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Prediction the Solubility of Polycyclic Aromatic Hydrocarbons in Subcritical Water by Using the CPA EOS

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Abstract The aim of this work is to describe the solubility of polycyclic aromatic hydrocarbons (PAHs) in subcritical water. To achieve this goal, first, a literature survey of the solubilities of PAHs in water and of naphthalene in mixtures of water and ethanol was made. Subsequently, the cubic plus association equation of state was used to describe the solubility of PAHs in the liquid phase. For accurate descriptions of the aqueous solubility of PAHs, the binary interaction parameters and cross-association volumes were regressed based on the experimental solubilities at atmospheric pressure. These regressed parameters are then used for subcritical water. Additionally, these parameters have been determined for the (naphthalene + ethanol) binary system. These regressed parameters have then been applied to predict the solubility of naphthalene in (ethanol + water) solutions. The results of the present model prove that it can be successfully applied for reproducing the solubilities of PAHs in the aqueous phase.

Keywords Polycyclic aromatic hydrocarbons · Subcritical water · CPA EOS · Solubility

List of symbols

a	Attractive parameter in the CPA EOS ($J \cdot m^3 \cdot mol^{-2}$)
AAD	Average absolute deviation (%)
assoc	Association part of the CPA EOS
b	Covolume in the EOS ($m^3 \cdot mol^{-1}$)
calc	Calculated result
exp	Experimental
g	Simplified radial distribution function
i, j	Components i and j
k_{ij}	Binary interaction parameter for the attractive parameter in the CPA EOS

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N	The number of experimental points
p	Pressure (Pa)
phys	Physical part of CPA EOS
R	Ideal gas constant ($J\cdot mol^{-1}\cdot K^{-1}$)
T	Temperature (K)
T_r	Reduced temperature
x_i	Mole fraction of each component i in each phase
X_A	Fraction of molecules not bonded at site A
Z	Compressibility factor
β^{AiBi}	The association volume
ε	The association energy ($J\cdot mol^{-1}$)
Δ	Association strength
η	Reduced density
ρ	Mole density ($mol\cdot m^{-3}$)

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) lead to environmental problems due to their toxicity and bioaccumulation. Also, PAHs cannot be removed by conventional methods such as biological degradation, coagulation, flocculation, sedimentation, filtration, or ozonation, so that the solubility of PAHs in various solvents has been an intriguing subject of researches in recent years. Among different solvents, subcritical water has been selected for most of the investigations because its solvating power dramatically increases when the temperature is above 100 °C [1]. Furthermore, since subcritical water is a nontoxic, inexpensive and readily available solvent, it can be beneficial for extraction of PAHs. Another way of enhancing the solubility of hydrophobic components such as PAHs in subcritical water is to apply an organic co-solvent. As a result, accurate knowledge of PAH solubilities in water is of importance [2, 3].

Although knowing the solubility of PAHs in water is important, values of the experimental solubilities of PAHs in water are limited. Therefore, a reliable thermodynamic model is required for the accurate description of PAH solubilities in water. In recent years, some modeling studies have been conducted on the solubility of PAHs in water. Oliveira et al. [2] modeled the solubility of polycyclic aromatic hydrocarbons (PAHs) in water. They used the cubic-plus-association (CPA) equation of state for the aqueous phase. The accurate results of this model proved that the CPA EOS can successfully describe the solubility of PAHs in the aqueous phase. Teoh et al. [3] utilized a static analytical equilibrium approach for measuring the solubility of anthracene and *p*-terphenyl in subcritical water over the temperatures range (393–473) K and the pressures range (50–150) bar. They concluded that temperature had the most significant influence on the solubility of PAHs in the aqueous phase. Subsequently, they applied the Peng–Robinson equation of state (PR EOS) to reproduce the solubilities of PAHs in subcritical water. The results of their model were in good agreement with experimental data. Raman and Chiew [4] compared the performance of various approaches for describing the phase equilibrium between solid PAHs and sub-critical water. To conduct this modeling investigation, they used different equations of state/Gibbs energy (EOSs/GE). They also compared the results of their model with the results of UNIFAC activity coefficient models. They found that the performance of their model was reasonably good, and the PR-LCVM model gave the best results.

