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Solubility of polycyclic aromatics in binary solvent mixtures using activity coefficient models

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) precipitation is one of the major problems in the hydrocracking units. In this investigation, pyrene and phenanthrene were selected because they were found to be in higher concentrations in the feed to hydrocracking units. Their solubilities were investigated in toluene solvent mixture of *iso*-octane and heptane over a temperature range from 293 to 323 K. The experimental solubility data were used to predict the interaction parameters for seven different solid–liquid equilibrium models. The following activity coefficient models were used; Wilson, NIBS/Redlich–Kister, UNIQUAC, modified UNIFAC, modified UNIFAC (Dortmund), Flory–Huggins and Sheng. The interaction parameters were expressed as a second-order polynomial function in temperature. In order to test the models, the average absolute deviation percentage (AADP) was used. The overall AADP was found to range from approximately 7 to 14%. The models can be arranged according to their accuracy in a descending order based on AADP as follows: NIBS/Redlich–Kister, Wilson, UNIQUAC, Sheng, Flory–Huggins, modified UNIFAC (Dortmund) and finally modified UNIFAC. All models used in this work gave reasonable results; however, the group contribution models can also be used as a predictive tool for the solubility measurement of pyrene and phenanthrene in other solvents containing the same groups of the solvents used in this study.

Keywords: Solid–liquid equilibria (SLE); Models; Pyrene; Phenanthrene; Toluene; *iso*-Octane; Heptane

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings. The precipitation of polycyclic aromatic hydrocarbons during the hydrocracking process is of the prime interest in petroleum and petrochemical industries. PAHs are difficult to crack and may build up in the recycle streams in the hydrocracking unit (HCR). High PAHs content in HCR feed may cause the following problems in the unit; accelerated coking and catalyst deactivation in the reactor section; reduction in heat transfer and possible plugging in the tubes of heat exchangers; fouling and plugging on valves-trays of fractionators.

Solid–liquid equilibrium data for a number of PAHs is becoming increasingly important in the petroleum industry. Solubility data for a number of polycyclic aromatic compounds have been published in the recent chemical literature. Zvaigzne and Acree [1] used successfully NIBS/Redlich–Kister equation and modified Wilson model to mathematically present the solubility of pyrene in alkane + 1-propanol and alkane + 2-propanol solvent mixtures. Also, the same authors tested the same models for predicting the solubility of pyrene in alkane and 1-octanol solvent mixtures, and reported very accurate results [2]. McHale et al. [3] had accurately represented the solubility of pyrene in binary alcohol + cyclohexanol and alcohol + pentanol solvent mixtures at 299.2 K using NIBS/Redlich–Kister equation. Furthermore, McHale et al. [4] used the same model to test the solubility of pyrene in binary alcohol + 2-methyl-2-butanol solvent mixtures at 299.2 K. The mathematical representation gave accurate results. Also, Hernandez et al. [5] studied

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the solubility of pyrene in binary solvent mixtures alkane + 2-butanol using the NIBS/Redlich–Kister equation. However, Mahmoud et al. [6] found that UNIFAC failed to accurately predict the solubility of pyrene in long chain normal alkanes. But, by readjusting UNIFAC parameters, they [6] found that reasonably good representations of the solubility diagrams were obtained. On the other hand, Lee et al. [7] successfully used both Wilson and NRTL models for representing the solubility of binary mixtures constituted of phenanthrene, acenaphthene, dibenzofuran, fluorene and diphenylmethane. Both UNIFAC and the modified UNIFAC (Dortmund) models were found to have better accuracy when describing the solubilities of pyrene, anthracene and fluranthene in polar organic solvents rather than non-polar organic solvents [8].

The objective of this investigation is to study the precipitation of the polycyclic aromatic compounds in the hydrocracking unit by studying experimentally the precipitation of pyrene and phenanthrene dissolved in toluene (as a typical aromatic) by addition of *iso*-octane (as a typical *iso*-paraffin) and heptane (as a typical paraffin) and modeling the precipitation of pyrene and phenanthrene using seven solid–liquid activity coefficient models.

