6% are obtained, lower than the experimental uncertainties.

The very good results obtained for fluorene, benz[a]anthracene, and triphenylene must be highlighted, for which no pure compound liquid density data were available in literature. Using CPA parameters of PAHs with the same number of rings, global average deviations smaller than 5% were obtained for these three PAHs. These good results show that the CPA EoS can be used as a predictive tool for the description of PAH aqueous systems when no liquid density or/and vapor pressure data are available for estimating the CPA pure compound parameters. The good predictive character of the model was already observed previously, for instance, while modeling the water solubility in fatty acid methyl esters.[23]

It should be noted that a previous work[17] on the liquid−liquid equilibria of water + several aromatics showed that the aromatic solubilities in water, using correlated k_{ij} and β_{ij} values, had typical deviations around 20%, thus showing that excellent
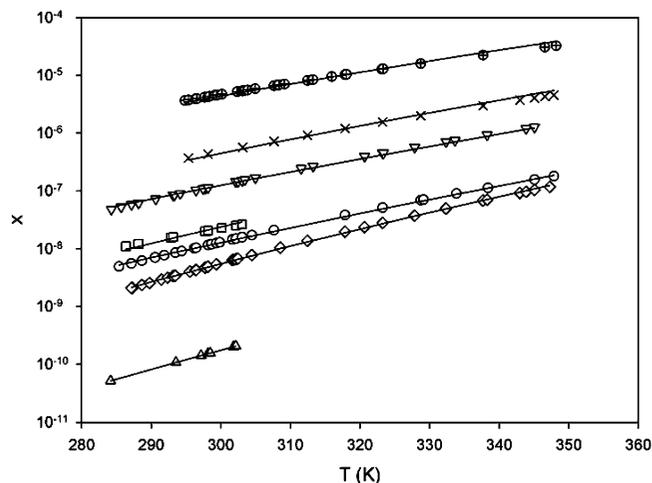
As can be seen, the model seems to correctly take into account the solvation phenomena present in these systems and to accurately describe the temperature dependence of the aqueous solubility of PAHs, as seen in Figure 1. Global average

Figure 1. PAH aqueous solubilities. Experimental ($\bigcirc$, pyrene; $\square$, fluoranthene; $\triangle$, chrysene; $\times$, acenaphthene; $\triangledown$, phenanthrene; $\oplus$, naphthalene; $\diamondsuit$, anthracene) and CPA results (—).

predictions of aqueous solubilities of PAHs are obtained from CPA using a single solvation parameter.

As discussed above, the solubilities of PAHs in pressurized hot water are of importance and the EoS model used here can be easily extended to high pressures.

Experimental data for the compounds previously studied were collected from the literature in pressurized hot water in the temperature range 313.15−498.15 K for pressures from 4 to 6.5 MPa.[49,54−58] A change in temperature affects considerably the solubilities while an increase in pressure results in a minor effect, unless the pressure changes are large. For instance, when the pressure is increased from 6 to 285 bar, the solubility of anthracene decreases only by an order of magnitude.[59]

The values for β_{ij} for each binary system previously estimated were used for the prediction of the solubilities. An excellent prediction of the experimental data was obtained, as shown in Figure 2 and Table 5, with global average deviations smaller than 21%. Higher deviations were obtained for chrysene, as well as before at ambient pressures, but this is among the studied PAHs the one with the lowest mole fraction solubilities, on the order of 10^{-10}. While comparing the modeled solubilities with the literature experimental values, the uncertainty of the experimental data due to the difficulty in measuring accurately such low solubilities should be recalled.
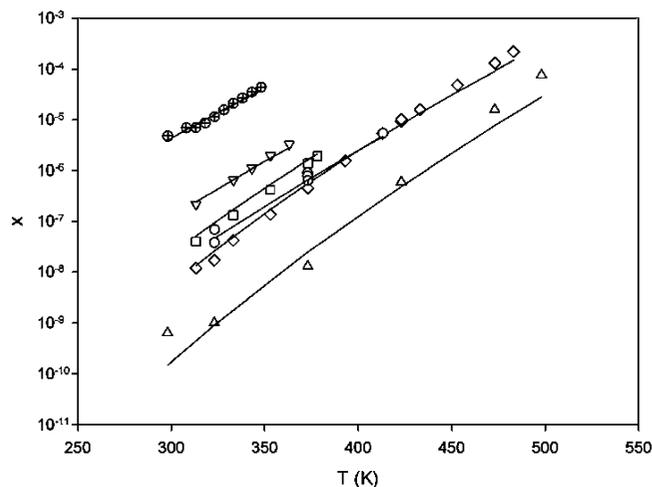

Figure 2. High pressure PAH aqueous solubilities. Experimental ($\bigcirc$, pyrene; $\square$, fluoranthene; $\triangle$, chrysene; $\triangledown$, phenanthrene; $\oplus$, naphthalene; $\diamondsuit$, anthracene) and CPA results (—).