Teoh et al. [5] measured the solubility of anthracene and *p*-terphenyl in a liquid mixture made up of subcritical ethanol and water. The temperatures and pressures of this study were in the range of (393–473) K and (50–150) bar, respectively. The experimental results showed that temperature and ethanol concentration had the most significant influence on the solubility of PAHs in the liquid phase. Then they successfully used the UNIQUAC, OUNIFAC, and M-UNIFAC models to reproduce the solubility of PAHs in the liquid phase. Escandell et al. [6] investigated the performance of the NRTL-PR model to model the solubility of solid PAHs in water. To validate this approach, they first used this model for the phase equilibrium of aromatic hydrocarbons and gasses containing carbon dioxide and ethane. Then they successfully applied their model to the PAH-water phase equilibrium.

Due to the importance of the solubility of PAHs in subcritical water, the present modeling investigation is dedicated to describe the solubility of PAHs including naphthalene, phenanthrene, acenaphthene, anthracene, pyrene, fluoranthene, fluorene, chrysene, *m*-terphenyl, benzo[a]pyrene, and *p*-terphenyl in water. The 4C and 2B association schemes are considered for water and ethanol, respectively. Similar to Oliveira et al. [2], the PAHs are considered as pseudo-associating species that can only have cross-association with water. For an accurate description of the solubility of PAHs in the liquid phase, the binary interaction parameter (k_{ij}) and cross-association volume ($\beta^{A_i B_j}$) have been adjusted according to experimental solubilities of PAHs in the liquid phase. Furthermore, the binary interaction parameters and cross-association volumes have been used for estimation of the solubilities in subcritical water. Also, the interaction parameters and cross-association volumes have been computed for (naphthalene + ethanol) and (ethanol + water) binary mixtures. These parameters are then used to predict the solubility of naphthalene in the (ethanol + water) binary solvent system. The performance of the present model is also discussed.

2 Description of the Model

2.1 CPA Equation of State

As was mentioned in the previous section, in the present modeling study, the CPA equation of state [7–13] has been selected to describe the phase equilibrium of systems made up of water, ethanol, and PAHs. To our knowledge, the CPA EOS has shown good performance for the phase equilibrium of aqueous systems, for example, water–alcohol mixtures.

The compressibility factor of the CPA EOS is composed of two main parts. The first is the physical part relating to the physical interactions between molecules. In this study, the Soave–Redlich–Kwong equation of state (SRK EOS) has been selected for the physical part. The second part relates to association between molecules. This type of association uses the Wertheim association theory [8]:

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

In Eq. 1, α denotes the energy parameter, b is the co-volume parameter, and ρ denotes the molar density of phases. The parameters of the association part, g and X_{Ai}, are the simplified radial distribution function [8] and the mole fraction of non-bonded molecules of i (at site A), respectively.

The most important parameter of the association part, X_{Ai}, is computed by solving Eq. 2.

$$X_{Ai} = \frac{1}{1 + \rho \sum\limits_{j} x_j \sum\limits_{i} X_{B_j} \Delta^{A_i B_j}} \tag{2}$$

The other parameter of the association model, the association strength ($\Delta^{A_i B_j}$), is calculated by using the following equation:

$$\Delta^{A_i B_i} = g(\rho) \left[\exp\left(\frac{\varepsilon^{A_i B_i}}{RT} \right) - 1 \right] b_{ii} \beta^{A_i B_i} \tag{3}$$

In Eq. 3, $\varepsilon^{A_i B_i}$ is the association energy and $\beta^{A_i B_i}$ represents the association volume.

In the present study, a simplified form of the hard-sphere radial distribution, $g(\rho)$, has been used [14]:

$$g(\rho) = \frac{1}{1 - 1.9\eta}, \quad \eta = \frac{1}{4} b\rho, \quad b_{ij} = \frac{b_i + b_j}{2} \tag{4}$$

Similar to previous investigations [7–14], a Soave-type energy parameter has been used for the CPA EOS:

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

In Eq. 5, T_r is the reduced temperature.

