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**Modelação da Solubilidade de Compostos
Aromáticos Policíclicos com CPA EoS**

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PAHs with the CPA EoS**



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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Engenharia Química, realizada sob a orientação científica do Professor Doutor João Araújo Pereira Coutinho do Departamento de Química da Universidade de Aveiro e pelo Doutor António José Queimada do Laboratório de Processos de Separação e Reacção da Faculdade de Engenharia da Universidade do Porto.

Dedico este trabalho aos meus queridos pais e à minha extraordinária irmã.

Obrigada por todo o apoio que sempre me deram e continuam a dar.

o júri

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palavras - chave

CPA EoS, Modelação, PAHs, Solubilidade, Água

resumo

Os hidrocarbonetos aromáticos policíclicos (PAHs) constituem uma família de compostos caracterizada por possuírem dois ou mais anéis aromáticos condensados. São no geral referenciados de contaminantes ambientais porque estão associados à combustão incompleta de materiais orgânicos, como por exemplo, a queima de combustíveis fósseis, incineração de resíduos e derrames de petróleo.

O estudo da solubilidade destes compostos em misturas aquosas é de grande importância, devido ao impacto que estes compostos têm na saúde pública e no meio ambiente, dado as suas propriedades cancerígenas.

Neste trabalho, a capacidade da equação de estado CPA para modelar a solubilidade em meio aquoso de vários PAHs numa ampla gama de temperatura, foi avaliada.

Esta equação de estado combina o termo Soave-Redlich-Kwong (SRK) para descrever as interações físicas com a contribuição de associação proposta por Wertheim, também usada em outras equações de estado, tais como as diferentes versões da SAFT. A CPA EoS já foi aplicada com sucesso a sistemas aquosos com alcanos, compostos aromáticos e álcoois.

Os resultados obtidos são muito próximos dos valores encontrados na literatura, sugerindo que a CPA EoS é um modelo adequado para correlacionar soluções aquosas de moléculas complexas de poluentes orgânicos.

keywords**CPA EoS, Modelling, PAHs, Solubility, Water****abstract**

The polycyclic aromatic hydrocarbons (PAHs) are a family of compounds characterized by having two or more aromatic rings condensed. They are referenced in general because they are environmental contaminants associated with the incomplete combustion of organic materials, such as the burning of fossil fuels and incineration of waste, and oil spills.

The solubility of these xenobiotics in aqueous mixtures must be monitored due to their impact on public health and the environment, because of their carcinogenic properties and their ubiquity in the environment.

In this work, the ability of the Cubic-plus-Association equation of state (CPA EoS) for modelling the aqueous solubility of several PAHs in a wide temperature range was evaluated.

This equation of state combines the Soave-Redlich-Kwong (SRK) EoS for describing the physical interactions with the association contribution proposed by Wertheim, also used in other associating equations of state, such as the different versions of SAFT. The CPA EoS had already been successfully applied to aqueous systems with alkanes, aromatics and alcohols.

The results obtained are in very close agreement with the literature data, suggesting that the CPA EoS is an adequate model for correlating aqueous solutions of complex molecules of organic pollutants.

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List of symbols

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

a_0 parameter in the energy term (a), $\text{Pa m}^6 \text{ mol}^{-2}$

a_{ij} cross-interaction energy parameter between molecules i and j

A_i site A in molecule i

b co-volume parameter, $\text{m}^3 \text{ mol}^{-1}$

c_1 parameter in the energy term, dimensionless

g radial distribution function

k_{ij} binary interaction parameter

OF objective function

P pressure, Pa

R gas constant, $\text{Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$

T temperature, K

T_c critical temperature, K

T_m melting temperature, K

V_m molar volume, $\text{m}^3 \text{ mol}^{-1}$

V_{vdw} van der Waals volume, $\text{m}^3 \text{ kmol}^{-1}$

X_{Ai} mole fraction of component i not bonded at site A

x_i liquid mole fraction of component i

Z compressibility factor

Greek letters

ρ molar density, mol m^{-3}

β_{ij} solvation parameter

$\Delta^{A_i B_j}$ association strength

ΔC_p difference of the liquid and solid molar heat capacities

$\varepsilon^{A_i B_j}$ association energy

$\beta^{A_i B_j}$ association volume

γ activity coefficient

φ fugacity coefficient

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“What is important is to keep learning, to enjoy challenge, and to tolerate ambiguity. In the end there are no certain answers.”

Martina Horner

1. Part

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) (figure 1) are globally distributed environmental contaminants, which attract considerable concern because of their known toxic and bioaccumulative effects. In humans, health risks associated to PAH exposure include cancer and DNA damage. The major sources affecting the presence and distribution of PAHs in the environment are anthropogenic. In the marine environment, these include large oil spills from tankers, oil discharges by all kinds of ships, and activities associated with offshore oil and gas exploration and production ^[1].

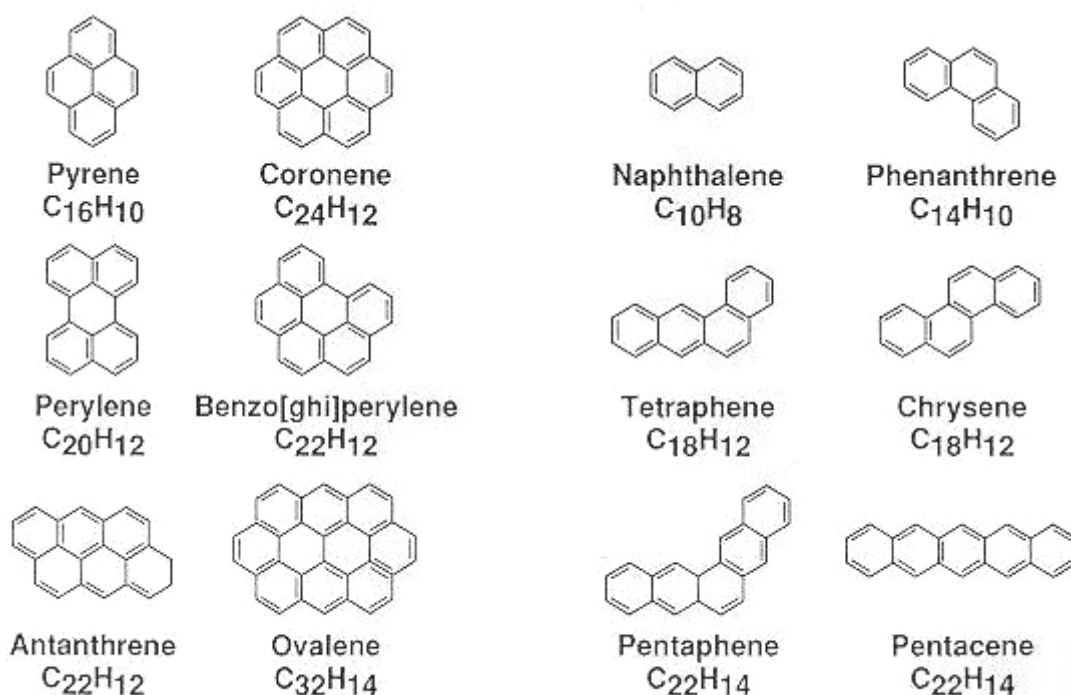


Figure 1 – Typical names and structures of some PAHs ^[2].

In the last two decades there have been numerous catastrophes involving oil tankers all around the world, like Exxon Valdez (Canada, 1989), Braer (Scotland, 1993), Haven (Italy, 1996), Sea Empress (Wales, 1996), Nakhodka (Japan, 1997), Erika (France, 1999) and Prestige (Spain, 2002).

The wreck of the Prestige oil tanker off the Galician coast, in November 2002, involved one of the greatest environmental catastrophes in European navigation in which the initial spill and subsequent leakage resulted in the release of nearly 63,000 tons of heavy oil during the period up to August 2003. According to the analysis made

by the Spanish National Research Council, the composition of the Prestige oil could be described as 50% aromatic hydrocarbons, 22% saturated hydrocarbons and 28% resins and asphaltene^[3]. This event mobilised a large number of volunteers, who collaborated in several tasks, such as cleaning beaches, rocks, sea and oil-contaminated birds.

Several epidemiological studies have been conducted to determine the consequences of the oil spills on human health^[3]. Human epidemiological studies have demonstrated the association of petroleum hydrocarbon exposures with various adverse health outcomes. Oil was reported in the past to be associated with acute myelogenous leukaemia. An increased risk of renal adenocarcinomas was seen for refinery and petrochemical workers and from occupational exposures to gasoline. The limited data available on dermal absorption of PAHs do suggest that these compounds are rather well absorbed via the skin of humans. The absorption is facilitated if PAHs are present in a solvent or oil^[4].

Although the fuel oil of Prestige did not seem to contain any of the six PAHs categorized by the International Agency for Research on Cancer (IARC) as probable or possible human carcinogens (naphthalene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and dibenz[ah]anthracene), and included in the 16 PAHs designated by the United States Environmental Protection Agency (USEPA) as primary contaminants^[3], some volunteers who helped in the cleanup developed cancer.

Sixteen PAHs are classified by the U.S. Environmental Protection Agency (USEPA) as priority pollutants, given their carcinogenic nature. These are presented in the following table.

Table 1 – List of the sixteen PAHs classified as priority pollutants by the USEPA ^[5].

	USEPA Priority pollutants (16 PAH)	IRAC Probable or possible Human carcinogens (6 PAH)	Borneff (6 PAH)	UNEP POPs Protocol Indicators for purpose of emission inventories
Napthalene	✓			
Acenaphthene	✓			
Acenaphthylene	✓			
Fluorene	✓			
Anthracene	✓			
Phenanthrene	✓			
Fluoranthene	✓		✓	
Pyrene	✓			
Benz[a]anthracene	✓	✓		
Chrysene	✓			
Benzo[b]fluoranthene	✓	✓	✓	✓
Benzo[k]fluoranthene	✓	✓	✓	✓
Benzo[a]pyrene	✓	✓	✓	✓
Dibenz[ah]anthracene	✓	✓		
Indeno[1,2,3- cd]pyrene	✓	✓	✓	✓
Benzo[ghi]perylene	✓		✓	

A subset of six of these PAHs has been identified by the International Agency for Research on Cancer (IARC) as probable or possible human carcinogens (IARC, 1987). The Borneff six PAHs have been used in some EC emission inventory compilations. Those PAHs to be used as indicators for the purposes of emissions inventories under the United Nations Environment Programme (UNEP) Persistent Organic Pollutants (POPs) Protocol are indicated in the final column of Table 1. As seen, most of the PAH's at the end of Table 1 are considered important hazardous chemicals by all institutions ^[5].

Since it was discovered that PAHs could be carcinogenic, they were the subject of many studies with the objective of trying to find out how dangerous they are to the environment and to all living beings.

The main environmental impact of PAHs is related to their health effects, focusing on their carcinogenic, mutagenic and teratogenic properties. The most potent

carcinogens have been shown to be benzo[a]anthracene, benzo[a]pyrene and dibenz[ah]anthracene ^[5]. The semi-volatile properties of PAHs make them highly mobile components throughout the environment, via deposition and re-volatilisation between air, soil and water bodies.

PAHs have several other sources beyond oil, although this is their primary source. PAHs can be found in bitumen and asphalt production plants, paper mills, aluminium production plants and industrial machinery manufacturers, fires of all types (bush, forest, agricultural, home heating, cooking, etc.), and the manufacture and use of preserved wood (creosote). Through the natural sources, PAHs can be formed from any naturally occurring fire, such as bushfires or forest fires. They occur in crude oil, shale oil, and coal tars. They are also emitted from active volcanoes ^[6].

PAHs are often resistant to biological degradation and are not efficiently removed by conventional physicochemical methods such as coagulation, flocculation, sedimentation, filtration or ozonation ^[7].

It is well established that the fate of PAHs in the environment is primarily controlled by their physicochemical properties. Since their aqueous solubility, volatility, hydrophobicity or lipophilicity vary widely, the differences among their distributions in aquatic systems, atmosphere and soil are significant. On the other hand, these compounds have relatively low vapor pressure and resistance to chemical reactions. As a result, they are persistent in the environment and show a tendency to accumulate in soils, sediments, and are also highly dispersed by the atmosphere.

As mentioned, different phase equilibria involving these molecules are important: vapor-liquid for volatilization, liquid-liquid for partitioning and solid-liquid for solubilization processes. Unfortunately, experimental solubility data are only available for a few compounds and some mixtures. Hence, having a thermodynamic model able to accurately and consistently predict the thermodynamic properties for PAHs is an essential step that will allow a better description of these processes, such as the chemical transformation process of crude oil or the incomplete combustion of hydrocarbon fuels ^[8].

