Fluid Phase Equilibria 334 (2012) 197–203

Contents lists available at SciVerse ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Short communication

Addition of the sulfhydryl group (—SH) to the PPR78 model: Estimation of missing group-interaction parameters for systems containing mercaptans and carbon dioxide or nitrogen or methane, from newly published data

Romain Privat, Jean-Noël Jaubert*

Université de Lorraine – Ecole Nationale Supérieure des Industries Chimiques (ENSIC), Laboratoire Réactions et Génie des Procédés (UPR CNRS 3349), 1 rue Grandville, B.P. 20451, F-54001 Nancy Cedex, France

ARTICLE INFO

Article history:
Received 14 June 2012
Received in revised form 3 August 2012
Accepted 6 August 2012
Available online 14 August 2012

Keywords:
Mercaptan
Sulfhydryl
PPR78
Predictive model
Binary interaction parameters
Nitrogen
Carbon dioxide
Methane
CPA

ABSTRACT

In 2008, the PPR78 model (Predictive Peng–Robinson 1978) was extended to mercaptan-containing systems by adding the sulfhydryl group (—SH), that is, by determining the values of the group-interaction parameters between the group —SH and the fourteen other groups already present in the PPR78 model. Unfortunately, due to a lack of experimental data reported in the open literature, it was not possible to characterize interactions between the group —SH and the three groups: ethane, CO_2 and N_2. Very recently, vapor–liquid equilibrium data for three binary systems containing methanethiol and respectively methane, nitrogen and carbon dioxide were however measured. It was thus decided to use these data to estimate two of the missing group-interaction parameters (—SH/CO_2 and —SH/N_2). For such systems, deviations observed with the PPR78 model are compared to those obtained with the CPA equation of state.

1. Introduction

The PPR78 model (Predictive Peng–Robinson 1978) is a well-established model able to predict with accuracy the phase behavior of natural gases, gas condensates and crude oils explaining why it is today integrated in famous process-simulation softwares like *ProSimPlus* or *PRO/II*. Any mixture containing alkanes, aromatics, naphthenes, CO_2, N_2, H_2S, and mercaptans can be predicted with such a model which combines the Peng–Robinson equation of state in its 1978 version, classical mixing rules and a group-contribution method for the estimation of the temperature-dependent binary interaction parameters $k_{ij}(T)$. In 2008, Privat et al. [1] decided to add the sulfhydryl group (—SH) to the PPR78 model, briefly presented hereafter. By considering – as far as possible – all the data sets available in the open literature, Privat et al. were able to estimate group-interaction parameters between group —SH and eleven other elementary groups: alkanes groups (CH_3, CH_2, CH, C and methane), aromatic groups (C_{aro}, CH_{aro}, $C_{fused\ aromatic\ rings}$), naphthenic groups ($CH_{2\ cyclic}$, $CH_{cyclic} \Leftrightarrow C_{cyclic}$) and group H_2S (hydrogen sulfide). In spite of a thorough bibliographic study, it was however not possible to find data allowing estimation of interactions {group ethane/group —SH}, {group CO_2/group —SH} and {group N_2/group —SH}.

In a very recent paper, Awan et al. published vapor–liquid equilibrium (VLE) data on three binary systems containing methanethiol (a mercaptan) and methane, nitrogen or carbon dioxide [2]. To the best of our knowledge, it is the very first time that experimental VLE data are reported for systems containing carbon dioxide or nitrogen and a mercaptan. These measurements clearly offer the opportunity to estimate two of the three missing sets of PPR78 group-interaction parameters mentioned above (between group CO_2 and group —SH and between group N_2 and group —SH). This is the main goal of the present paper.

Although already estimated in 2008 [1], group-interaction parameters between groups —SH and methane were re-determined using the new data on the binary system methanethiol + methane measured by Awan et al. [2].

* Corresponding author. Fax: +33 3 83 17 51 52.
E-mail addresses: romain.privat@univ-lorraine.fr (R. Privat), jean-noel.jaubert@univ-lorraine.fr, Jean-Noel.Jaubert@ensic.inpl-nancy.fr (J.-N. Jaubert).

0378-3812/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.fluid.2012.08.007

Table 1
Nomenclature used for the six PPR78 groups considered in this study.

Group chemical structure	Group number
—CH_3	1
—CH_2	2
Methane (CH_4)	5
Carbon dioxide (CO_2)	12
Nitrogen (N_2)	13
—SH	15

In the last part of this paper, the performances of the PPR78 model and the Cubic-Plus-Association (CPA) EoS are evaluated and compared.

2. A short presentation of the PPR78 model

The PPR78 model relies on the Peng–Robinson equation of state (EoS) [3] with classical Van der Waals mixing rules [1,4–10]. In the PPR78 model, the binary-interaction parameters $k_{ij}(T)$, depend on temperature and are calculated by a group-contribution method through the following expression:

$$k_{ij}(T) = \frac{-(1/2)\left[\sum_{k=1}^{N_g}\sum_{l=1}^{N_g}(\alpha_{ik}-\alpha_{jk})(\alpha_{il}-\alpha_{jl})A_{kl}\cdot(298.15/(T/\mathrm{K}))^{(B_{kl}/A_{kl})-1}\right] - [(\sqrt{a_i(T)}/b_i)-(\sqrt{a_j(T)}/b_j)]^2}{2[(\sqrt{a_i(T)\cdot a_j(T)})/(b_i\cdot b_j)]} \quad (1)$$

In Eq. (1), a_i and b_i are pure-component Peng–Robinson parameters [1,3–10]. N_g is the number of different groups defined by the method (for the time being, fifteen groups are defined and $N_g = 15$). α_{ik} is the fraction of molecule i occupied by group k (occurrence of group k in molecule i divided by the total number of groups present in molecule i). $A_{kl} = A_{lk}$ and $B_{kl} = B_{lk}$ (where k and l are two different groups) are constant group-interaction parameters determined in our previous papers [1,4–10].

