Generalized Correlation of Binary Interaction Parameters in Cubic Equations of State for Hydrocarbon/CO₂, Hydrocarbon/H₂S and CO₂/H₂S Systems

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In the present work, we develop a predictive corresponding-states correlation for the binary interaction parameters of systems composed of hydrocarbons (HC), up to C_{10}, with CO_2 and H_2S. Experimental data were collected from the literature for 12 HC/CO_2 systems (1017 data points for 90 isotherms), 7 HC/H_2S systems (293 data points for 27 isotherms), and the CO_2/H_2S systems (61 data points for 19 isotherms). Optimal k_{ij} were computed using the isofugacity method of Paunović et al. Computations were made for the van der Waals, Redlich-Kwong and Peng-Robinson equations of state, with the cohesion functions of Soave, Gibbons and Laughton, Stryjek and Vera, Twu et al., and our own group. Analysis of the results showed that k_{ij} are essentially the same for each binary pair and equation of state, regardless of the cohesion function used, thus making them true system properties. Average deviations obtained with the present correlation range from 2.5% to 4.5% for compositions, and from 1.5% to 4.0% for pressures, depending on the equation of state and type of binary pair. The correlation has also been used successfully in predicting vapor-liquid equilibria of ternary and higher mixtures involving these same components.

1. Introduction

Cubic equations of state are still widely used for representing phase equilibria of mixtures of industrial importance, notably in the natural gas and petroleum industry where there are mixtures of hydrocarbons and inorganic gases such as CO_2, H_2S, H_2 and N_2. Their applicability is based on their algebraic simplicity, versatility and precision. The general form for the 2P1T (2 parameters, one dependent on temperature) cubic equations of state (CEOS) is:

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + k_1 b v + k_2 b^2}$$ (1)

where a and b, the cohesion parameter and the covolume, are specific to each substance and are calculated from their critical properties as:

$$a = a_c \alpha(T_r); \quad a_c = \Omega_{ac} \frac{R^2 T_c^2}{P_c}; \quad b = \Omega_{bc} \frac{R T_c}{P_c}$$ (2)

Depending on the values of k_1, k_2, Ω_{ac}, and Ω_{bc} different versions of the CEOS are obtained, as shown in Table 1.

Table 1. Cubic equation of state constants

CEOS	k_1	k_2	Ω_{ac}	Ω_{bc}
van der Waals (VW)	0	0	27/64	1/8
Redlich-Kwong (RK)	1	0	0.427480	0.076640
Peng-Robinson (PR)	2	-1	0.457235	0.077796

Wilson (1964) and later Soave (1972) introduced a temperature dependence in the cohesion parameter, through the so called "cohesion function" or "alpha function" $\alpha(T_r)$, in order to improve the prediction of vapor pressures of single components. Most modern CEOS incorporate this function, and many different expressions have been proposed, such as those shown in Table 2. These functions may have one, two or more fluid specific parameters, which in some cases can be correlated in terms of physical properties (typically the acentric, ω, and the critical compressibility, Z_c factors).

Table 2: Cohesion functions considered in the present work

Authors	Cohesion function
Soave (1972) (S72)	$\alpha = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2$
Soave (1979) (S79)	$\alpha = 1 + (1 - T_r)\left(m + \dfrac{n}{T_r}\right)$
Gibbons and Laughton (1984) (GL)	$\alpha = 1 + m(T_r - 1) + n\left(\sqrt{T_r} - 1\right)$
Stryjek and Vera (1986) (SV)	$\alpha = \left\{1 + \left[m + n\left(1 - \sqrt{T_r}\right)(0.7 - T_r)\right]\left(1 - \sqrt{T_r}\right)\right\}^2$
Twu et al. (1991) (TW)	$\alpha = T_r^{n(m-1)} e^{l\left(1 - T_r^{nm}\right)}$
Stamateris and Olivera (1996) (SOF)	$\alpha = T_r\left[1 + \dfrac{m}{n-1}(1 - T_r^{1-n})\right]$

The extension of CEOS to mixtures is achieved through the introduction of mixing rules that take into account the interaction between components. Although there are several mixing rules intended for different type of systems, the classical "one-fluid" or van der Waals mixing rule (Eq. 3) has been found accurate enough to represent mixtures containing light hydrocarbons and gases such as CO_2 and H_2S.

$$a_m = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \sqrt{a_i a_j}\left(1 - k_{ij}\right) \quad b_m = \sum_{i=1}^{n} x_i b_i$$

$$\tag{3}$$

Here k_{ij} is the binary interaction parameter (BIP), which is an empirical factor introduced to increase the accuracy of the CEOS through a better representation of unlike pair interactions. This improved performance is obtained at the expense of losing

part of the predictive capability of the CEOS, which now must rely on the availability of experimental data for the calculation of the BIP. Therefore, it is highly desirable to have an estimation tool for these parameters.