The five pure component parameters ($\varepsilon^{A_i B_i}$, $\beta^{A_i B_i}$ for the association term, and a_0, c_1, and b for the SRK term) are obtained for each component by fitting the experimental vapor pressure and liquid density data. For this fitting, the objective function is:

$$OF = \sum_{i}^{N_p} \left(\frac{P_i^{\exp} - P_i^{\text{calc}}}{P_i^{\exp}} \right)^2 + \sum_{i}^{N_p} \left(\frac{\rho_i^{\exp} - \rho_i^{\text{calc}}}{\rho_i^{\exp}} \right)^2 \tag{6}$$

where N_p is the number of experimental points. Subscripts "exp" and "calc" denote experimental data and calculation results, respectively.

In this study, the 4C association scheme has been considered for water:

$$X_A = X_B = X_C = X_D = \frac{-1 + \sqrt{1 + 8\rho\Delta^{AC}}}{4\rho\Delta^{AC}} \tag{7}$$

$$\Delta^{AA} = \Delta^{AB} = \Delta^{BB} = \Delta^{CC} = \Delta^{CD} = \Delta^{DD} = 0 \\ \Delta^{AC} = \Delta^{AD} = \Delta^{BC} = \Delta^{BD} \neq 0 \tag{8}$$

Also, the 2B association scheme has been applied for ethanol.

$$X_A = X_B = \frac{-1 + \sqrt{1 + 4\rho\Delta^{AB}}}{2\rho\Delta^{AB}} \tag{9}$$

$$\Delta^{AA} = \Delta^{BB} = 0 \\ \Delta^{AB} \neq 0 \tag{10}$$

The polycyclic aromatic hydrocarbons (PAHs) are considered as pseudo-associating components. To our knowledge, these components can only have cross-association with water and they do not have self-association [2, 15]. It is known that the cross-association

energy ($\varepsilon^{A_iB_i}$) and cross-volume parameter ($\beta^{A_iB_i}$) are required for cross-associating molecules. In the present model, the cross-association energy between PAHs and water has been set equal to half of the one for water, and the cross-volume parameter is regressed based on the minimization of the average absolute deviation (AAD) of PAHs solubility in the liquid phase:

$$AAD = \frac{1}{N_p} \sum_{i=1}^{N_p} \left(\frac{x_i^{\text{exp}} - x_i^{\text{calc}}}{x_i^{\text{exp}}} \right)^2 \tag{11}$$

In Eq. 11, x_i is the mole fraction of PAH in the liquid phase.

The classical van der Waals mixing rule has been used for the cubic parameters of the CPA EOS:

$$a = \sum_i \sum_j a_{ij} x_i x_j \tag{12}$$

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{13}$$

$$b = \sum_i b_i x_i \tag{14}$$

In Eqs. 11–13, x_i denotes the mole fraction of component i in the liquid phase, and k_{ij} is the binary interaction parameter of the model.

2.2 Solid–Liquid Equilibrium

To describe the solubility PAHs in the aqueous phase, the phase equilibrium has to be considered, so the fugacity (f_2) of solute (PAH) is equal in the aqueous and solid phases:

$$f_2^L = f_2^S \tag{15}$$

in which component 2 is considered as the solute and subscripts L and S denote liquid and solid phases, respectively. The fugacity of the dissolved PAH in the aqueous phase can be expressed in terms of the fugacity of the pure PAH in a liquid state:

$$f_2^L = \gamma_2 x_2 f_2^{L_0} \tag{16}$$

In Eq. 16, γ_2 is the activity coefficient of a PAH in the aqueous phase, x_2 is the mole fraction of PAH in the aqueous phase and $f_2^{L_0}$ represents the fugacity of the pure PAH in its hypothetical liquid state. According to Eqs. 15 and 16, the following equation is obtained.

$$\ln(x_2) = \ln\left(\frac{f_2^S}{f_2^{L_0}} \right) - \ln(\gamma_2) \tag{17}$$

On the other hand, the ideal solubility can be expressed as follows:

$$\ln\left(\frac{f_2^S}{f_2^{L_0}} \right) = \ln\left(x_2^{\text{id}} \right)$$

$$= \frac{\Delta H_{\text{fus}}}{RT_{m_2}} \left(\frac{T_{m_2}}{T} - 1 \right) + \frac{\Delta C_p}{R} \left(\frac{T_{m_2}}{T} - 1 \right) + \frac{\Delta C_p}{R} \ln\left(\frac{T}{T_{m_2}} \right) - \int_{p^{\text{sat}}}^{p} \frac{V_2^L - V_2^S}{RT} dp \tag{18}$$

Here, ΔH_{fus} and T_{m_2} are the fusion enthalpy and normal melting point of the PAH, respectively.

