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Predictive method of hydrogen solubility in heavy petroleum fractions using EOS/G^E and group contributions methods

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ABSTRACT

Hydrogen solubility in heavy petroleum fractions was modelled with Peng-Robinson cubic equation of state combined with the UNIFAC solution model (EoS/G^E) through a modified Huron-Vidal mixing rule (MHV1). As critical properties and molecular structure of heavy petroleum fractions are entering parameters in this thermodynamic model, the thermodynamic characterization procedure by contribution of functional groups proposed by Carreón-Calderón et al. (2012) was taken as starting point in order to develop a predictive method for estimating hydrogen solubility in such fractions. The functional groups considered in the original work were reviewed and modified, improving predictions and avoiding adjustment of model parameters. Besides, a procedure of mass distribution for the hydrogen-carbon ratio (HCR) of the petroleum fraction is proposed so that the hydrogen solubility can be estimated when more than one heavy petroleum fraction is present. This approach was tested with twelve heavy petroleum fractions in a wide range of pressure and temperature. These fractions include coal liquids, refinery products and a bitumen from Athabasca. The total average deviation was about 15%.

1. Introduction

Hydrogen solubility is a key parameter in designing and operating several processes in chemical and petroleum industries. For instance, hydroprocess in the refining industry, and more recently in situ upgrading, needs experimental data and theoretical models to predict VLE behavior of hydrogen and hydrocarbons (pure components or petroleum fractions). Several authors have pointed out the influence of VLE on selectivity and conversions [1–5]. Luz M. Chavez et al. [6] presented a detailed review concerning experimental and theoretical VLE behavior of hydrocarbons and hydrogen. Among all the thermodynamic methods commonly used to predict hydrogen solubility in petroleum fractions, cubic equations of state (CEoS) are the most used because their mathematical simplicity and their predictive capabilities. They are the classical models for high pressure and temperature predictions, being suitable for multicomponent mixtures modelling as well. However, some parameters of CEoS have to be fitted to experimental VLE data in order to obtain more accurate results [7–12]. Privat et al. [13] and Ulrich [14] reported some problems with respect to VLE modelling of mixtures containing hydrogen and hydrocarbons because of the quantum nature of hydrogen and the molecular asymmetry. The unusual phase behavior of these systems leads to type-III phase diagrams, which show peculiar characteristics in its phase equilibrium modelling. For instance, Le Guennec et al. [15] analyzed consistency for alpha functions from CEoS, finding that special shapes are shown and that specific regression necessities are required in the case of quantic fluids. To overcome such difficulties, models combining CEoS with G^E models are reported in literature, for example, Jun-Wei et al. [16] predict VLE of binary mixtures of hydrogen and defined hydrocarbons using PPR78 [17], which estimates binary interaction parameters through functional group contributions. This thermodynamic model as well as anyone using group contribution methods is, in principle, a candidate for being used in phase equilibrium calculations in the presence of hydrogen and petroleum fractions. However, in this work, the original PR equation of state will be used because this is still one of the most employed equation in petroleum industry.

Methods based on regular solution theory are also reported in literature, where the solubility parameter is calculated through

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Notation

A	parameter of the equation of state
A_d	coefficient in Eqs. (14)–(16)
A_H	coefficient in Eq. (19)
a	attraction parameter from PR-EOS
A1–A3	coefficients in Eq. (6)
B	parameter of the equation of state
B_d	coefficient in Eqs. (14)–(16)
b	co-volume parameter from PR-EOS
FG	number of functional groups types
F_{Obj}	objective Function
RHC	hydrogen carbon ratio
MW	molecular weight of a petroleum fraction
M_+	molecular weight of the plus fraction
N	number of data points
P	pressure
P_b	bubble pressure
P_c	critical Pressure
p_c	contribution to P_c by functional groups
R	universal constant of gases, 8.31441 J/mol K
$AAD\%$	absolute average deviation $= \frac{100}{N}\sum_{i=1}^{N}\left(\frac{\lvert x_i^{Exp}-x_i^{Cal}\rvert}{x_i^{Exp}}\right)$
T	temperature
T_c	critical temperature
V	molar volume, m^3/mol
V_c	critical volume, m^3/mol
v_C	contribution to V_c by functional groups
x	mole fraction
Z	compressibility factor

Greek letters

α	coefficient in Eq. (25)
β	coefficient in Eq. (25)
γ	activity coefficient
Δv	group volume increment in Eq. (4)
ϕ	fugacity coefficient
ρ	mass density, kg/m^3
ν	number of functional groups
χ	coefficient in Eq. (25)
ω	acentric factor
ψ	group interaction parameter