Because of their importance and toxic behaviour, their solubility in different solvents is of considerable interest. Polycyclic aromatic hydrocarbons have toxic impact on the environment when washed from contaminated soils by ground and surface water and for this reason PAH solubility in water is most frequently studied.

The solubility can be modelled quantitatively for a series of solutes in a single solvent or for a series of solvents for a single solute. Most PAH solubility studies until now have expressed the solubility of a single solute in a series of pure solvents or binary mixtures of solvents ^[9].

There are several models that had already been applied to determine the phase equilibria of these compounds, such as Quantitative Structure Property Relationships (QSPR) ^[9, 10], activity coefficient models such as the Universal Function Activity Coefficient (UNIFAC) ^[11, 12], and equations of state such as the Statistical Associating Fluid Theory (SAFT) ^[8].

Quantitative Structure Property Relationships (QSPR) are a class of models which use multivariate statistical methods to model relevant properties as a function of molecular structure parameters, called descriptors.

While such descriptors can themselves be experimental properties of the molecule, it is generally more useful to use descriptors derived mathematically from either the 2D or the 3D molecular structure, since this allows derived relationships to be extended to the prediction of properties of compounds for which data are not available ^[13].

For example, a QSPR was used for modeling the solubility of polyaromatic hydrocarbons and fullerene in 1-octanol and n-heptane. In that work, two general QSPR models were developed, describing the solubility of PAHs and fullerene in two different ways. It was shown that the solubility of PAH's in nonpolar solvents (as n-heptane) and mid polar solvents (such as 1-octanol) is influenced by its size but also by charges in polycycles which can contribute to solvation. With this model it was possible to correctly predict the solubility of fullerene (C₆₀) ^[9].

Some properties of PAHs, including their solubility, were also described by a QSPR in another work ^[10]. It was concluded that the use of a single descriptor could only capture part of the property of interest, or of some occurring process, which is far from satisfactory. The use of multivariate regression instead, is a great improvement by correlating physical properties with molecular parameters, thus resulting in better results. Using five descriptors for modelling the solubility, only 4 in 14 compounds had an error greater than 10% ^[10].

UNIFAC ^[11, 14] is a thermodynamic model based on the description of the excess gibbs energy. On this model, each molecule is considered the sum of functional groups, and the thermodynamic properties of the solution are computed in terms of the

functional group properties. The activity coefficient obtained from UNIFAC consists of two parts: a combinatorial contribution, due mostly to differences in molecular size and shape, and a residual contribution, arising mostly from differences in intermolecular attractive forces ^[11]. The utility of UNIFAC has previously been demonstrated, successfully predicting the solubility of large hydrophobic molecules, such as PAHs in various organic liquids^[15].

The UNIFAC model is quite attractive because, while there are a large number of organic compounds, the number of functional groups that make up these compounds is small. Hence, it is possible to estimate activity coefficients for a large number of organic compounds from a small number of functional group parameters ^[14]. A study that aimed to evaluate the revised UNIFAC interaction parameters to predict solubilities of a vast number of organic compounds of environmental concern in both aqueous and nonaqueous solvents, can be found in literature ^[14]. A good agreement was observed between the UNIFAC-predicted and literature-reported aqueous solubilities for eleven groups of compounds, i.e., short-chain alkanes, alkenes, alcohols, chlorinated alkanes, alkyl benzenes, chlorinated benzenes, polycyclic aromatic hydrocarbons, polychlorinated biphenyls (PCBs), anilines, phenols, and organohalide insecticides (DDT and lindane). Similarly, UNIFAC successfully predicted the co-solvency of PCB in methanol/water solutions. The error between predicted and literature-reported aqueous solubilities was larger for three groups of chemicals: long-chain alkanes, phthalates, and chlorinated alkenes ^[14].

Besides UNIFAC, other activity coefficient models were used to model the solubility of polycyclic aromatics in binary solvent mixtures, such as: Wilson, Non-Random Two Liquid (NRTL), NIBS/Redlich–Kister, Universal Quasi-Chemical (UNIQUAC), Flory–Huggins and Sheng ^[16].

Zvaigzne and Acree ^[17] used successfully the NIBS/Redlich–Kister equation and the modified Wilson model to describe the solubility of pyrene in alkane + 1-propanol and alkane + 2-propanol solvent mixtures. Also, the same authors tested the same models for correlating the solubility of pyrene in alkane and 1-octanol solvent mixtures, and reported very accurate results ^[18]. McHale et al. ^[19] had accurately represented the solubility of pyrene in binary alcohol + cyclohexanol and alcohol + pentanol solvent mixtures at 299.2 K using the NIBS/Redlich–Kister equation. Furthermore, McHale et al. ^[20] used the same model to test the solubility of pyrene in binary alcohol + 2-methyl-2-butanol solvent mixtures at 299.2 K, obtaining accurate results. Hernandez et al. ^[21]

studied the solubility of pyrene in binary solvent mixtures of alkanes + 2-butanol using the NIBS/Redlich–Kister equation. Lee et al. [22] successfully used both Wilson and NRTL (non-random two liquid) models for representing the solubility of binary mixtures constituted of phenanthrene, acenaphthene, dibenzofuran, fluorene and diphenylmethane.

The comparison between these models, in terms of average absolute deviations [16], resulted in the following classification in descending order: NIBS/Redlich–Kister (6.8%), Wilson (7.6%), UNIQUAC (9.6%), Sheng (10.6%), Flory–Huggins (13%), modified UNIFAC (Dortmund) (13%) and modified UNIFAC (14%).

Another class of thermodynamic models for describing fluid phase equilibria are the equations of state. Aqueous solutions require equations of state that explicitly deal with hydrogen bonding and solvation effects. Two of the most used are the Statistical Associating Fluid Theory (SAFT) [23] and the Cubic plus Association (CPA) equation of state [24-26].

SAFT is a class of equations of state based on perturbation theory. Here, molecules are considered as chains of identical spherical segments that may form associating links with other molecules. Different versions of SAFT use different expressions for some individual contributions for the total residual Helmholtz energy, depending on the assumptions made [27-30].

SAFT has already been applied for PAH's phase equilibria. The group contribution method for SAFT pure compound parameters proposed by Tamouza et al. [28] was used for the calculation of vapor pressures and saturated liquid volumes of pure polycyclic aromatic hydrocarbons (PAHs) using three versions of SAFT: PC-SAFT [31, 32], SAFT-VR [33] and a slightly modified version [34] of original SAFT. Both vapor pressure and liquid saturation volume calculated for PAHs by this approach compared well with experimental data. The prediction of some binary mixtures with other PAHs, heptane and toluene, without binary interaction parameters ($k_{ij} = l_{ij} = 0$), agreed with the experimental data within a few percent [8]. The main difficulty in the validation of the method, as mentioned by the authors, was the lack of sufficient experimental data. More data are needed for a better evaluation of the predictive ability of the SAFT model.

The cubic-plus-association (CPA) equation of state 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 ^[25]. The fact that the SAFT and CPA models explicitly take into account the interactions encountered in mixtures of associating compounds makes them applicable to multicomponent, multiphase equilibria for systems containing associating components.

CPA was previously applied to the phase equilibrium of mixtures containing alcohols, glycols, water, amines, organic acids and aromatic or olefin hydrocarbons ^[26, 35-38]. Recently, CPA has been applied to mixtures containing aromatic or olefin hydrocarbons together with water, alcohols, or glycols ^[25, 39, 40]. The results of these studies showed excellent results for liquid - liquid equilibrium (LLE) of water aromatics/ olefins and for both the water and hydrocarbon solubilities. For water-aromatics /olefins, only a “solvating” parameter is fitted from equilibrium data, and the interaction parameter of the physical term is obtained from a water/aliphatic hydrocarbon correlation. The results of these works demonstrate that the CPA EoS is a flexible thermodynamic tool for modelling vapor-liquid and liquid-liquid equilibrium of aqueous multicomponent mixtures containing alcohols or glycols and aliphatic, aromatic, and olefinic hydrocarbons ^[39].

In this work, it will be shown that the CPA EoS is able to produce an excellent description of the solubilities in water of several PAHs in a broad range of temperatures.

CPA can provide an accurate description of the solid-liquid equilibria of aqueous mixtures with PAHs, being only necessary a single association volume (solvating) parameter, β_{ij} , to model the water solubility of these compounds.

2. Part

MODEL

The accurate description of vapor–liquid equilibrium (VLE), liquid–liquid equilibrium (LLE), solid-liquid equilibrium (SLE) and gas solubility data for a multi-component system is the key to a successful process design and simulation. The two most popular approaches used for the calculation of multi-component phase equilibria are the excess Gibbs energy models (G^E) which are widely used for low-pressure applications and equations of state (EoS) traditionally used for high-pressure applications.

The main advantage of the G^E models lies in the ability to handle highly non-ideal systems using well defined liquid theories and the availability of a group contribution method such as UNIFAC^[41] for estimating the binary interaction parameters in the residual contribution. The main drawback of these methods lies in dealing with permanent gases and supercritical components, high pressures and inconsistencies close to the critical region. Some G^E models also require significant amounts of data to regress their parameters.

On the other hand, the EoS method is capable of handling supercritical and subcritical components in a consistent manner^[42]. Cubic equations of state such as the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) are by far the most used. Still, cubic equations of state perform poorly for associative and polar molecules and provide a bad description of the liquid phase volume of long-chain molecules.

The breakthrough in the modelling of highly polar systems, such as aqueous systems, came with the development of the statistical associating fluid theory (SAFT)^[43] and the cubic plus association (CPA) EoS^[25, 26, 40, 43].

In this work, CPA was used because it performs superiorly for aqueous systems, as shown by several authors^[25, 26, 35, 38-40, 44-46] and is also mathematically simpler, thus substantially simplifying and accelerating the phase equilibrium calculations when compared with SAFT. Another advantage is the presence of a cubic term that proved to be adequate for the correct description of the phase equilibria of hydrocarbon systems.

The CPA EoS, proposed by Kontogeorgis and co-workers^[24-26], 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^[45, 47, 48]. Using a generalized

cubic term (SRK: $\delta_1 = 1, \delta_2 = 0$; PR: $\delta_1 = 1 + \sqrt{2}, \delta_2 = 1 - \sqrt{2}$) the cubic and association contributions to the Helmholtz energy are the following:

$$A^{cubic} = \frac{an}{b(\delta_2 - \delta_1)} \ln\left(\frac{1 + b\rho\delta_1}{1 + b\rho\delta_2}\right) - nRT \ln(1 - b\rho) \quad (1)$$

$$A^{assoc} = RT \sum_i n_i \sum_{A_i} \left[\ln(X_{A_i}) - \frac{X_{A_i}}{2} + \frac{1}{2} \right] \quad (2)$$

The CPA EoS, can be expressed for mixtures in terms of pressure P , as:

$$P = P^{cubic} + P^{assoc} = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - \frac{1}{2} \frac{RT}{V_m} \left(1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (3)$$

or in terms of the compressibility factor as:

$$Z = Z^{phys.} + Z^{assoc.} = \frac{1}{1 - b\rho} - \frac{a\rho}{RT(1 + b\rho)} - \frac{1}{2} \left(1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (4)$$

where a is the energy parameter, b the co-volume parameter, ρ is the density, g the simplified radial distribution function^[44], 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 $\Delta^{A_i B_j}$ 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:

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (5)$$

where the association strength $\Delta^{A_i B_j}$ is expressed as:

$$\Delta^{A_i B_j} = g(\rho) \left[\exp\left(\frac{\varepsilon^{A_i B_j}}{RT}\right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (6)$$

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

The simplified radial distribution function, $g(\rho)$ is given by ^[44]:

$$g(\rho) = \frac{1}{1 - 1.9\eta} \quad \text{where} \quad \eta = \frac{1}{4} b \rho \quad \text{while} \quad b_{ij} = \frac{b_i + b_j}{2} \quad (7)$$

These $\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ 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 inert components, e.g., 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 (critical data and acentric factor).

When regressing the pure component parameters, the mostly used objective function is:

$$OF = \sum_i^{NP} \left(\frac{P_i^{\text{exp.}} - P_i^{\text{calc.}}}{P_i^{\text{exp.}}} \right)^2 + \sum_i^{NP} \left(\frac{\rho_i^{\text{exp.}} - \rho_i^{\text{calc.}}}{\rho_i^{\text{exp.}}} \right)^2 \quad (8)$$

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

$$a(T) = a_0 \left[1 + c_1 \left(1 - \sqrt{T_r} \right) \right]^2 \quad (9)$$

where $T_r = T/T_c$ being T_c the critical temperature.