Equation 1 can be simplified by considering the following assumptions: (1) ΔC_p is small, particularly when the operating temperature and melting point of PAH are not very different; (2) the influence of the pressure on the fugacity of the PAH is not significant. Therefore, Eq. 18 can be simplified as follows:

$$\ln\left(x_2^{\text{id}}\right) = \frac{\Delta H_{\text{fus}}}{RT_{m_2}}\left(\frac{T_{m_2}}{T} - 1\right) \tag{19}$$

By substituting $\ln\left(\frac{f_2^{\text{S}}}{f_2^{\text{L0}}}\right) = \ln\left(x_2^{\text{id}}\right)$ in Eq. 17, the following expression is obtained:

$$x_2^{\text{id}} = \gamma_2 x_2 \tag{20}$$

The activity coefficient of a PAH can be also expressed in terns of the fugacity coefficient of the PAH in the aqueous mixture (ϕ_2^{L}) and the corresponding one in the hypothetical liquid state (ϕ_2^{L0}).

$$\gamma_2 = \frac{\phi_2^{\text{L}}}{\phi_2^{\text{L0}}} \tag{21}$$

Based on Eqs. 20 and 21, the following equation is obtained:

$$\ln(x_2) = \ln\left(\frac{\phi_2^{\text{L0}}}{\phi_2^{\text{L}}}x_2^{\text{id}}\right) \tag{22}$$

Combining Eqs. 19 and 22, the following equation can be written:

$$x_2 = \frac{\phi_2^{\text{L0}}}{\phi_2^{\text{L}}}\exp\left(-\frac{\Delta H_{\text{fus}}}{RT_{m_2}}\left(\frac{T_{m_2}}{T} - 1\right)\right) \tag{23}$$

In this work, the fugacity coefficient of the PAH in the aqueous mixture (ϕ_2^{L}) and the one in the hypothetical liquid state (ϕ_2^{L0}) are computed by using the CPA EOS.

3 Results and Discussion

3.1 Pure Fluids

Before applying the CPA EoS for the specified binary and ternary systems, the pure-component parameters of the CPA EOS can be determined based on a simultaneous regression of saturated vapor pressures and liquid densities. Also, the critical properties, liquid density and vapor pressure data are taken from [16]. The CPA equation of state has been applied to naphthalene, phenanthrene, acenaphthene, anthracene, pyrene, fluoranthene, fluorene, chrysene, m-terphenyl, benzo[a]pyrene, and p-terphenyl, and water. The results of these calculations are reported in Table 1. In this table, the normal melting temperature and enthalpy of fusion of the compounds are also presented [17]. One can see that the calculated results are in good agreement with the experimental data.

Table 1 Pure component CPA parameters, deviations in the description of saturation pressures and liquid densities, and values of critical temperature (T_c), critical pressure (P_c), acentric factor, normal melting temperature (T_m), and enthalpy of fusion

Compound	T_c (K)	P_c (bar)	w	T_m (K)	$\Delta_{fus}H$ (kJ·mol⁻¹)	a_0 (Pa·m⁶·mol⁻²)	c_1	b (×10⁴ m³·mol⁻¹)	ε (J·mol⁻¹)	β	AAD (%) P^σ	ρ_{liq}
Naphthalene	748.35	40.51	0.302	353.42	19.00	3.7373	0.8596	1.3307	–	–	0.32×10^{-4}	0.25×10^{-2}
Phenanthrene	869.25	29	0.495	372.15	16.28	6.4284	0.8604	2.1592	–	–	0.88×10^{-4}	0.30×10^{-2}
Acenaphthene	808.58	31	0.381	372.44	21.50	5.3400	1.0704	1.4099	–	–	0.031	0.023
Anthracene	873	29	0.489	488.91	29.37	6.5357	0.8728	2.1685	–	–	0.93×10^{-2}	0.13×10^{-2}
Azulene	773.48	38.97	0.355	–	–	4.2601	0.8053	1.4298	–	–	0.058	0.057
Fluoranthene	905	26.10	0.588	383.34	18.74	7.9620	0.8920	2.4977	–	–	0.49	0.16
Fluorene	870	47	0.349	385.15	18.74	4.3446	0.9300	1.3334	–	–	0.37×10^{-2}	0.75×10^{-2}
Chrysene	979	23.90	0.604	528.65	26.15	9.0333	1.1570	2.9507	–	–	0.42×10^{-2}	0.15
Benzoic acid	751	44.70	0.604	395.55	17.31	3.2474	1.3451	1.2103	–	–	0.04	0.01
m-Terphenyl	924.85	35.06	0.558	360.15	22.59	7.9720	1.2766	1.9002	–	–	0.072	0.028
p-Terphenyl	925.95	33.24	0.528	487.05	35.60	7.9040	1.2883	2.0067	–	–	0.20×10^{-2}	0.022
Water	647.30	221.20	0.344	–	–	0.1214	0.6700	0.1450	16655	0.069	1.35	0.80

