

CORRELATION OF MULTIPHASE EQUILIBRIA FOR ASYMMETRIC MIXTURES BY A UNIFIED MODEL

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The simple DDLC-EOS unified model proposed in the previous paper was extended to describe the multiphase equilibrium behavior of highly asymmetric mixtures.

Liquid-liquid equilibrium data of 25 binary and 5 ternary systems as well as vapor-liquid-liquid equilibrium data of five binary systems were correlated with this model and the Soave-Redlich-Kwong equation.

Results show that for systems consisting of associating substances, fitting accuracies of the proposed model have been significantly improved.

For systems of alkanes or alkylbenzenes with carbon dioxide or ethane as a common component, the average deviations of this model were also found to be lower than those of the conventional method with either temperature-independent or temperature-dependent binary interaction parameters.

Introduction

Studies of high-pressure phase behavior have penetrated several fields of industrial application, such as the enhanced-oil-recovery (EOR) process, coal gasification and liquefaction, supercritical fluid extraction and biochemical technology. Special attention has recently been focused on the multiphase equilibrium behavior of homologous series of heavy hydrocarbons with carbon dioxide or light hydrocarbons as a common component.

These mixtures are important constituent binaries of the crude oil usually encountered in the EOR process. However, carbon dioxide and heavy hydrocarbons differ widely in molecular size and chemical nature. The former is known to be partially miscible with all normal alkanes from heptane up to the higher molecular-weight ones lower than heneicosane.

An adequate thermodynamic model is of prime importance for describing the partially miscible behavior of these highly asymmetric mixtures, both for design purposes and for promoting insight to a better understanding of immiscibility phenomena.

However, it appears that the conventional cubic equation of state is not usually capable of correlating such multiphase behavior. Both the Patel-Teja and Peng-Robinson equations of state were found to be very poor in correlating LLE behavior with conventional mixing rules.⁵⁾

Several authors^{10,11,23)} have attempted with some success to introduce the density-dependent local-composition concept into the mixing rule of the cubic equation of state. This introduction has greatly extended the applicability of the EOS model to more complex mixtures and provides the possibility of using a single model for all equilibrium phases.

In this paper, LLE data of 25 binary and five ternary systems, and VLLE data of five binary systems were

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correlated by applying the proposed model²²⁾ and the Soave-Redlich-Kwong equation of state¹⁷⁾ to test their applicabilities. In comparison with the conventional method, better results were obtained by this model with either temperature-independent or temperature-dependent binary interaction parameters.

1. Simple DDLC-EOS Unified Model

The proposed model is similar in formulation with the ordinary equation of state:

$$P = RT/(v - b) - a/v(v + b) \quad (1)$$

The attractive parameter of a mixture may be expressed as a function of temperature, density and composition:

$$a = \sum x_i \sum x_j a_{ji}^o (1 - C_{ji} E_{ji} / \sum x_k E_{ki}) \quad (2)$$

where

$$C_{ii} = C_{jj} = 0$$

The pair-attractive parameter a_{ji}^o in the conformal reference state can be calculated by the conventional combining rule:

$$a_{ji}^o = (\alpha_i a_{ci} \alpha_j a_{cj})^{0.5} \quad (3)$$

The attractive parameter of pure component i at its critical point, a_{ci} , and its temperature correction factor α_i are similar to those of the SRK equation.

The nonconformal parameter E_{ji} is defined as

$$E_{ji} = \exp[-C_{ji} a_{ji}^o \ln(1 + b/v) / RTb] \quad (4)$$

E_{ji} values may be considered as a measure of local-composition effects. At the low density limit, Eq. (2) reduces to the conventional quadratic mixing rule with one binary interaction parameter while E_{ji} approaches unity. For LLE and VLLE, since local-composition effects in both liquid phases cannot be neglected, values of E_{ji} are expected to depart from unity. Especially for nonpolar asymmetric mixtures, E_{ji} deviates significantly from unity with increasing pressure as was shown elsewhere.²³⁾ Calculated results of all systems investigated demonstrate these local-composition effects.

2. Correlation Procedure

The criteria of multiphase equilibria among all existing phases are the equalities of temperature, pressure and fugacity of each component in every phase.

$$f_i^l = f_i^H = f_i^v \quad (5)$$

If the fugacity is expressed in terms of the fugacity coefficient ϕ_i , Eq. (5) becomes:

$$\phi_i^l x_i^l = \phi_i^H x_i^H = \phi_i^v y_i \quad (6)$$

The above equation provides a direct method for

multiphase equilibrium calculations in case we have an equation of state which is capable of accurately describing limited miscibility phenomena. The fugacity coefficient of component i for the proposed model can be found in the Appendix of reference 22. The compressibility factor Z should be calculated by Eqs. (1) and (2), while a_{ji}^o by Eq. (3).