The objective of the present work is the computation of BIP for binary mixtures of fluids often found in the natural gas industry, such as paraffinic hydrocarbons (from C1 to C10), and the inorganic gases carbon dioxide and hydrogen sulphide. We then proceed to develop a corresponding-states correlation for these BIP in order to provide a predictive method for estimation of BIP for ill-defined fluids or when experimental data is scarce.

2. Calculation of Binary Interaction Parameters

The BIP are usually adjusted from vapor-liquid equilibria (VLE) data of binary systems. Different objective functions have been proposed for this purpose, such as minimizing the differences between experimental and calculated pressures, or similarly compositions in the vapor phase. In the present work the method proposed by Paunović et al. (1981), which minimizes the differences between the fugacities of vapor and liquid phases at equilibrium, is applied. This method has the advantage of significantly reducing the computational effort, because it does not require iterative calculations of the VLE, and providing a good compromise between minimization of the deviations of pressure and vapor compositions. However, it is limited to data sets that fully include the equilibrium temperatures, pressures and compositions of both phases. The objective function to minimize is:

$$F = \sum_{m=1}^{n} \left(\frac{|f_i^L - f_i^V|}{f_i^V} + \frac{|f_j^L - f_j^V|}{f_j^V} \right)_m$$

(4)

In the present work, we studied 12 binary systems of CO_2 and paraffinic hydrocarbons from C1 to C10 with a total of 90 isotherms and 1017 data points; 7 binary systems of H_2S and C1-C10 paraffins with a total of 27 isotherms and 293 points; and the binary system CO_2/H_2S with 19 isotherms and 61 points. The BIP were computed for the original form of the Soave-Redlich-Kwong CEOS (RK CEOS with S72 alpha function), and also for the VW, RK and PR CEOS with the S79, GL, SV and SOF cohesion functions, using the constants m and n computed by Figueira (2005), Figueira et al. (2006) and Figueira et al. (2007). The TW cohesion function was also considered but only for the RK and PR CEOS. This made up a total of 16 CEOS/$\alpha(T_r)$ combination, for each of which the BIP were optimized for each binary system and isotherm.

In general, the BIP were found to be temperature dependent. Figure 1 shows that BIP tend to increase with temperature, at a much steeper rate as the critical temperature of the heavier component is approached. The same behavior was observed by Estévez et al. (1988), who attributed it not only to greater molecular interactions, but also to the need to compensate for the inadequacies of CEOS in the critical region. We also found, Figure 1a, that BIP calculated for the same CEOS and different cohesion functions do not exhibit great variation (only 0.6% for VW and RK and 0.5% for PR), and can therefore be considered as dependent only on the binary pair and CEOS, allowing the

use of the same (averaged) BIP for any $\alpha(T_r)$. Moreover, the differences between BIP for the VW and RK CEOS were found to be negligible (0.1%), so that the same BIP can be used for both CEOS. We thus proceeded to formulate two corresponding states correlations, one for the PR and the other jointly for the RK and VW CEOS, using the average of optimized BIP for each isotherm and system.
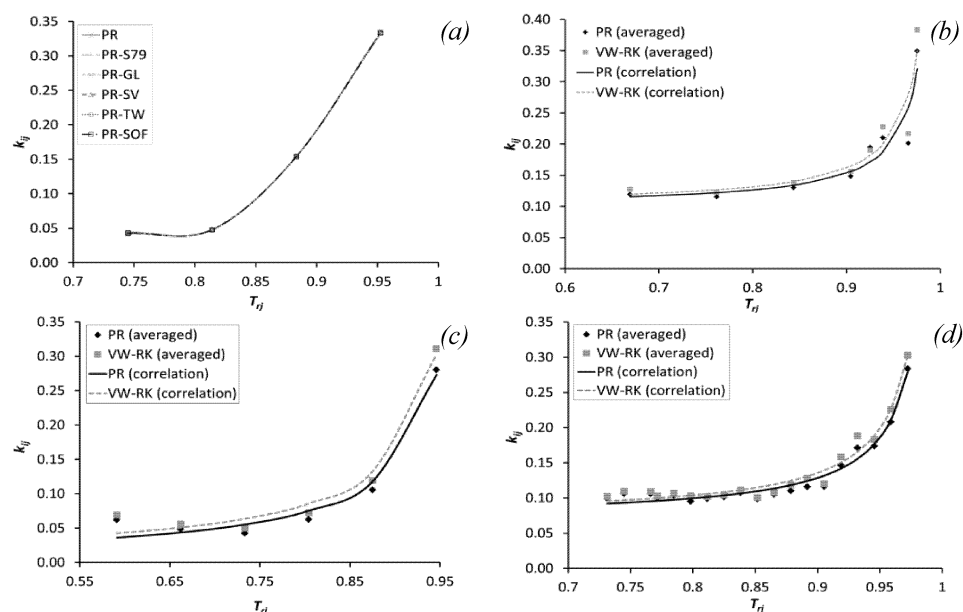

Figure 1. BIP behaviour with temperature: (a) Optimized for H$_2$S/neopentane, and correlated for (b) CO$_2$/isobutane (c) H$_2$S/n-pentane, and (d) CO$_2$/H$_2$S systems.