According to the PPR78 group-decomposition scheme, six groups (—SH, —CH_3, —CH_2, methane, CO_2, N_2) are necessary to build the five molecules (methanethiol, ethanethiol, methane, CO_2, N_2) involved in this work. These groups are numbered as mentioned in Table 1, following the nomenclature previously adopted [1,4–10].

Table 2
Pure-component properties and data sources.

Name	Source	T_c (K)	P_c (bar)	ω
Methyl mercaptan (methanethiol)	[11]	470.00	72.30	0.150
Ethyl mercaptan	[12][a]	499.15	54.90	0.188
Methane	[11]	190.56	45.99	0.011
Carbon dioxide	[11]	304.12	73.74	0.225
Nitrogen	[11]	126.20	33.98	0.037

[a] The reason for which two different data sources were considered is explained in [1].

According to Eq. (1), the six following group-interaction parameters have thus to be determined: $\begin{cases} A_{15-5} \\ B_{15-5} \end{cases}$, $\begin{cases} A_{15-12} \\ B_{15-12} \end{cases}$ and $\begin{cases} A_{15-13} \\ B_{15-13} \end{cases}$.

Note that the three group-interaction parameters $\begin{cases} A_{15-1} \\ B_{15-1} \end{cases}$, $\begin{cases} A_{15-2} \\ B_{15-2} \end{cases}$ and $\begin{cases} A_{1-2} \\ B_{1-2} \end{cases}$, were determined in previous works [1,4].

The regression procedure used to estimate the three sets of A_{kl} and B_{kl} parameters is similar to the one previously used [1,4–10]. It is briefly reminded hereafter.

1. Values of $T_{c,i}$, $P_{c,i}$ and ω_i (acentric factor) for each pure compound i are required to estimate parameters a_i and b_i involved in Eq. (1). These values and their sources are given in Table 2 for the six molecules considered in this study.
2. A databank containing VLE data is developed. In the present case, it contains data from [2] (for binary systems methanethiol + methane, methanethiol + CO_2 and methanethiol + N_2) and [13] (for binary systems methanethiol + methane and ethyl mercaptan + methane).
3. A_{kl} and B_{kl} parameters are fitted on VLE data using the quasi-Newton BFGS method [14]. The objective function to be minimized is defined as follows:

$$\begin{cases} F_{\mathrm{obj}} = \dfrac{F_{\mathrm{obj,bubble}} + F_{\mathrm{obj,dew}}}{n_{\mathrm{bubble}} + n_{\mathrm{dew}}} \\ F_{\mathrm{obj,bubble}} = 100\displaystyle\sum_{i=1}^{n_{\mathrm{bubble}}} \frac{|\Delta x|}{2}\left(\frac{1}{x_{1,\mathrm{exp}}} + \frac{1}{x_{2,\mathrm{exp}}}\right)_i \quad \text{with} \quad |\Delta x| = |x_{1,\mathrm{exp}} - x_{1,\mathrm{calc}}| = |x_{2,\mathrm{exp}} - x_{2,\mathrm{calc}}| \\ F_{\mathrm{obj,dew}} = 100\displaystyle\sum_{i=1}^{n_{\mathrm{dew}}} \frac{|\Delta y|}{2}\left(\frac{1}{y_{1,\mathrm{exp}}} + \frac{1}{y_{2,\mathrm{exp}}}\right)_i \quad \text{with} \quad |\Delta y| = |y_{1,\mathrm{exp}} - y_{1,\mathrm{calc}}| = |y_{2,\mathrm{exp}} - y_{2,\mathrm{calc}}| \end{cases} \quad (2)$$

n_{bubble} and n_{dew} are the number of bubble points and dew points respectively. x_i is the mole fraction of component i in the liquid phase and y_i is the mole fraction of component i in the gas phase. Subscript *exp* stands for an experimental value. $x_{i,\mathrm{calc}}$ and $y_{i,\mathrm{calc}}$ are the mole fractions of component i respectively in the liquid and gas phases, calculated at given experimental values of temperature and pressure using the PPR78 model.

3. Estimation or re-estimation of group-interaction parameters between the group sulfhydryl (—SH) and three other groups

As explained before, six groups are involved in mixtures considered in this work (groups number 1, 2, 5, 12, 13, 15). This section aims at studying and quantifying the three group interactions {group 15–group 5}, {group 15–group 12} and {group 15–group 13}.

3.1. Interaction between group —SH and group methane

This interaction was already studied in a previous work [1]: the A_{15-5} and B_{15-5} parameters were determined from 128 bubble-point data [13] on two binary systems