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:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (10)$$

being k_{ij} a binary interaction parameter fitted from binary equilibrium data and,

$$b = \sum_i x_i b_i \quad (11)$$

Although aromatic hydrocarbons are themselves non-self-associating, it is well known that aromatic compounds are able to cross associate (solvate) with water [49-51]. For extending the CPA EoS to mixtures containing cross-associating molecules, combining rules for the association energy (ε^{AiBj}) and volume parameters (β^{AiBj}) are required [52]. Different sets of combining rules have been proposed by several authors [52-55], including not solely for ε^{AiBj} and β^{AiBj} but also for the cross-association strength, Δ^{AiBj} :

$$\varepsilon^{AiBj} = \frac{\varepsilon^{AiBi} + \varepsilon^{AjBj}}{2}, \quad \beta^{AiBj} = \frac{\beta^{AiBi} + \beta^{AjBj}}{2} \quad (12), \text{ referred as the CR-1 set}$$

$$\varepsilon^{AiBj} = \frac{\varepsilon^{AiBi} + \varepsilon^{AjBj}}{2}, \quad \beta^{AiBj} = \sqrt{\beta^{AiBi} \beta^{AjBj}} \quad (13), \text{ referred as the CR- 2 set}$$

$$\varepsilon^{AiBj} = \sqrt{\varepsilon^{AiBi} \varepsilon^{AjBj}}, \quad \beta^{AiBj} = \sqrt{\beta^{AiBi} \beta^{AjBj}} \quad (14), \text{ referred as the CR- 3 set}$$

$$\Delta^{AiBj} = \sqrt{\Delta^{AiBi} \Delta^{AjBj}} \quad (15), \text{ referred as the CR- 4 set (or Elliot rule)}$$

For systems aromatic(s) + water, as is the case of this master's thesis, only water is a self-associating molecule, having ε^{AiBj} and β^{AiBj} values different from zero. Aromatics are non-self-associating molecules so ε^{AiBj} and β^{AiBj} are zero for these molecules. Thus, a different procedure is required to obtain the cross-associating energy and volume. Folas *et al.* [39] 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 (β_{ij}^{AB}) is used as an adjustable parameter, fitted to equilibrium data. This methodology, has been successful applied to mixtures with water or glycols and aromatic ^[39, 40] or olefinic hydrocarbons.

For estimating the β^{AiBj} parameter the following objective function was employed:

$$OF = \sum_i^{NP} \left(\frac{x_i^{calc.} - x_i^{exp.}}{x_i^{exp.}} \right)^2 \quad (16)$$

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 ^[26]. For aromatics a single association site is considered, cross-associating with water, as suggested by some theoretical and experimental evidence ^[50, 51].

Equations to describe the SLE for binary systems are well established in the literature ^[56].

Considering the formation of a pure solid phase and neglecting the effect of pressure (melting temperature and enthalpy, heat capacities and Poynting term), the solubility of a solute *s* can be calculated from the following generalized expression that relate the reference state fugacities:

$$\ln \frac{f_s^{liq}(T, P)}{f_s^{sol}(T, P)} = \left[-\frac{\Delta_{fus}H}{R} + \frac{\Delta C_p T_m}{R} \right] \left(\frac{1}{T} - \frac{1}{T_m} \right) + \frac{\Delta C_p}{R} \ln \frac{T_m}{T} \quad (17)$$

where $\Delta_{fus}H$ is the enthalpy of fusion, T is the absolute temperature, T_m is the melting temperature, ΔC_p is the difference of the liquid and solid molar heat capacities and R the gas constant.

Neglecting the heat capacity terms with respect to the enthalpic term we obtain the following expression for the solubility, while using an activity coefficient model:

$$x_s = \frac{1}{\gamma_s} \exp \left\{ \left[-\frac{\Delta_{fus}H_s}{R} \right] \left(\frac{1}{T} - \frac{1}{T_{m,s}} \right) \right\} \quad (18)$$

Where γ is the activity coefficient.

Eq. 19, is used instead, whenever an equation of state is selected:

$$x_s = \frac{\varphi_s^L}{\varphi_s^L} \exp \left[-\frac{\Delta_{fus}H_s}{R} \left(\frac{1}{T} - \frac{1}{T_{m,s}} \right) \right] \quad (19)$$

Where φ is the fugacity coefficient and subscript 0 refer to pure component.

3. Part

RESULTS AND DISCUSSION

This work began with the compilation and selection of available data, required for the development and evaluation of the thermodynamic model used. Thus an extensive literature search was made to collect data on critical temperature, vapour pressure and saturated liquid density as a function of temperature, and melting temperatures and enthalpies for polycyclic aromatic compounds. It was possible to obtain data for 25 compounds ^[57].

Table 2 – List of PAH's with available data and their chemical formula.

Compound	Chemical Formula
1-ethylnaphthalene	C ₁₂ H ₁₂
1,2,3,4-tetrahydronaphthalene	C ₁₀ H ₁₂
1-butylnaphthalene	C ₁₄ H ₁₆
1-nonylnaphthalene	C ₁₉ H ₂₆
1-decylnaphthalene	C ₂₀ H ₂₈
1-propylnaphthalene	C ₁₃ H ₁₄
n-hexylnaphthalene	C ₁₆ H ₂₀
2,6-dimethylnaphthalene	C ₁₂ H ₁₂
2,7-dimethylnaphthalene	C ₁₂ H ₁₂
2,6-diethylnaphthalene	C ₁₄ H ₁₆
1-phenylnaphthalene	C ₁₅ H ₁₈
1-n-hexyl-1,2,3,4-tetrahydronaphthalene	C ₁₆ H ₂₄
1-n-pentylnaphthalene	C ₁₆ H ₁₂
1-methylnaphthalene	C ₁₁ H ₁₀
naphthalene	C ₁₀ H ₈
2-methylnaphthalene	C ₁₁ H ₁₀
2-ethylnaphthalene	C ₁₂ H ₁₂
anthracene	C ₁₄ H ₁₀
pyrene	C ₁₆ H ₁₀
fluoranthene	C ₁₆ H ₁₀
acenaphthalene	C ₁₂ H ₈
chrysene	C ₁₈ H ₁₂
acenaphthene	C ₁₂ H ₁₀
phenanthrene	C ₁₄ H ₁₀
fluorene	C ₁₃ H ₁₀

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

Correlations indicated by the DIPPR database:

$$P^{\sigma} = \exp \left[A + \frac{B}{T} + C \times \ln T + D \times T^E \right] \quad (20)$$

and

$$\rho_{liq} = \frac{A}{B \left[1 + \left(1 - \frac{T}{C} \right)^D \right]} \quad (21)$$

lead to values for the vapour pressures (P^{σ}) and saturated densities of the liquid (ρ_{liq}), covering the range of reduced temperatures from 0.45 to 0.85 (Appendix A). This temperature range covers most of the liquid phase region, from close to the triple point up to close to the critical point. Still, it should be noted that the accuracy of the DIPPR correlations far from the region where experimental data are available is frequently questionable.

Through a simultaneous regression of vapour pressure and liquid density data, the three parameters of the physical part (a_0 , b , c_1) of the CPA-EoS were estimated for all compounds previously listed in table 2. A FORTRAN routine based on a modified Marquardt algorithm for non-linear least squares was used for this purpose^[58]. This routine was obtained from the Harwell subroutine library (<http://hsl.rl.ac.uk/archive/cou.html>) and allows constrained regression of the CPA parameters, in the sense that the user can set up a range of allowed values for each parameter, thus avoiding the regression of parameters with non-physical meaning.

The pure compound parameters for the studied polycyclic aromatic hydrocarbons (and water) are reported in table 3.

Table 3 – Pure component CPA parameters and deviations on the description of saturation pressures and liquid densities.

Compound	a_0 (Pa m ⁶ mol ⁻²)	c_1	b (x10 ⁴ m ³ mol ⁻¹)	V_{vdw} (m ³ kmol ⁻¹)	ε (J mol ⁻¹)	β	% AAD	
							P^σ	ρ_{liq}
1-ethylnaphthalene	4.92	1.00	1.47	0.10			1.56	0.58
1,2,3,4-tetrahydronaphthalene	3.87	0.91	1.25	0.08			0.97	0.51
1-butylnaphthalene	6.25	1.13	1.83	0.12			1.07	1.06
1-nonylnaphthalene	10.63	1.21	2.79	0.17			0.52	2.66
1-decyl naphthalene	11.55	1.24	3.00	0.18			0.50	2.87
1-propylnaphthalene	5.71	0.99	1.65	0.11			2.02	1.15
n-hexylnaphthalene	7.79	1.24	2.21	0.14			0.92	1.66
2,6-dimethylnaphthalene	5.14	1.00	1.53	0.10			0.84	1.59
2,7-dimethylnaphthalene	5.16	1.00	1.53	0.10			1.97	1.95
2,6-diethylnaphthalene	6.43	1.06	1.78	0.12			1.37	1.72
1-phenylnaphthalene	6.95	1.19	2.01	0.12			0.61	1.76
1-n-hexyl-1,2,3,4-tetrahydronaphthalene	8.06	1.21	2.33	0.14			0.95	2.02
1-n-pentylnaphthalene	6.95	1.19	2.01	0.13			1.10	1.17
1-methylnaphthalene	4.37	0.93	1.32	0.09			0.58	0.74
naphthalene	3.75	0.86	1.17	0.07			0.75	0.46
2-methylnaphthalene	4.50	0.90	1.34	0.09			3.14	0.88
2-ethylnaphthalene	5.07	0.94	1.49	0.10			0.85	0.75
anthracene	6.50	0.88	1.58	0.10			0.48	0.36
pyrene	7.86	0.93	1.77	0.11			0.72	2.87
fluoranthene	7.92	0.88	1.81	0.11			2.56	3.05
acenaphthalene	5.34	1.07	1.61	0.08			0.93	0.63
chrysene	9.19	1.15	2.04	0.13			0.61	2.08
acenaphthene	4.90	0.93	1.37	0.09			0.36	1.10
phenanthrene	6.26	0.93	1.56	0.10			0.48	1.01
fluorene	4.49	0.89	1.16	0.09			0.59	0.81
water	0.12	0.67	0.145			16655	0.73 ^[59]	0.82 ^[59]
Average deviation							1.06	1.42

The average absolute deviation (AAD) is calculated using the following equation: $\%AAD = \frac{1}{NP} \sum_{i=1}^{NP} ABS \left[\frac{x_{exp,i} - x_{calc,i}}{x_{exp,i}} \right] \times 100$, where x can be the vapour pressure or the liquid density.

As can be seen from table 3, a good description of vapour pressures and liquid densities is achieved with CPA, with a global average deviation of 1.1 % for vapour pressure (figure 2) and 1.4 % for liquid density (figure 3).

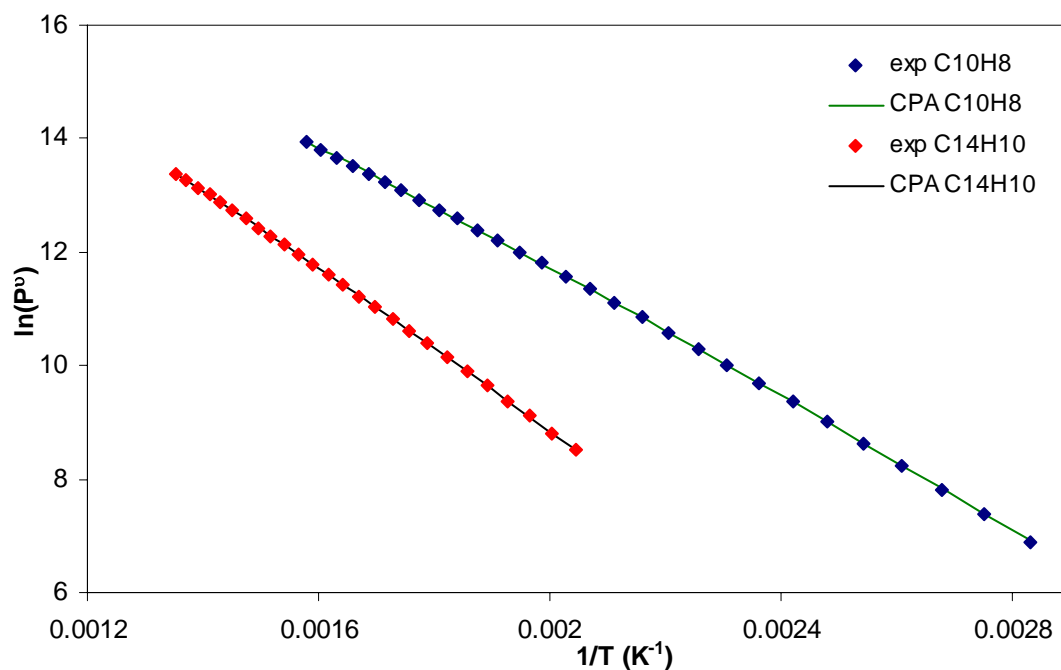


Figure 2 – Vapour pressure as a function of $1/T$ for naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$).