3.2 Binary Systems of PAH and Water

This section reports the experimental and modeled solubilities of PAHs in water. These PHAs contain naphthalene, phenanthrene, acenaphthene, anthracene, pyrene, fluoranthene, fluorene, chrysene, m-terphenyl, benzo[a]pyrene, and p-terphenyl. Also, the modeling has been done for the solubility of naphthalene in ethanol. The thermodynamic conditions of experimental data are listed in Table 2. The experimental solubility data over the specified pressure and temperature ranges are taken from [18–22].

As was mentioned above, the present model uses the CPA EOS to determine the phase equilibria of these systems. The PAHs are considered as components that can only have cross-association with water and ethanol, so no self-association has been assumed for the PAHs [2]. Similar to many investigations, the water and ethanol are considered as 4C and 2B scheme fluids, respectively. Based on the available experimental solubilities at atmospheric pressure, the constant binary interaction coefficients (k_{ij}) (independent of temperature), and cross-volume parameters (β_{ij}), are regressed only for atmospheric pressure but they are used for high pressures. The results of the correlations are presented in Table 3.

Based on Table 3, it is found that the modeling results are in good agreement with the experimental solubility data. The average absolute deviations of the solubilities are between 3.51 and 26.18% for these specified systems. The computed solubilities versus

Table 2 k_{ij} and β_{ij} values and CPA modeling results at atmospheric pressure

Compound (+ water)	T (K)	P (bar)	N_p	k_{ij}	β_{ij}	AAD (%)
Naphthalene	298.35–318.05	1	5	− 0.0772	0.0211	2.2788×10^{-2}
Phenanthrene	277.15–303.05	1	9	− 0.2156	0.0117	0.55
Acenaphthene	295.35–347.85	1	13	− 0.0071	0.0116	6.6209×10^{-2}
Anthracene	278.35–301.85	1	7	− 0.1971	0.0656	1.1194×10^{-2}
Pyrene[a]	277.85–303.05	1	7	− 0.1498	0.0106	2.17
Fluoranthene	281.25–303.05	1	5	− 0.2273	0.0525	0.55
Fluorene	279.75–304.25	1	6	− 0.0123	0.0188	0.13
Chrysene	279.65–301.85	1	6	− 0.2447	0.0564	0.15
m-Terphenyl	287.00–322.00	1	8	0.0132	0.0125	1.5
Benzo[a]pyrene[a]	283.15–303.15	1	5	− 0.2018	0.0090	8.55

[a]For pyrene and benzo[a]pyrene, the three parameters of the SRK term (a_0, c_1, b) are calculated in the conventional manner (from critical data and the acentric factor)