Table 5. CPA Modeling Results for High Pressure PAH Aqueous Solubilities

compound	AAD, %
naphthalene	11.4
anthracene	22.4
pyrene	21.2
fluoranthene	23.5
chrysene	51.6
phenanthrene	8.1
global AAD, %	20.3

Previous attempts to correlate these aqueous solubilities at elevated pressures were based only on straightforward relations for the temperature dependence of the solubilities, or on activity coefficient models such as UNIFAC.[28] Some of the authors providing the experimental data also suggested semiempirical relationships using pure component properties and a first-order group contribution scheme to correlate the solubility of PAHs in pressurized hot water. The reported deviations are much higher than the ones provided by the CPA EoS, 44%, demonstrating the higher accuracy of the thermodynamic model used in this work for describing aqueous binary systems containing PAHs, in comparison with the models based on semiempirical relations.

The ability of the CPA EoS for describing the phase equilibria of the hydrocarbon + water systems was already successfully demonstrated for a large number of compounds in a broad range of pressures and temperatures.[17] The great advantage of this association equation of state is its particular applicability to model solubilities of water and hydrocarbons at high pressures that simple correlations or the excess Gibbs energy models in cubic equation of state mixing rules (EoS G^E), such as the modified Huron−Vidal (MHV2), do not cover.[60]

The very good results obtained for the solubilities of several polycyclic aromatic hydrocarbons in water suggest that the CPA EoS is an adequate model for predicting the aqueous solutions of complex molecules of organic pollutants in a broad range of thermodynamic conditions.

4. Conclusions

In this work the cubic-plus-association (CPA) equation of state was for the first time successfully applied to describe the solubility of several polycyclic aromatic hydrocarbons in water.

CPA pure compound parameters were estimated for 25 PAHs, and very good results for the vapor pressures and liquid densities were achieved, with global deviations below 1.1% and 1.4%, respectively. Pure predictions of the aqueous solubility of PAHs, not taking into account the cross-association between the water and the aromatic ring, are below 60%. If the solvation between a self-associating molecule and a non-self-associating molecule is taken into account using a single fitting parameter, the solubilities can be correlated within 6% deviation.

The capability of the CPA EoS to predict the aqueous solubility of solid polycyclic aromatic hydrocarbons at high pressures was also investigated. It is shown that this model can be used as a predictive tool with global average deviations of only 20% for solubilities of PAHs in pressurized hot water.

The very good predictive performance of the CPA EoS was also shown when successfully modeling the water solubilities of PAHs for which no liquid density data were available, using only the CPA pure compound parameters of other compounds with similar structures. In this manner the CPA EoS can be used to predict many other systems of environmental interest containing less-studied organic contaminants.

The results obtained for the solubility of several polycyclic aromatic hydrocarbons in water are in close agreement with the literature data, suggesting that the CPA EoS is an adequate model for predicting the aqueous solutions of complex molecules of organic pollutants in a broad range of thermodynamic conditions.

Acknowledgment

Nomenclature

a_0 = parameter in the energy term
a_{ij} = cross-interaction energy parameter between molecules i and j
A_i = site A in molecule i
b = covolume parameter
c_1 = parameter in the energy term, dimensionless
g = radial distribution function
k_{ij} = binary interaction parameter
OF = objective function
P = pressure
R = gas constant
T = temperature
T_c = critical temperature
T_m = melting temperature
T_r = reduced temperature
V_m = molar volume
V_{vdw} = van der Waals volume
X_{A_i} = mole fraction of component i not bonded at site A
x_i = liquid mole fraction of component i
Z = compressibility factor

Greek Symbols

ρ = molar density
β_{ij} = solvation parameter
$\Delta^{A_iB_j}$ = association strength
ΔC_p = difference of liquid and solid molar heat capacities
$\Delta_{fus}H$ = enthalpy of fusion
$\beta^{A_iB_j}$ = association volume
$\varepsilon^{A_iB_j}$ = association energy
η = reduced fluid density
φ = fugacity coefficient

Superscripts

exp = experimental
calc = calculated
assoc = association
phys = physical

Subscripts

i, j = pure component indices

Abbreviations

AAD = average absolute deviation ($\%AAD = 1/NP\sum_{i=1}^{NP} ABS[(x_{exp,i} - x_{calc,i})/x_{exp,i}] \times 100$)

CPA = cubic plus association
EoS = equation of state
G^E = excess molar Gibbs energy
MHV2 = second-order modified Huron−Vidal mixing rules
PAHs = polycyclic aromatic hydrocarbons
SAFT = statistical associating fluid theory
SLE = solid−liquid equilibria
SRK = Soave−Redlich−Kwong
UNIFAC = universal functional activity coefficient model

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