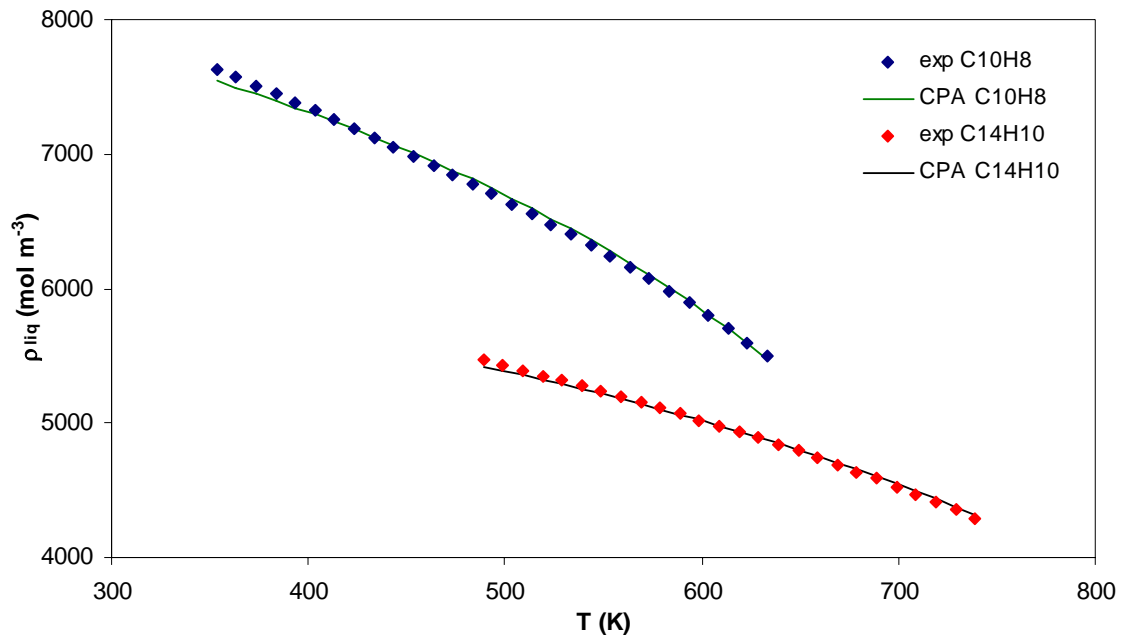


Figure 3 – Liquid density as a function of temperature for naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$).

As frequently pure component vapour pressure and liquid density data are not available, a following point in this thesis was to try to establish some correlations for the CPA parameters based on some known property. Previous works with CPA suggested using the van der Waals volume (VDWV) to correlate the cubic term CPA parameters ^[60]. Plots of a_0 and b as a function of the van der Waals volume are presented in Figures 4-5, where it can be seen that linear correlations can be established, particularly for the

b parameter: $a_0 = 73.89 V_{vdw} - 1.66$, $R^2 = 0.87$ and

$b = 0.0018 V_{vdw} - 2 \times 10^{-5}$, $R^2 = 0.95$.

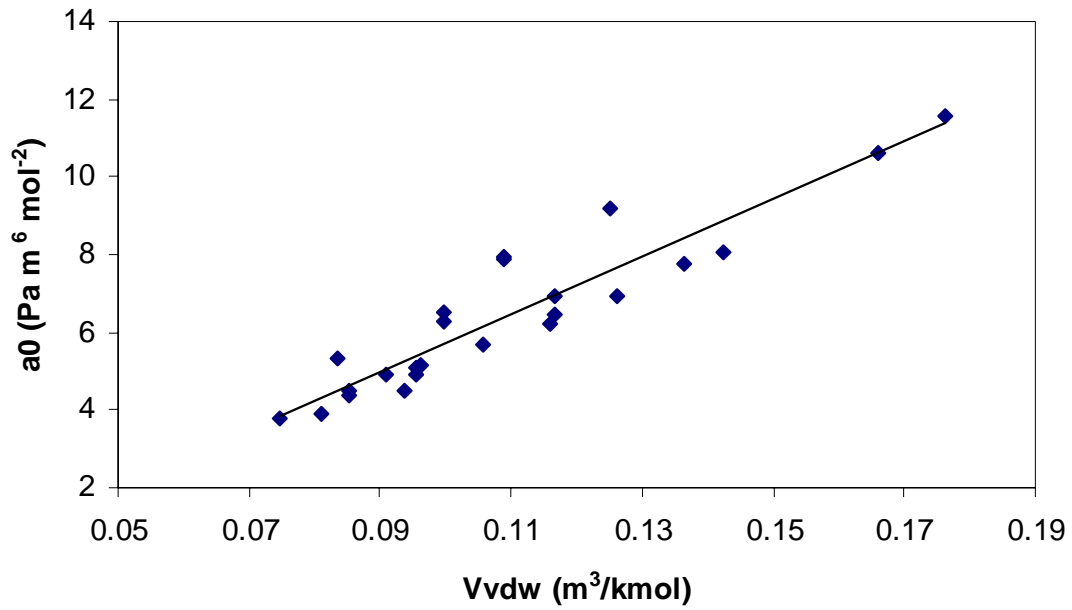


Figure 4 – Correlation of the a_0 parameter with the van der Waals volume.

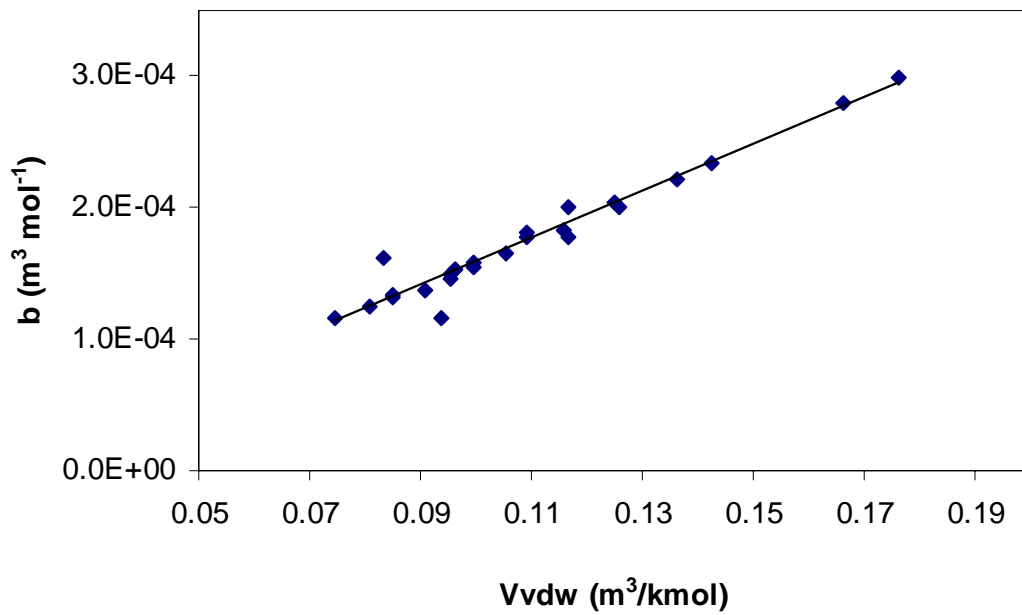


Figure 5 – Correlation of the b parameter with the van der Waals volume.

For the c_1 parameter, it was found that the plot vs. the van der Waals volume presented considerable scatter, thus preventing the establishment of any correlation. In order to reduce the scatter of the c_1 data, this parameter was re-estimated with new values of a_0 and b obtained from the proposed van der Waals volume correlations. Their values along with the obtained deviations in pressure and density are reported in table 4.

Table 4 – Correlated parameters (a_0 and b from van der Waals correlations) and deviations on the description of saturation pressures and densities.

Compound	a_0 (Pa m ⁶ mol ⁻²)	c_1	b (x10 ⁴ m ³ mol ⁻¹)	% AAD	
				P^σ	ρ_{liq}
1-ethylnaphthalene	5.25	0.87	1.48	9.87	1.03
1,2,3,4-tetrahydronaphthalene	4.19	0.68	1.22	14.7	4.07
1-butylnaphthalene	6.76	0.96	1.84	11.6	1.68
1-nonylnaphthalene	10.48	1.21	2.74	0.56	3.32
1-decyl naphthalene	11.23	1.26	2.92	1.88	3.61
1-propylnaphthalene	6.00	0.88	1.66	8.39	1.61
n-hexylnaphthalene	8.27	1.09	2.21	10.4	2.39
2,6-dimethylnaphthalene	5.31	0.86	1.50	6.87	3.34
2,7-dimethylnaphthalene	5.31	0.87	1.50	7.08	3.65
2,6-diethylnaphthalene	6.83	1.01	1.86	4.45	3.75
1-phenylnaphthalene	6.81	1.19	1.86	3.50	1.77
1-n-hexyl-1,2,3,4-tetrahydronaphthalene	8.72	1.01	2.32	14.4	3.07
1-n-pentylnaphthalene	7.51	1.01	2.03	11.9	1.82
1-methylnaphthalene	4.49	0.83	1.30	5.87	2.42
naphthalene	3.72	0.78	1.11	3.83	5.67
2-methylnaphthalene	4.49	0.83	1.30	4.77	3.98
2-ethylnaphthalene	5.25	0.84	1.48	6.32	1.66
anthracene	5.56	1.35	1.55	20.0	1.37
pyrene	6.26	1.52	1.72	37.5	1.75
fluoranthene	6.26	1.43	1.72	37.0	3.20
acenaphthalene	4.37	1.03	1.27	4.58	28.9
chrysene	7.45	1.84	2.01	29.1	0.93
acenaphthene	4.92	0.97	1.40	1.92	2.22
phenanthrene	5.56	1.24	1.55	20.9	0.93
fluorene	5.12	0.89	1.45	0.47	0.72
Average deviation				11.1	3.55

Average deviations of 11.1 % for vapour pressure and 3.6 % for liquid density were obtained.

Even though, we have tried to achieve a better fit for the parameters, it was not possible to keep the good descriptions obtained previously in Table 3, as can be seen by the average deviations. This is due to the high sensitivity of the vapour pressure estimates on the a_0 parameter. Thus, in the subsequent work, we used the values of the parameters reported on table 3, which provided the best fit to the physical properties of the compounds under study. As will be seen, the PAH's aqueous solubility database that could be compiled contained data only for compounds already present in Table 3, thus the use of correlations for the CPA parameters was not necessary.

Having estimated the pure compound parameters, it is now possible to describe binary mixtures. An extensive literature search to collect experimental solubility data of PAHs, in a large temperature range was carried. Information on the collected data is reported in Table 5.

Due to the difficulty in measuring experimentally the solubility of these compounds, it was only possible to collect data for seven PAHs: naphthalene, anthracene, pyrene, fluoranthene, chrysene, acenaphthene and phenanthrene (figure 6).