Table 3 CPA modeling results for high pressure

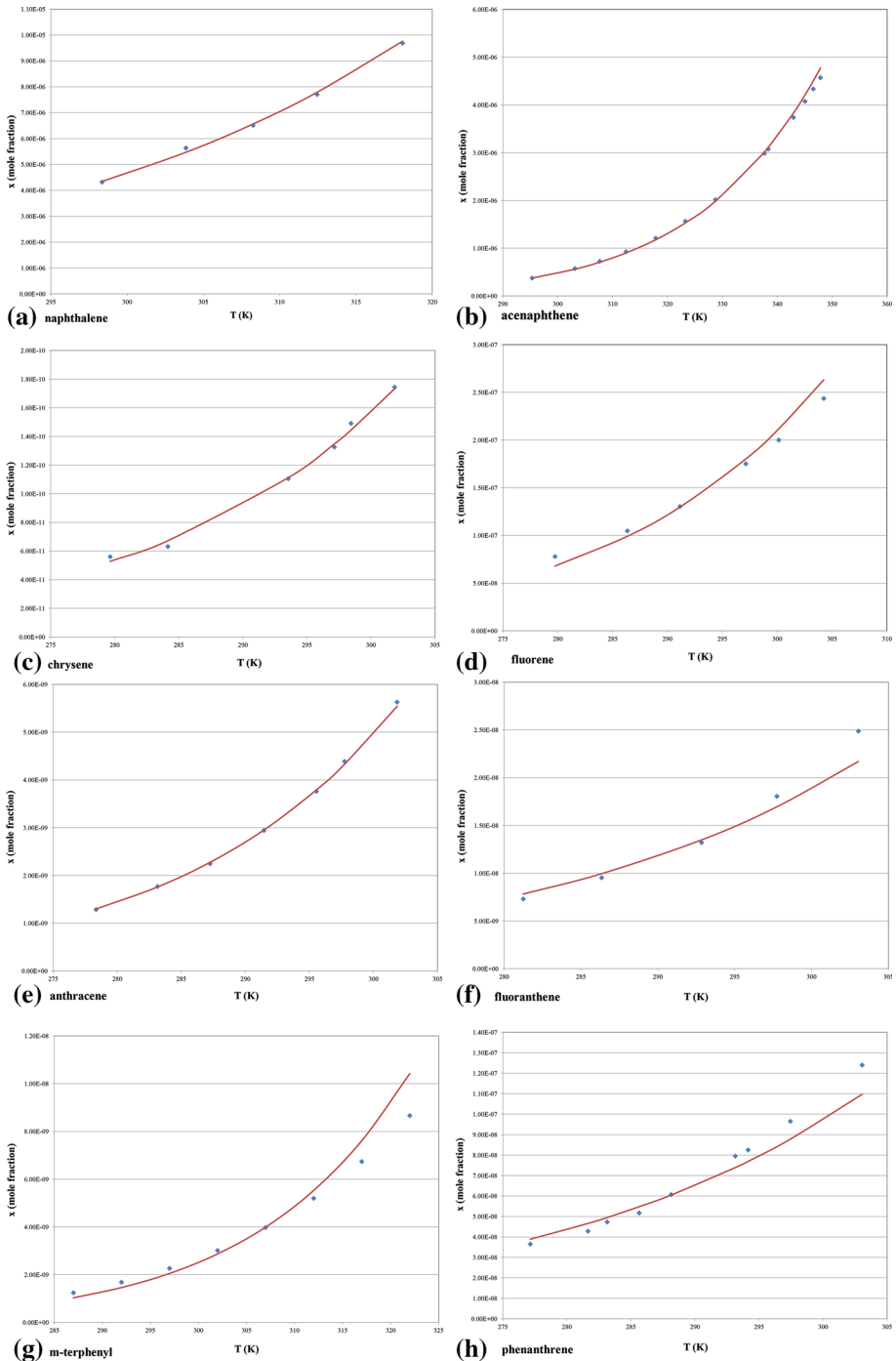| Compound (+ water)	T (K)	p (bar)	N_p	AAD (%)
Naphthalene	313.2–348.2	50	8	3.51
Phenanthrene	313.2–363.2	50	5	13.01
Anthracene	313.2–433.2	50	7	22.32
Fluoranthene	313.2–378.2	50	5	26.18
Fluorene	313.2–383.2	50	6	6.91
p-Terphenyl	393.15–473.15	50	7	10.03

Fig. 1 PAH aqueous solubilities at atmospheric pressure: experimental (diamond) and CPA (continuous line) results
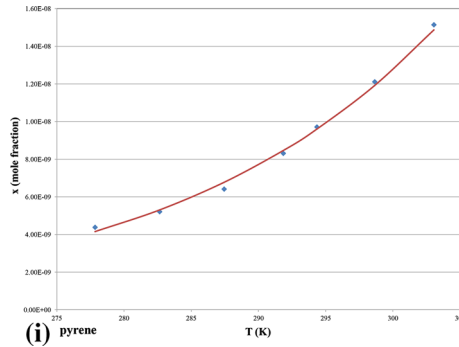
Fig. 1 continued

temperatures at atmospheric pressure and high pressures are presented in Figs. 1 and 2, respectively.