3. Generalized Correlation of Binary Interaction Parameters

Several generalized correlations have appeared in the literature for temperature dependent BIP. Kato et al. (1981) correlated BIP of CO$_2$/hydrocarbon systems for the PR CEOS in terms of the acentric factor of the hydrocarbon. A similar proposal was presented by Valderrama et al. (1988) for five different CEOS. Estévez et al. (1988) studied binary systems of hydrocarbons, CO$_2$ and H$_2$S and formulated a generalized BIP correlation in terms of the Thompson mean radius of gyration and the Lyman-Danner association parameter for three CEOS.

In order to generate the present correlations, several temperature dependencies were considered. The functional form that showed better agreement with the behavior of the optimized BIP was that proposed by Estévez et al. (1988), Eq. (5), where $T_{rf} = T/T_{cf}$, is the reduced temperature of the heavier compound of the binary pair.

$$k_{if} = c - \frac{d}{|1 - T_{rf}|}$$

(5)

However, in the present work a different parameterization for the constants c and d is proposed, as it was found that they are directly related to the acentric factor of the hydrocarbon. Table 3 shows the generalized expressions for systems containing CO_2/HC, H_2S/HC and CO_2/H_2S. The correlation coefficients of Eq. (5) are 0.876 for CO_2/HC, 0.938 for H_2S/HC and 0.968 for CO_2/H_2S.

Table 3: Generalized correlations for c and d obtained in the present work

System	CEOS	c	d
CO_2/HC	VW-RK	$-0.5832\omega^2 + 0.3387\omega - 0.00561$	0.09731
	PR	$-0.6910\omega^2 + 0.4373\omega - 0.02426$	0.09731
H_2S/HC	VW-RK	$-0.003881\omega^2 + 0.02706\omega - 0.01149$	$0.04769\omega^2 - 0.04959\omega + 0.00892$
	PR	$0.06936\omega^2 + 0.002577\omega - 0.01187$	$0.10930\omega^2 - 0.17940\omega + 0.030390$
CO_2/H_2S	VW-RK	0.006378	0.07190
	PR	0.005781	0.07062

4. BIP Correlation Performance for VLE Calculations

Figure 2 shows the absolute average relative deviations (AARD) in the prediction of bubble pressures (P_b) and vapor compositions (y_i) for the cohesion functions considered in the present work with: no BIP $(k_{ij} = 0)$, optimized BIP (specific for each system, isotherm and CEOS), and correlated BIP (from Eq. (5)). The dramatic improvement of the predictions is clearly seen when optimized BIP are introduced in the mixing rule. For instance, the AARD for the CO_2/HC systems are reduced by almost one order of magnitude, while for H_2S/HC the reduction is about a half. Figure 2 also shows an excellent performance of the correlation proposed in the present work, with AARD of the same order of those obtained with optimized BIP. Average deviations obtained with the correlations of Eq. (5) range from 2.5% to 4.5% for compositions, and from 1.5% to 4.0% for pressures, depending on the equation of state and type of binary pair.
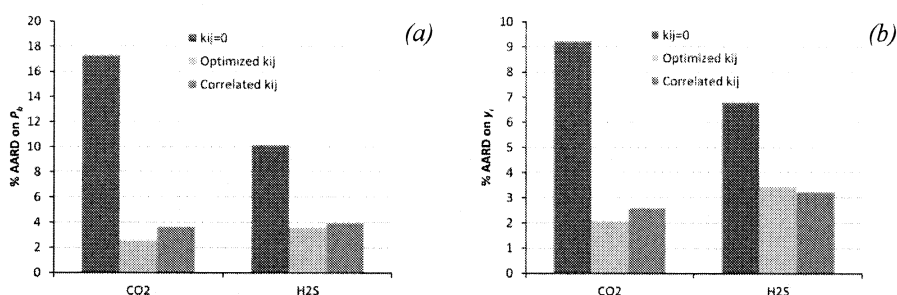

Figure 2. AARD on prediction of (a) bubble pressures, and (b) vapor compositions.

5. Conclusions

A generalized temperature dependent correlation for BIP for systems containing CO_2, H_2S and paraffinic hydrocarbons was developed. These correlations only require values of critical temperature of the heaviest component and acentric factor of hydrocarbon present in the mixture. Evaluation of these correlations showed that the BIP calculated

from them reproduce experimental VLE data with virtually the same accuracy as the optimized BIP.

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