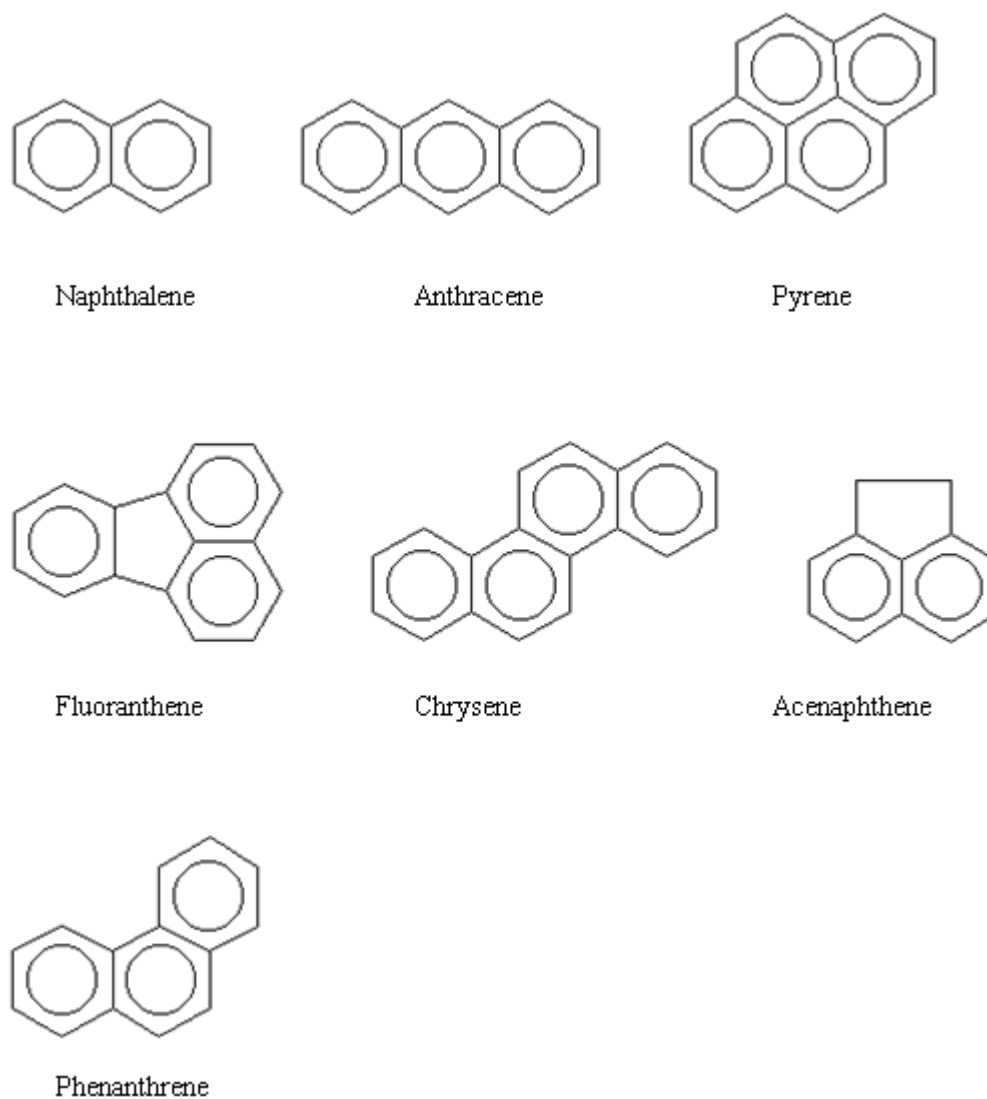


Figure 6 – Structure of PAHs with aqueous solubility data.

Table 5 – Range of temperature and solubility ^[61-67] for the different PAHs.

Compound	Temperature (K)	Solubility (S/g.m ⁻³)
naphthalene	273.15 - 348.15	13.74 – 258
anthracene	273.15 - 347.25	0.022 – 1.19
pyrene	273.15 - 347.85	0.049 – 2.21
fluoranthene	281.25 - 303.05	0.0821 – 0.2796
chrysene	279.65 - 302.15	0.00071 – 0.0022
acenaphthene	273.15 - 347.85	1.45 – 40.8
phenanthrene	273.15 - 346.55	0.39 – 15.2

The first approach to the modelling of the aqueous solubility of PAH's with CPA was done in a completely predictive manner, using k_{ij} and β_{ij} equal to zero. The deviations thus obtained between the CPA predictions and the experimental data are reported in Table 6.

Table 6 – CPA modelling results using $k_{ij} = \beta_{ij} = 0$.

Compound	% AAD
naphthalene	48.5
anthracene	63.5
pyrene	62.4
fluoranthene	84.9
chrysene	75.0
acenaphthene	36.9
phenanthrene	39.4

Taking naphthalene as an example, it can be observed that although a significant difference between the predicted and experimental solubilities were observed, both followed the same trend with temperature, as shown in Figure 7 below. It should also be noted that the experimental data presents some scatter, in some cases (as close to room temperature) with deviations among different points similar to the deviations between the predictions and the data. It should also be stressed that a previous work ^[40] on the liquid-liquid equilibria of water + several aromatics showed that the aromatic solubilities in water, using correlated k_{ij} and β_{ij} had typical deviations around 20 %, thus showing that very good predictions of PAH's aqueous solubilities can be obtained from CPA.

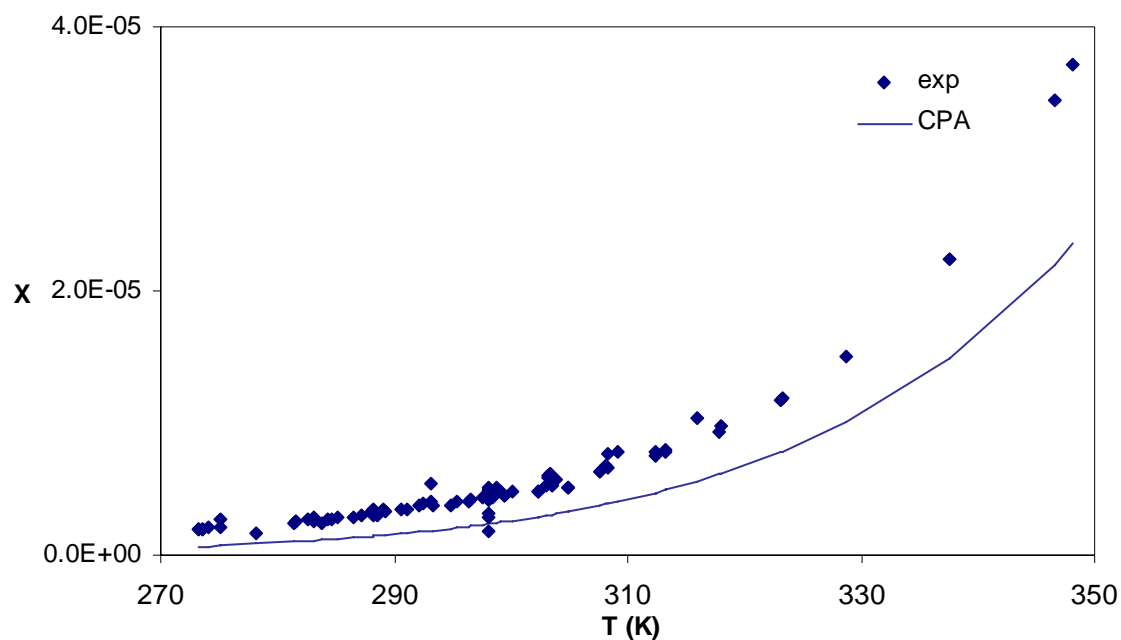


Figure 7 – Naphthalene aqueous solubility: experimental and CPA predictions.

Since it is difficult to measure accurately the solubility of these compounds, some compounds have a wide dispersion of values for the same temperature. For example in the case of pyrene, for a temperature of 25 °C a great dispersion of values exists, as shown in Figure 8 below, and this also happens for some of the other compounds studied.

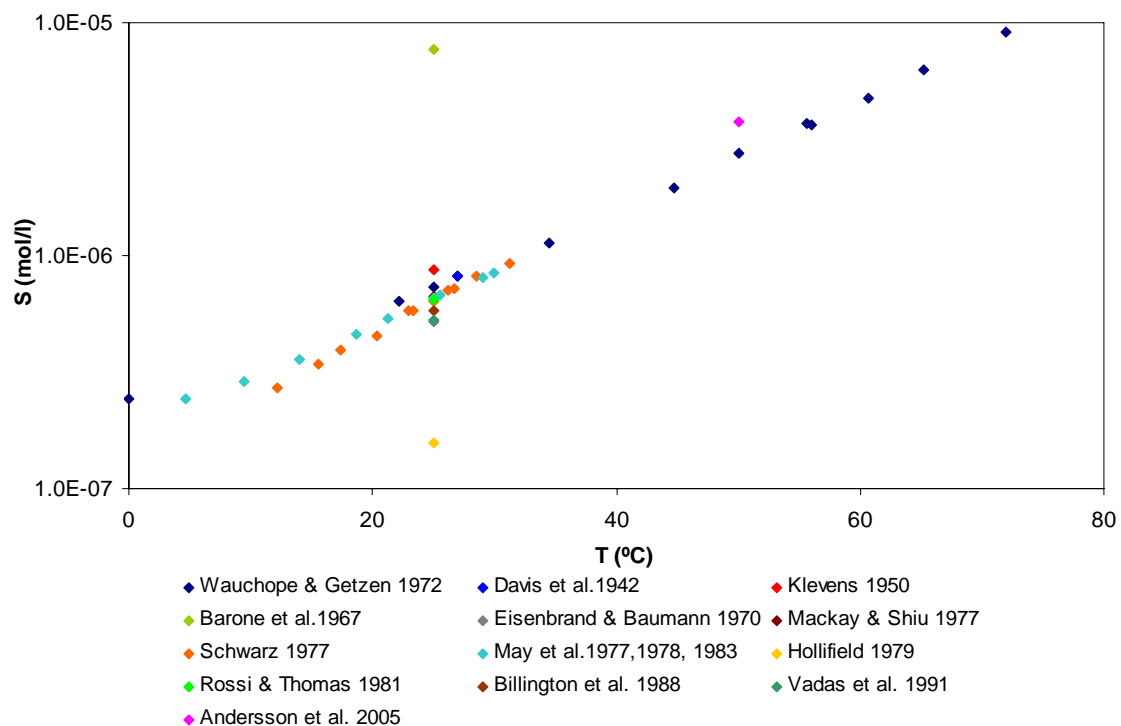


Figure 8 – Values collected in the literature for the solubility of pyrene ^[62, 64, 65, 68-80].

Being verified that for the PAHs, the experimental points present a large scatter, 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. Moreover, a number of compounds had solubility data going through a minimum at low temperatures. This data was also discarded as CPA and other models are not able to adequately describe this region. Further, to minimize the scattering of the experimental data, correlations of the solubilities were obtained for each compound. The deviations of the model where then estimated relatively to these correlations (Table 7) being reported in Table 8.

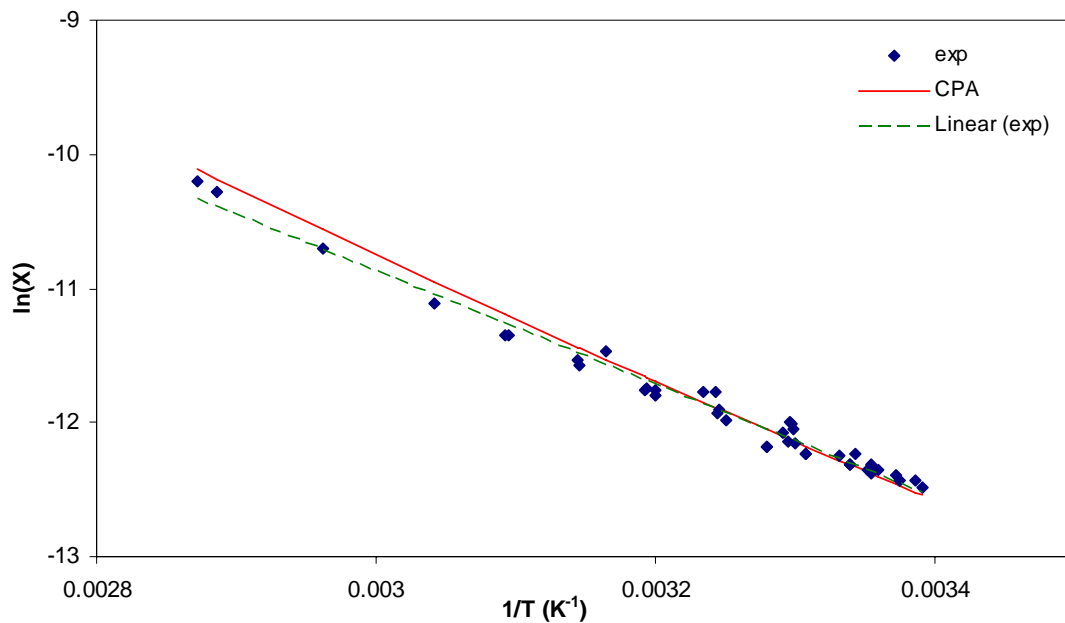


Figure 9 – Van't Hoff naphthalene solubility plot.