3.3 Ternary System of (Water + Ethanol) + Naphthalene

In the previous section, the results for the binary mixtures show the accuracy and reliability of the present model for these mixtures. Hence, the present model can be applied to predict the phase equilibrium for ternary mixture of (water + ethanol) + naphthalene. The constant binary interaction coefficients and cross-volume parameters regressed in the previous section are used in this section for prediction. Also, modeling has been done for the solubility of naphthalene in pure ethanol. For the binary system naphthalene + ethanol, k_{ij} is obtained equal to 0.007 with AAD of 0.79%. To our knowledge, the available binary interaction coefficient of (water + ethanol) binary mixture is taken from Folas et al. as equal to $-$ 0.11 [23]. The experimental phase equilibrium data are taken from [24]. The temperature range of this ternary system is in the range of (298.25–318.05) K. Table 4 compares the experimental phase equilibrium data and the results of the present model for (water + ethanol) + naphthalene at the specified temperatures and atmospheric pressure. The *AAD* values are 1.39, 9.22 and 12.53% for this ternary system when the present model is used. These results prove that the applied model is capable of predicting the solubility of naphthalene in water + ethanol solutions. Aqueous solubilities of naphthalene in (water + ethanol) solutions at various mole fractions of ethanol (water) are shown in Fig. 3. The same method has been applied in the previous work for predicting the solubility of β-carotene in subcritical (water + ethanol) solutions [25].

4 Conclusions

The cubic-plus-association equation of state (CPA EOS) was applied to describe the phase equilibrium of PAH/water binary systems and (water + ethanol) + naphthalene ternary mixtures. First, the binary interaction coefficients and cross-volume parameters of the PAH/water and naphthalene/ethanol binary systems were fitted based on the experimental solubility of PAHs. After the successful performance of the present model was obtained for
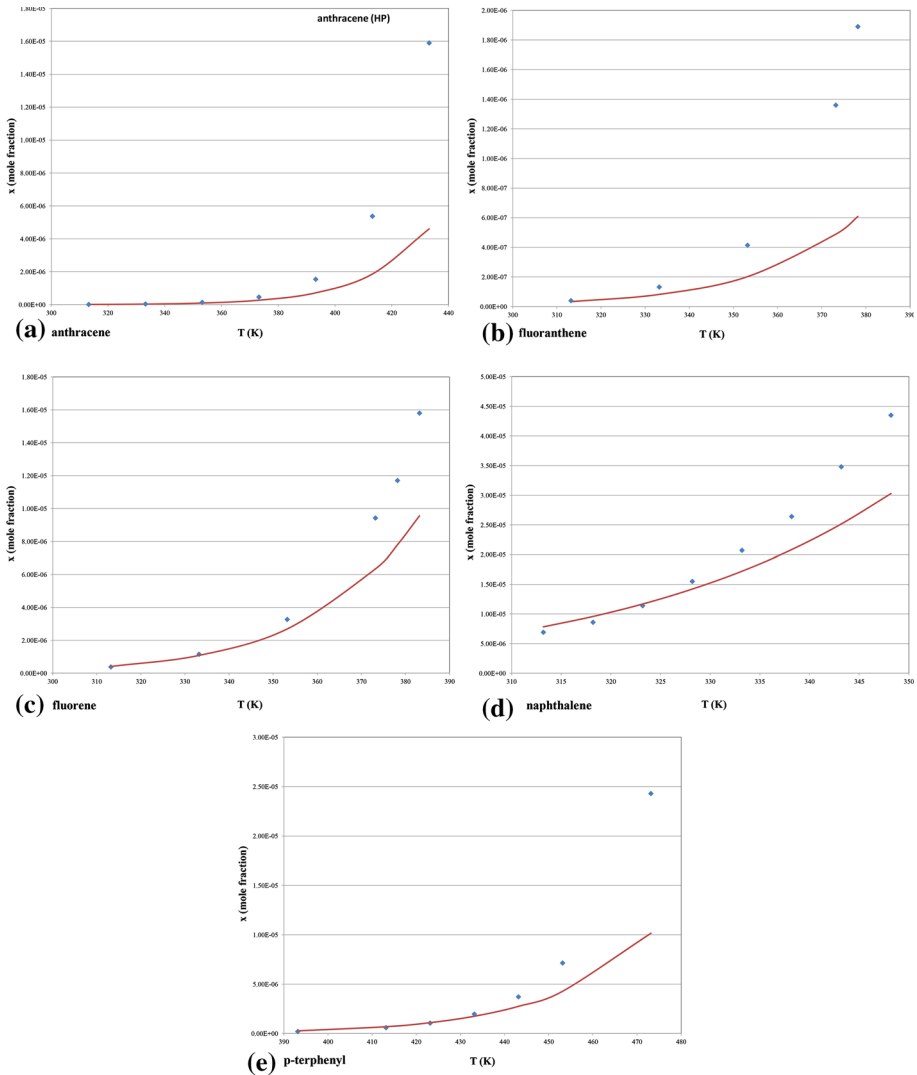
Fig. 2 PAH aqueous solubilities at pressure of 50 bar: experimental (diamond) and CPA (continuous line) results