Superscripts

Cal	calculated data
L	liquid phase
Exp	experimental data

Subscripts

i	functional group i or pure component i
j	undefined petroleum fractions j or pure component

correlations based on easy measurable bulk properties of the petroleum fraction. However, these methods are limited to model binary mixtures, that is, systems formed by hydrogen and one petroleum fraction [18,19]. Saajanletho et al. measured hydrogen solubility in petroleum fractions and tested some of the methods previously mentioned [20,21]. Among their developments, a thermodynamic characterization procedure based on the PNA (paraffinic, naphthenic and aromatic) content was used to estimate EoS input parameters; however, binary interaction parameters were adjusted in order to obtain better agreement between calculated and experimental data with petroleum fractions. Lei et al. [22] presented an experimental and modelling study of hydrogen solubility in a catalytic diesel from a molecular point of view by means of a COSMOS-RS model. Good agreement between their experimental observations and calculated data is showed, but a sensitivity analysis of the molecular structure was carried out due to the uncertainty of the diesel molecular structure.

Recently, a new method to estimate hydrogen solubility in petroleum fractions has been published by Aguilar-Cisneros et al. [23]. They used a characterization procedure based on group contributions methods [24] for estimating input parameters of a CEoS/G^E model, with which predictions of VLE for binary mixtures of hydrogen and heavy petroleum fractions (0.892–1.0297 g/cm^3) were carried out over a wide range of pressure (0.26–24.85 MPa) and temperature (323.15–623.15 K) conditions. Good agreement between calculated and experimental data was achieved but a correction factor was needed to improve hydrogen solubility calculations in petroleum fractions having molecular weights above 500 g/mol. Besides, the method was limited to binary systems. The aim of this work is to extend this method to multicomponent mixtures of hydrogen and petroleum fractions and to avoid adjustment of model parameters, obtaining thus a predictive method of the hydrogen solubility in petroleum fractions.

2. Characterization procedure

The thermodynamic characterization method is based on that suggested by Carreón-Calderón et al. [25]. This method is used to estimate parameters entering into CEoS/G^E models (critical properties and a molecular pseudostructure) by a Gibbs free energy minimization process, which is subject to linear constraints of molecular weight (MW) and density (ρ) of the corresponding petroleum fraction. Either Marrero-Gani (MG) [26] or Joback-Reid (JR) [27] group contribution method combined with GCVOL [28] method are used in such minimization process as relationships that connects critical properties and liquid density with functional groups. Nine functional groups are considered to construct the so-called molecular pseudostructure so that the UNIFAC [29] solution model can be used into CEoS/G^E models. This procedure was successfully tested for modelling phase equilibria and densities of light and heavy crude oil [25,30] but not for modelling mixtures containing hydrogen and hydrocarbons, especially in the case of heavy petroleum fractions. For hydrogen solubility in petroleum fractions, the procedure was modified by Aguilar-Cisneros et al. [23] by including the hydrogen-carbon ratio (HCR) as third constraint in the minimization process in order to construct a molecular pseudostructure of the petroleum fraction in a better accordance with its actual chemical nature. The Gibbs free energy used as the objective function is expressed in terms of the liquid fugacity coefficient (ϕ_i^L) as follows:

$$\min_{\upsilon_1,\upsilon_2,\cdots,\upsilon_{FG}\geqslant 0} \phi_i^L[T_{Ci}(\upsilon_1,\upsilon_2,\cdots,\upsilon_{FG}),P_{Ci}(\upsilon_1,\upsilon_2,\cdots,\upsilon_{FG}),\omega_i(\upsilon_1,\upsilon_2,\cdots,\upsilon_{FG})] \tag{1}$$

where T_C, P_C and ω are the critical temperature, critical pressure and acentric factor, respectively, whereas FG is the number of functional group types considered. The needed expression for estimating ϕ_i^L depends on the selected CEoS. In case of Peng-Robinson (PR) equation [31], fugacity coefficient can be determined from:

$$ln(\phi_i^L) = (Z^L-1)-ln(Z^L-B)-\frac{A}{2\sqrt{2}B}ln\left(\frac{Z^L+(\sqrt{2}+1)B}{Z^L-(\sqrt{2}-1)B}\right) \tag{2}$$

where $Z^L = Pv^L/(RT)$ is the compressibility factor of the liquid phase, whereas A and B are Peng-Robinson parameters. P and T are the pressure and temperature of the system, respectively. For the minimization process stated by Eq. (1), the pressure is set equal to 0.101325 MPa and the temperature equal to 288.71 K; that is, the standard conditions at which the bulk properties of petroleum fractions