Table 7 – PAH's correlations of solubility data.

Compound	Correlation	R ²
naphthalene	$\ln(x) = -4026.38\left(\frac{1}{T}\right) + 1.75$	0.982
anthracene	$\ln(x) = -6698.70\left(\frac{1}{T}\right) + 3.34$	0.990
pyrene	$\ln(x) = -5712.29\left(\frac{1}{T}\right) + 0.89$	0.998
fluoranthene	$\ln(x) = -4541.10\left(\frac{1}{T}\right) - 2.47$	0.756
chrysene	$\ln(x) = -4821.67\left(\frac{1}{T}\right) - 6.52$	0.930
acenaphthene	$\ln(x) = -4899.82\left(\frac{1}{T}\right) + 1.79$	0.994
phenanthrene	$\ln(x) = -5277.20\left(\frac{1}{T}\right) + 1.72$	0.991

Using these selected solubility data values it was possible to show that the predicted CPA solubilities had a lower error than previously estimated, as shown in Table 8.

Table 8 – Deviation of the CPA predictions from the selected data

Compound	% AAD
naphthalene	41.9
anthracene	60.4
pyrene	60.3
fluoranthene	84.6
chrysene	74.8
acenaphthene	32.6
phenanthrene	38.8

The predictions presented do not take into account the solvation occurring on aromatic + water systems. As mentioned before, the CPA model takes into account this phenomena through the β_{ij} parameter. A following point addressed in this thesis was thus, to evaluate the effect of this solvating parameter on the PAH's solubility results obtained from CPA.

Taking into account previous studies ^[40] a common value for all PAHs, of 0.051 was used as a first approximation. The results obtained are reported in the following table.

Table 9 – CPA results using $\beta_{ij}=0.051$.

Compound	% AAD
Naphthalene	33.3
Anthracene	6.8
Pyrene	15.1
Fluoranthene	54.2
Chrysene	19.5
Acenaphthene	65.7
Phenanthrene	63.9

Comparing the values presented in Tables 8 and 9 we can see that, with this first approach, we were able to considerably reduce the error for all compounds with the exception of acenaphthene and phenanthrene. For these two compounds the error unexpectedly increased while using a value of 0.051 instead of zero, for β_{ij} .

In the following figure we have the influence of the β_{ij} value for two PAHs: naphthalene and acenaphthene.

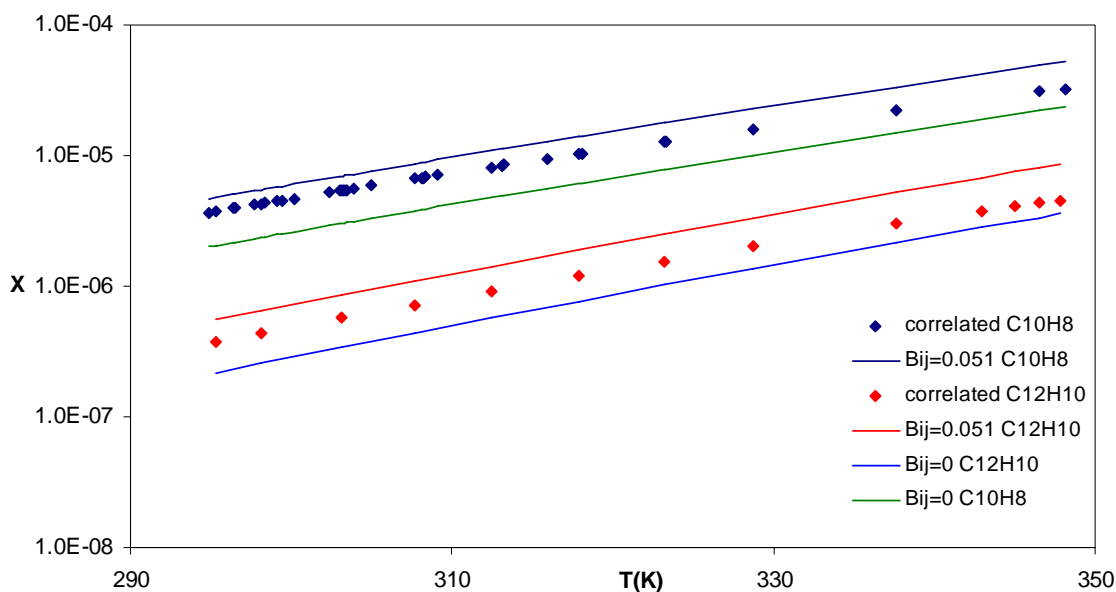


Figure 10 – Naphthalene and acenaphthene aqueous solubility (correlated data and CPA predictions using two values for β_{ij}).

As could be seen in the previous table, the use of a constant β_{ij} for all PAH's reduced considerably the deviations for six of the eight PAH's, while for the other two the deviations unexpectedly increased. In order to better check the influence of the solvation parameter for each binary PAH + water, these were regressed from the experimental solubility data. The results for the β_{ij} parameter and CPA deviations are presented in the next table and the model is compared with the experimental data on Figures 11-17.

Table 10 – Regressed β_{ij} values and CPA modelling results.

Compound	β_{ij}	% AAD
naphthalene	0.0269	5.55
anthracene	0.0455	2.45
pyrene	0.0403	2.94
fluoranthene	0.1425	6.41
chrysene	0.0749	11.8
acenaphthene	0.0193	9.22
phenanthrene	0.0186	4.21

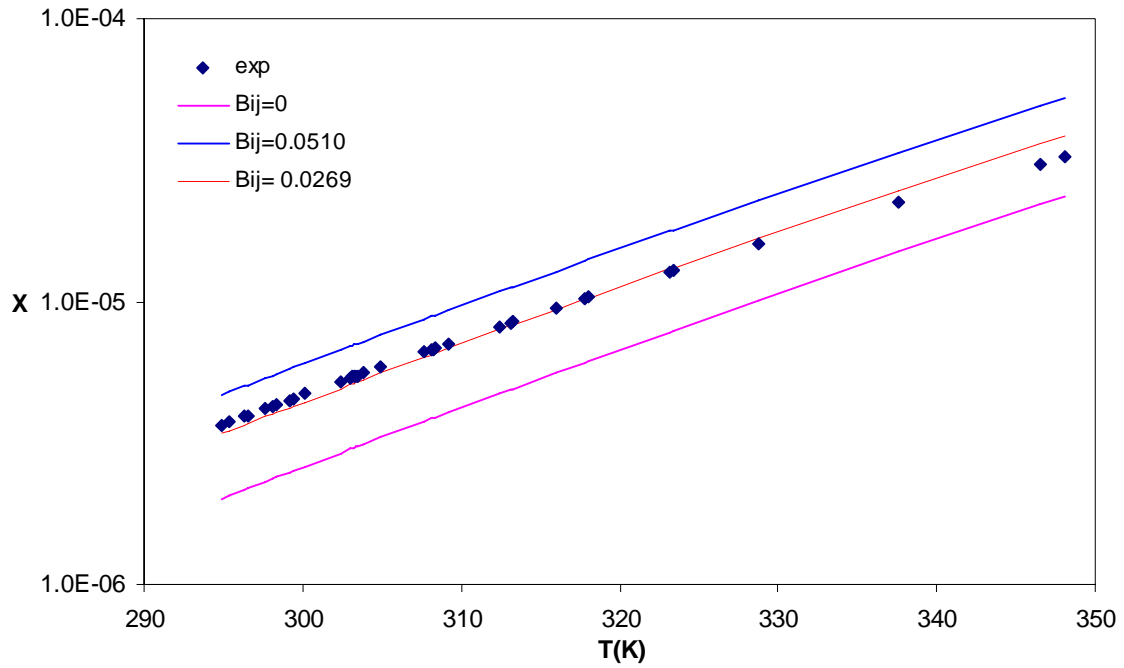


Figure 11 – Naphthalene solubility in the aqueous phase for several values of β_{ij} .

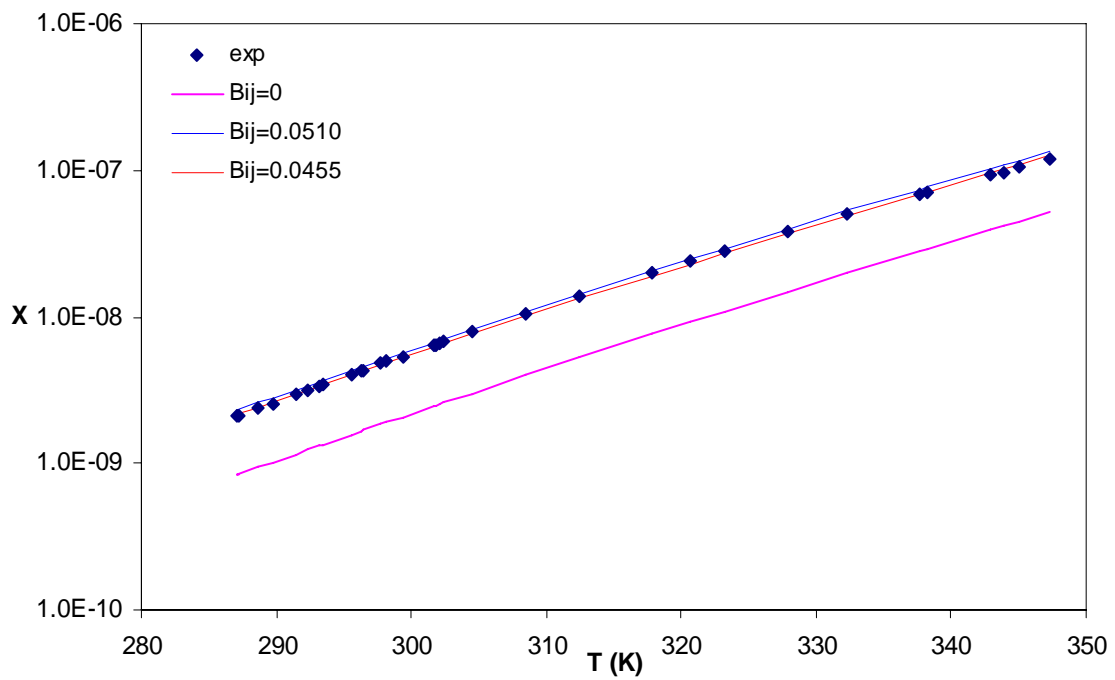
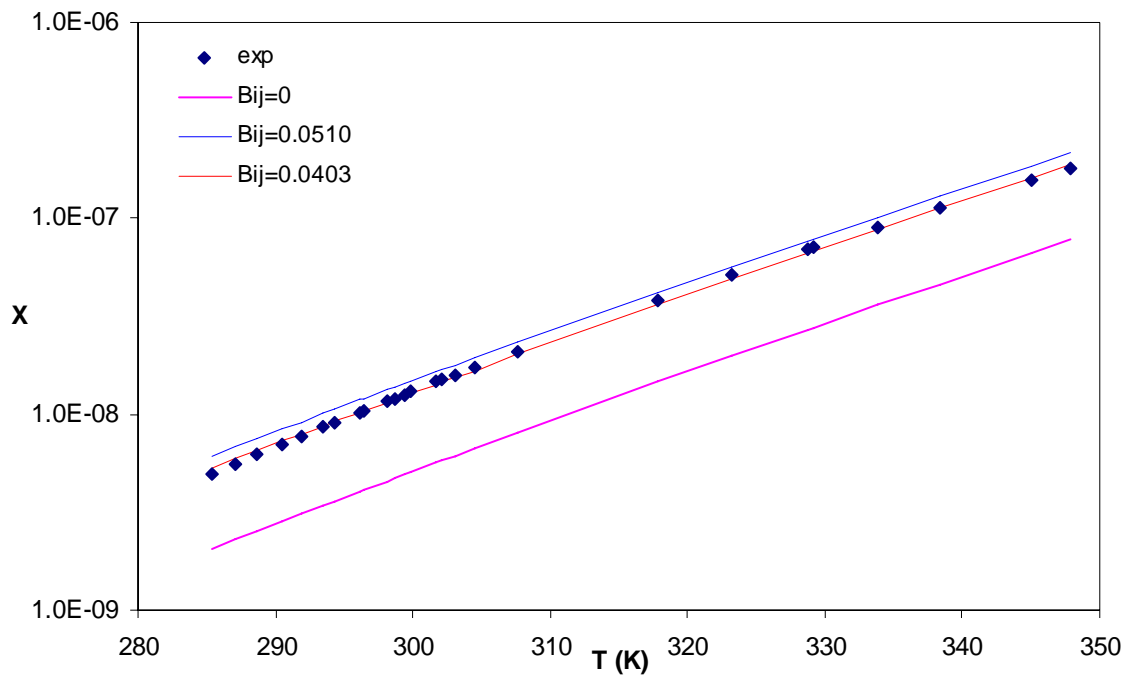
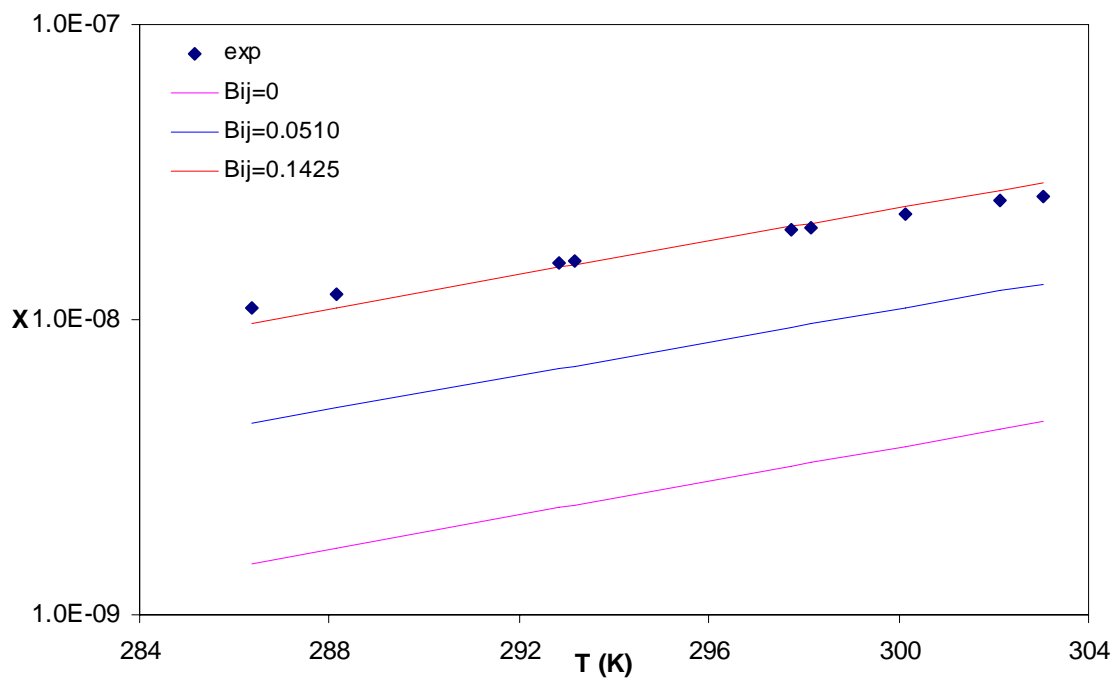