2. Solid–liquid equilibria models

The solid–liquid equilibria (SLE) calculations can be calculated by [9]:

$$\ln(\alpha_i) = \ln(\gamma_i x_i) = -\frac{\Delta H_\mathrm{f}}{RT_\mathrm{t}}\left(\frac{T_\mathrm{t}}{T}-1\right)+\frac{\Delta C_\mathrm{p}}{R}\left(\frac{T_\mathrm{t}}{T}-1\right) -\frac{\Delta C_\mathrm{p}}{R}\ln\frac{T_\mathrm{t}}{T}-\frac{\Delta H_\mathrm{p}}{RT}+\frac{\Delta S_\mathrm{p}}{R} \quad (1)$$

where α_i is the activity of component i, γ_i the activity coefficient of component i, x_i the mole fraction of component i in the liquid phase, ΔH_f the molar enthalpy of fusion of the solute at the triple-point temperature T_t, ΔC_p the molar heat capacity of the pure solute, ΔH_p the molar enthalpy change of the solid-phase transition and ΔS_p is the molar entropy change of the solid-phase transition. For most substances, there is little difference between the triple point temperature and the normal melting point temperature, also there is a negligible difference between the enthalpies of fusion at these two temperatures. Thus, to a good approximation, we can substitute normal melting temperature (T_m) for triple point (T_t), and can assume that ΔH_f is essentially the same at the two temperatures. In addition, in Eq. (1), the two terms in the right-hand side containing ΔC_p term almost cancel each other and of less importance than the remaining terms. Therefore, a simplified form of this equation can be used. For the two studied PAHs in this investigation, only phenanthrene exhibited a solid-phase transition that starts at 314–360 K (Lee et al. [7]), which lies within its melting point (372.5 K [7]) and the system temperature (ranged from 293 to 323 K). ΔH_p and ΔS_p for phenanthrene are 1.3 kJ/mol and 3.85 J/(mol K), respectively (Lee et al. [7]).

2.1. Wilson model

Wilson [10] expressed the activity coefficient for component i in a mixture as follows:

$$\ln\gamma_i = 1-\ln\left(\sum_{j=1}^{c}x_j\Lambda_{ij}\right)-\sum_{k=1}^{c}\left(\frac{x_k\Lambda_{ki}}{\sum_{j=1}^{c}x_j\Lambda_{kj}}\right) \quad (2)$$

where c is the number of the components in the mixture. Λ_{ij} is a model parameter which is expressed by:

$$\Lambda_{ij} = a_{ij}+b_{ij}T+c_{ij}T^2 \quad (3)$$

2.2. Combined NIBS/Redlich–Kister equation

For prediction of solute solubilities in a binary solvent system, the following expression of a combined NIBS/Redlich–Kister equation (suggested by Acree et al. [11–13]) can be used:

$$\ln x_\mathrm{A}^\mathrm{sat} = x_\mathrm{B}^0\ln(x_\mathrm{A}^\mathrm{sat})_\mathrm{B}+x_\mathrm{C}^0\ln(x_\mathrm{A}^\mathrm{sat})_\mathrm{C}+x_\mathrm{B}^0x_\mathrm{C}^0\sum_{i=0}^{N}S_i^*(x_\mathrm{B}^0-x_\mathrm{C}^0)^i \quad (4)$$

where x_B^0 and x_C^0 are the initial mole fractions of the binary solvent as if solute A is not present and $x_\mathrm{A}^\mathrm{sat}$ is the saturated mole fraction solubility of the solute in pure solvent i. $S_i{}^*$ is the model parameter and it is expressed as the following:

$$S_i^* = a_i+b_iT+c_iT^2 \quad (5)$$

2.3. UNIQUAC model

The activity coefficient for any component i can be calculated by the UNIQUAC model as follows [9]:

$$\ln\gamma_i = \ln\frac{\Phi_i^*}{x_i}+\frac{z}{2}q_i\ln\frac{\theta_i}{\Phi_i^*}+l_i-\frac{\Phi_i^*}{x_i}\sum_{j=1}^{m}x_jl_j -q'_i\ln\left(\sum_{j=1}^{m}\theta'_j\tau_{ij}\right)+q'_i-q'_i\sum_{j=1}^{m}\frac{\theta'_j\tau_{ij}}{\sum_{k=1}^{m}\theta'_k\tau_{kj}} \quad (6)$$

where

$$l_j = \frac{z}{2}(r_j-q_i)-(r_j-1) \quad (7)$$

The segment fraction Φ_i^* and area fractions θ_i and θ'_i are given by:

$$\Phi_i^* = \frac{r_ix_i}{\sum_{j=1}^{m}r_jx_j},\qquad \theta_i = \frac{q_ix_i}{\sum_{j=1}^{m}q_jx_j},\qquad \theta'_i = \frac{q'_ix_i}{\sum_{j=1}^{m}q'_ix_j} \quad (8)$$