binary systems, this model was used for prediction of naphthalene solubility in (water + ethanol) solvent mixtures. The predicted solubilities of naphthalene in (water + ethanol) solutions are in good agreement with the experimental data that were obtained from the literature.

Table 4 CPA modeling results for naphthalene in the (water + ethanol) mixed solvents

Mole fraction of ethanol	T (K)	N_p	AAD (%)
0.0159	298.25–318.05	5	1.39
0.0329	298.55–317.55	4	12.53
0.0508	298.05–317.55	5	9.22
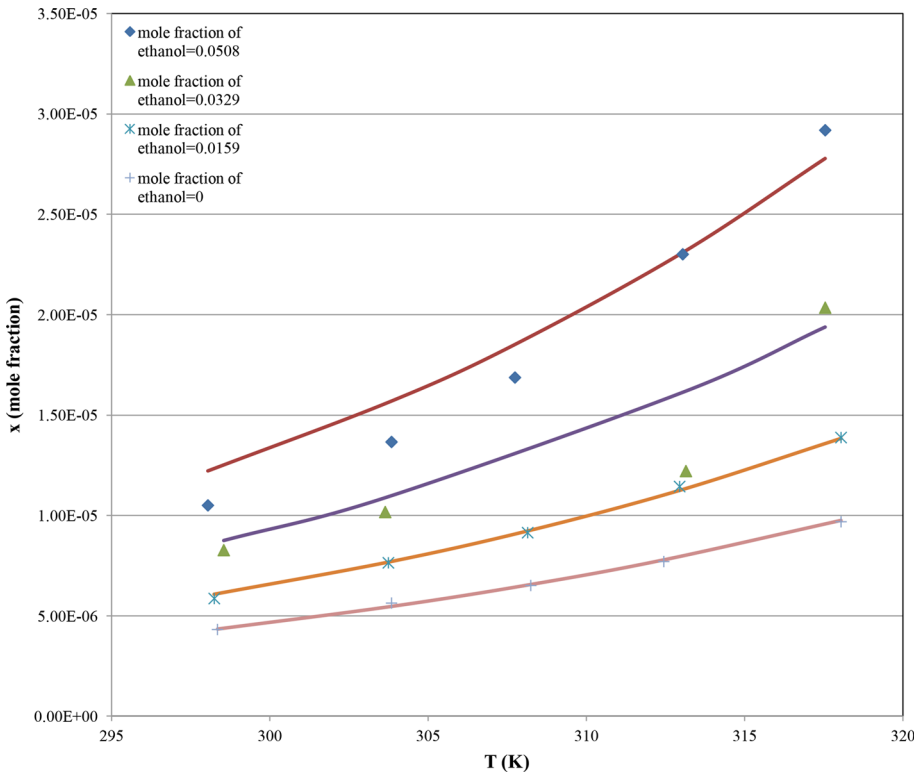
Fig. 3 Naphthalene aqueous solubility in (water + ethanol) solutions at various mole fractions of ethanol (water): experimental (dots) and CPA (solid lines) results

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