Figure 12 – Anthracene solubility in the aqueous phase for several values of β_{ij} .

Figure 13 – Pyrene solubility in the aqueous phase for several values of β_{ij} .Figure 14 – Fluoranthene solubility in the aqueous phase for several values of β_{ij} .

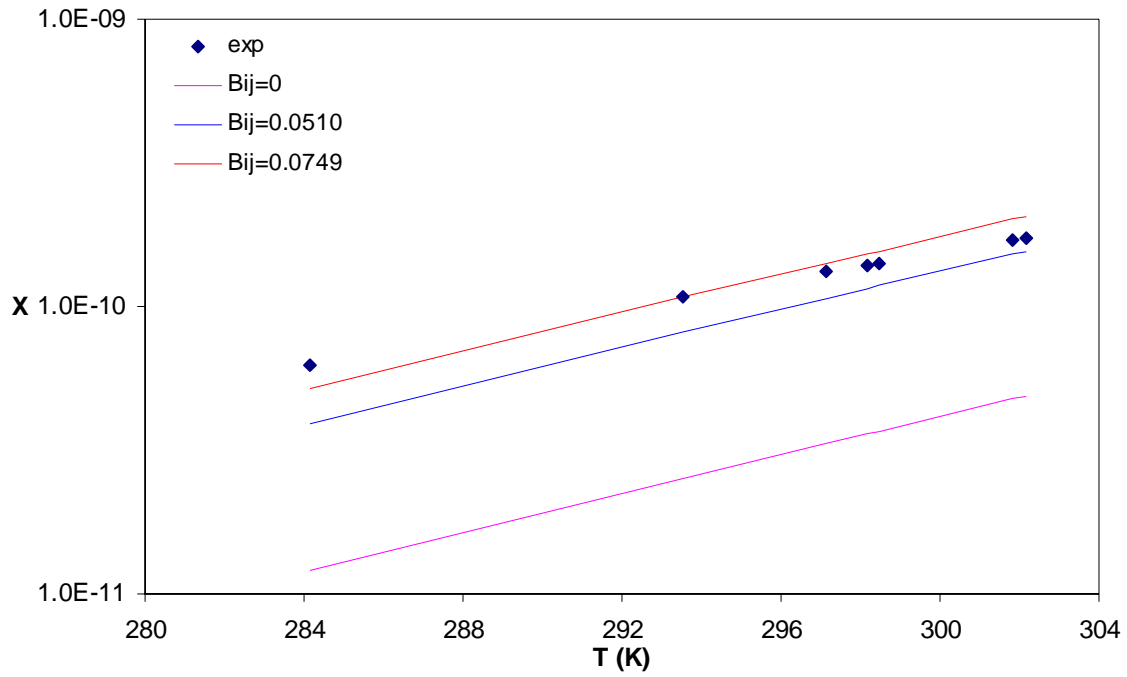


Figure 15 – Chrysene solubility in the aqueous phase for several values of β_{ij} .

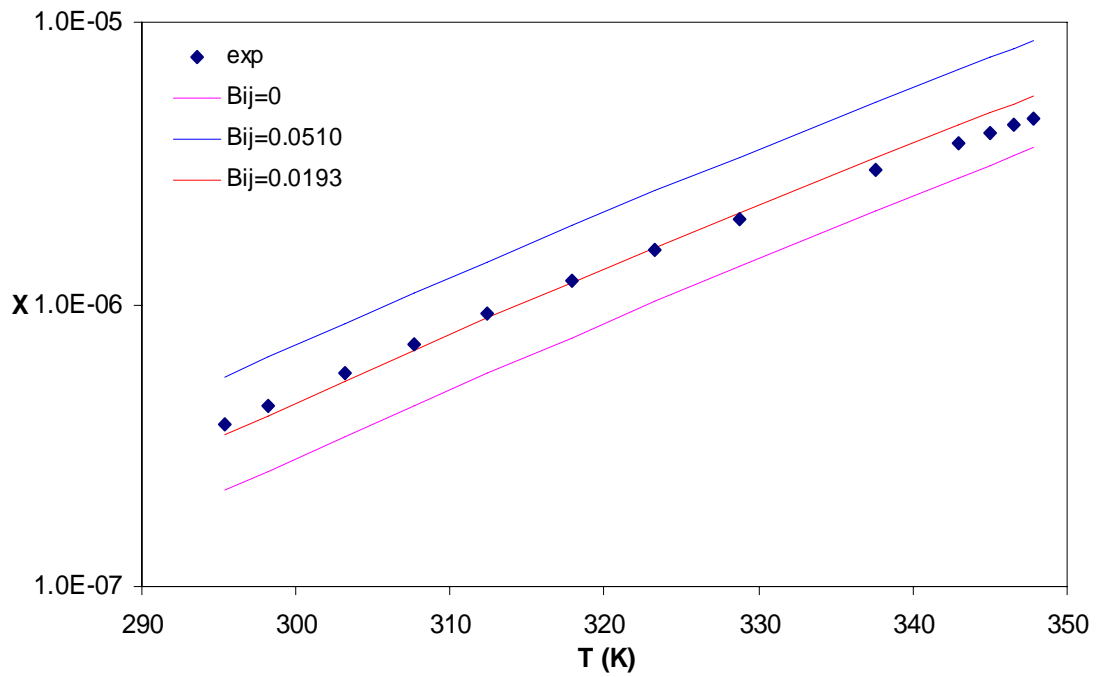


Figure 16 – Acenaphthene solubility in the aqueous phase for several values of β_{ij} .

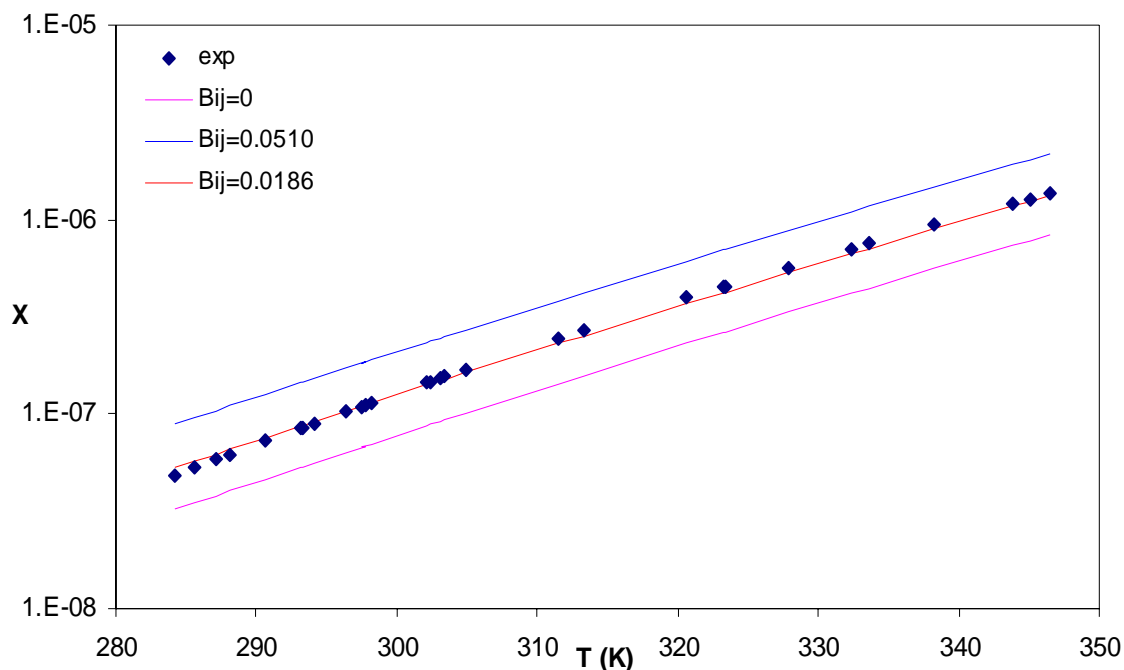


Figure 17 – Phenanthrene solubility in the aqueous phase for several values of β_{ij} .

As can be seen, the model considering the water-aromatic ring “association” seems to correctly take into account the solvation phenomena existent in these systems.

In spite of the excellent results obtained in this work for PAHs + water systems, some attempts to correlate the β_{ij} parameter with the aromaticity, thus increasing the model predictivity, were considered, but these did not seem to be very consistent.

Besides the solvation parameter, β_{ij} , an additional binary interaction parameter in the cubic term of CPA, k_{ij} is frequently employed. In a previous work where liquid-liquid equilibria of water + aromatics were studied, it was shown that the effect of k_{ij} was mostly significant on the hydrocarbon rich phase^[40]. Still in this thesis both the binary interaction parameter k_{ij} and the cross-association volume β_{ij} were also fitted simultaneously to experimental equilibrium data. The results obtained didn't improve considerably the results reported above, reducing the model predictivity.

The global aromaticity of PAHs has been the subject of a series of studies^[81].

In this work, the aromaticity of the PAHs was analyzed based in nucleus independent chemical shift (NICS).

Aromaticity is a complex and multidimensional physicochemical phenomenon that greatly affects many molecular properties such as magnetism, reactivity, and relative energy. The nucleus-independent chemical shift (NICS) is a generally accepted and widely used criterion for measuring aromaticity since its introduction by Schleyer et al.^[81]. It is defined as the negative value of the absolute magnetic shielding computed at any point of interest in the molecule, usually at the ring centers. It is therefore related to the magnetic consequences of aromaticity.

In this work, a relationship between the aromaticity and the β_{ij} value for each compound (figure 18) was evaluated. Nevertheless it was not possible to establish any correlation between the β_{ij} and the aromaticity. One can only conclude loosely that β_{ij} increases with aromaticity.

Table 11 – Values of the surface area (TSA) (Appendix B) and β_{ij} of PAHs.

Compound	β_{ij}	TSA (Å ²)
naphthalene	0.0269	160
anthracene	0.0455	210
pyrene	0.0403	220
acenaphthene	0.0193	172
phenanthrene	0.0186	205

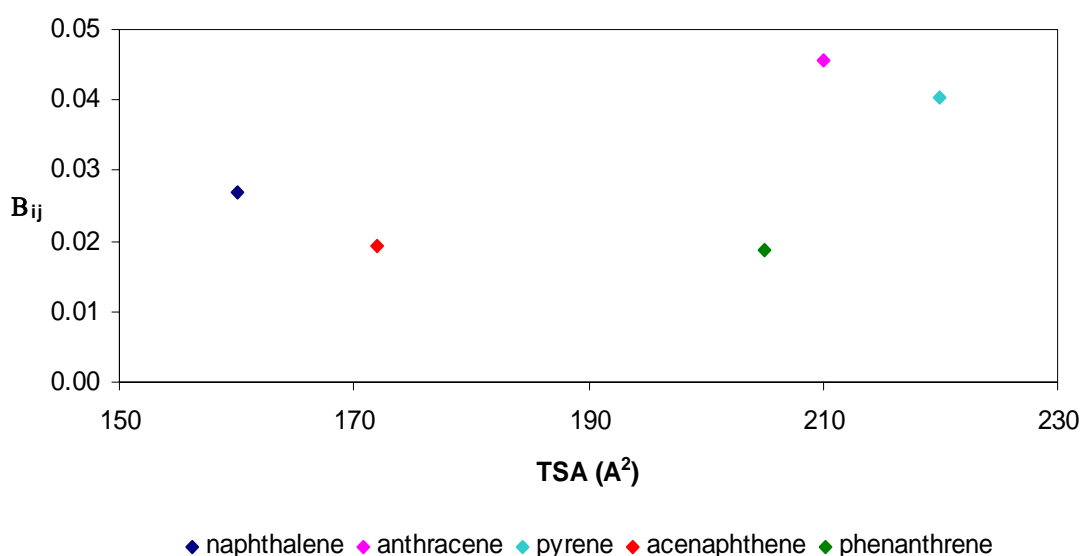


Figure 18 – β_{ij} values as a function of the surface area of PAHs.

4. Part

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, in a broad temperature range.

CPA pure compounds parameters were estimated for 25 PAH's and very good results for the vapour pressures and liquid densities were achieved, with global deviations inferior to 1.06 % and 1.42% respectively, covering the range of reduced temperatures from 0.45 to 0.85. Correlations for these parameters with the carbon number were not possible to propose resulting in higher global deviations, 11.1 % for the vapour pressures and 3.55% for the liquid densities.

It was shown that the solvation phenomena between a self associating molecule and a non-self-associating molecule, that takes place in the PAHs + water systems, can be successfully modelled with single and small cross-association parameters fitted to equilibrium data.

The results obtained for the solubility of several polycyclic aromatic hydrocarbons in water are in close agreement with the literature data, with global deviations inferior to 6.08 %, suggesting that the CPA EoS is an adequate model for correlating aqueous solutions of complex molecules of organic pollutants.

5. Part

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Appendix A

 Table A.1 – Parameters used in the correlation of liquid density (ρ_{liq})^[57].

Compound	A x10 ¹	B x10 ¹	C	D x10 ¹	T (K)
1-ethylnaphthalene	4.88	2.54	776	2.64	259.34 - 776
1,2,3,4-tetrahydronaphthalene	6.77	2.78	720	2.88	237.38 - 720
1-butylnaphthalene	4.00	2.53	792	2.83	253.43 - 792
1-nonylnaphthalene	2.27	2.27	849	3.02	284.15 - 849
1-decylnaphthalene	2.10	2.25	859	3.07	288.15 - 859
1-propylnaphthalene	4.39	2.52	782	2.81	264.55 - 782
n-hexylnaphthalene	3.42	2.54	813	3.01	255.15 - 813
2,6-dimethylnaphthalene	4.73	2.46	777	3.19	293.15 - 777
2,7-dimethylnaphthalene	3.56	2.14	775	2.84	293.15 - 775
2,6-diethylnaphthalene	3.85	2.42	807	2.86	322.15 - 807
1-phenylnaphthalene	3.68	2.42	849	2.90	318.15 - 849
1-n-hexyl-1,2,3,4-tetrahydronaphthalene	3.28	2.53	779	3.09	200 - 779
1-n-pentylnaphthalene	3.69	2.53	803	2.86	248.79 - 803
1-methylnaphthalene	5.48	2.54	772	2.80	242.67 - 772
naphthalene	6.35	2.58	748.4	2.77	333.15 - 748.4
2-methylnaphthalene	5.49	2.56	761	2.79	307.73 - 761
2-ethylnaphthalene	4.95	2.57	771	2.67	265.75 - 771
anthracene	4.71	2.61	873	2.35	488.93 - 873
pyrene	3.35	2.21	936	2.86	288.72 - 936
fluoranthene	3.47	2.27	905	2.86	383.33 - 905
acenaphthalene	4.86	2.64	792	2.86	289.15 - 792
chrysene	2.94	2.20	979	2.86	288.72 - 979
acenaphthene	3.99	2.20	803.15	2.40	366.56 - 803.15
phenanthrene	4.56	2.52	869	2.48	372.38 - 869
fluorene	6.50	2.60	870	2.86	387.94 - 870

Table A.2 – Parameters used in the correlation of vapour pressure (P^{σ})^[57].

Compound	A	B	C	D	E	T(K)
1-ethylnaphthalene	79.51	-10051	-7.83	2.50E-18	6	259.34 - 776
1,2,3,4-tetrahydronaphthalene	137.23	-10620	-17.91	1.45E-02	1	237.38 - 720
1-butylnaphthalene	119.49	-12706	-13.71	4.53E-06	2	253.43 - 792
1-nonylnaphthalene	90.31	-13035	-9.05	1.12E-18	6	284.15 - 849
1-decylnaphthalene	92.78	-13504	-9.36	1.07E-18	6	288.15 - 859
1-propylnaphthalene	86.51	-10646	-8.82	3.28E-18	6	264.55 - 782
n-hexylnaphthalene	126.57	-14052	-14.55	4.24E-06	2	255.15 - 813
2,6-dimethylnaphthalene	57.43	-8669.8	-4.73	8.68E-19	6	383.32 - 777
2,7-dimethylnaphthalene	50.87	-8274.7	-3.81	5.90E-19	6	368.81 - 775
2,6-diethylnaphthalene	63.29	-9908.2	-5.44	6.40E-19	6	322.15 - 807
1-phenylnaphthalene	83.32	-12017	-8.12	1.08E-18	6	318.15 - 849
1-n-hexyl-1,2,3,4-tetrahydronaphthalene	90.71	-11947	-9.21	1.88E-18	6	200 - 779
1-n-pentylnaphthalene	88.85	-11825	-8.95	1.78E-18	6	248.79 - 803
1-methylnaphthalene	67.57	-8737	-6.34	1.64E-06	2	242.67 - 772
naphthalene	62.96	-8137.5	-5.63	2.27E-18	6	353.43 - 748.4
2-methylnaphthalene	88.40	-10133	-9.17	4.27E-18	6	307.73 - 761
2-ethylnaphthalene	114.75	-11322	-13.31	5.71E-06	2	265.75 - 771
anthracene	65.07	-10251	-5.75	1.12E-18	6	488.93 - 873
pyrene	77.42	-12225	-7.33	8.22E-19	6	423.81 - 936
fluoranthene	167.64	-14930	-22.24	1.66E-02	1	383.33 - 905
acenaphthalene	74.68	-10061	-7.09	1.40E-18	6	362.65 - 792
chrysene	91.90	-14944	-9.06	4.89E-19	6	531.15 - 979
acenaphthene	71.25	-9584	-6.78	1.47E-06	2	366.56 - 803.15
phenanthrene	72.96	-10943	-6.79	1.09E-18	6	372.38 - 869
fluorene	129.09	-12347	-16.06	1.05E-02	1	387.94 - 870

Table A.3 – Parameters for critical temperature (T_c), critical pressure (P_c), acentric factor (w), enthalpy of fusion and range of temperature ^[57].

Compound	T_c (K)	$P_c \times 10^{-6}$ (Pa)	w	$\Delta H_f \times 10^{-7}$ (J kmol ⁻¹)
1-ethylnaphthalene	775.36	3.16	0.4073	1.63
1,2,3,4-tetrahydronaphthalene	719.16	3.56	0.3161	1.25
1-butylnaphthalene	792.00	2.64	0.4951	2.51
1-nonylnaphthalene	848.50	1.69	0.6168	-
1-decylnaphthalene	858.50	1.57	0.6415	-
1-propylnaphthalene	781.58	2.95	0.4554	1.76
n-hexylnaphthalene	812.73	2.19	0.5874	2.41
2,6-dimethylnaphthalene	776.29	3.04	0.4177	2.33
2,7-dimethylnaphthalene	776.63	3.13	0.4477	2.34
2,6-diethylnaphthalene	807.00	2.58	0.5118	2.03
1-phenylnaphthalene	849.00	2.63	0.5309	-
1-n-hexyl-1,2,3,4-tetrahydronaphthalene	776.00	1.91	0.5888	-
1-n-pentylnaphthalene	807.00	2.58	0.5118	2.34
1-methylnaphthalene	773.52	3.69	0.3521	0.97
naphthalene	748.49	4.05	0.3021	1.90
2-methylnaphthalene	761.05	3.45	0.3751	1.75
2-ethylnaphthalene	772.25	3.15	0.4213	1.47
anthracene	875.46	3.07	0.4857	2.94
pyrene	937.08	2.61	0.4257	1.74
fluoranthene	915.33	2.61	0.5438	1.87
acenaphthalene	795.67	3.28	0.3987	0.69
chrysene	982.38	2.40	0.6030	2.62
acenaphthene	808.58	3.10	0.3816	2.15
phenanthrene	871.14	3.08	0.5054	1.68
fluorene	842.67	3.85	0.3665	1.96

Appendix B

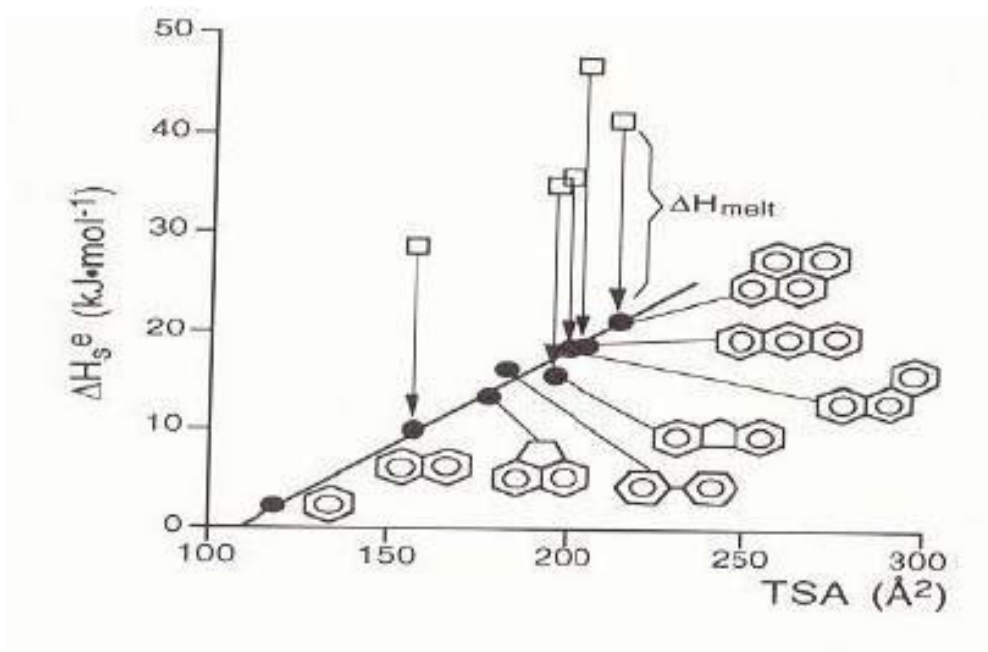


Figure B.1 – Enthalpies of solution related to surface area of the molecule.