Eq. (6) may be applied to solve for the equilibrium compositions of all phases at a given temperature and pressure. The regression analysis required for determining the binary interaction parameters C_{ji} is to solve a set of nonlinear functions. The Simplex method of Nelder and Mead¹⁴⁾ needs no differentiation procedure and has no convergence problems with arbitrary initial values. So it was applied to obtain the optimal parameters and the deviations between the experimental and calculated values with the following objective function:

$$OF = \sum_j^m [x_{1,exp}^I - x_{1,cal}^I]_j^2 + (x_{1,exp}^{II} - x_{1,cal}^{II})_j^2 + (y_{1,exp} - y_{1,cal})_j^2 \quad (7)$$

However, the vapor compositions calculated for both liquid phases must be confirmed to be identical in order to avoid trivial solutions.

3. Temperature-Dependence of Binary Parameters

It is known that temperature-independent binary parameters usually overestimate the two-liquid phase near the critical region. Since we assumed that the binary parameter C_{ji} was proportional to the coordination number z_i , which could be derived as a function of temperature, density and composition, it would be interesting to investigate the temperature-dependence of these parameters.

We calculated C_{ji} for each datum point by an exact fit to the equilibrium compositions of two liquid phases at corresponding temperature and pressure. The C_{ji} values obtained were found to be different from point to point in several systems. As an example, when plotted against temperatures, they exhibit approximately a straight line as shown in Fig. 1 for the carbon dioxide-nonylbenzene system, where k_{12} values of the SRK equation were also plotted.

It is evident that both C_{21} and C_{12} decrease steadily with increasing temperature, while k_{12} exhibits only a minor decrease over a temperature range of 40 K. This indicates that the conventional mixing rule cannot yield good results for such highly asymmetric mixtures.

From Fig. 1 we may expect the binary parameters to be a linear function of temperature.

For the SRK equation:

$$k_{12} = a + bT$$

Table 1. Correlation of liquid-liquid equilibria for binary asymmetric Mixtures

No.	System	Temperature Range [K]	Pressure Range [MPa]	Datum Point	SRK			DDLC-SRK				Ref.
					k_{12}	$\Delta x_1^I \times 100$	$\Delta x_1^{II} \times 100$	C_{12}	C_{21}	$\Delta x_1^I \times 100$	$\Delta x_1^{II} \times 100$	
1	Carbon dioxide (1) + Tridecane (2)	255.16–278.95 (UCST)	2.076–3.933	14	0.108 $a=0.075$ $b=0.098$	3.55 0.61 1.20	1.82	0.207 $c=0.188$ $d=1.233$	0.324 $e=0.266$ $f=0.727$	3.09 0.36	1.12 0.50	6
		(LCST) 311.21–313.91	8.192–8.692	12	0.100	0.41 1.16		0.160	0.061	0.32	0.47	
2	Carbon dioxide (1) + Octylbenzene (2)	233.77–309.28	1.027–8.006	27	$a=0.097$ $b=0.252$	0.51 1.08		$c=0.155$ $d=1.063$	$e=0.206$ $f=0.017$	0.39	0.46	4
3	Carbon dioxide (1) + Pentadecylbenzene (2)	275.62–302.35	3.709–7.062	21	$a=0.105$ $b=0.400$	0.45 2.02		$c=0.169$ $d=0.723$	$e=0.206$ $f=1.169$	0.36	0.16	3
4	Ethane (1) + Methanol (2)	267.50–309.57	2.026–5.176	5	0.009	14.59 12.01		0.501	−0.193	0.37	1.71	9
5	Carbon dioxide (1) + Water (2)	298.20	6.420	4	−0.1057	1.16 1.64		−0.219	0.228	0.12	0.74	20
Average						3.04 2.99				0.72 0.74		

$$\Delta x_1^I = \left\{ \sum_i^m (x_{1,exp}^I - x_{1,cal}^I)^2 / m \right\}^{0.5}, \quad \Delta x_1^{II} = \left\{ \sum_j^m (x_{1,exp}^{II} - x_{1,cal}^{II})^2 / m \right\}^{0.5}$$

$$\text{SRK: } k_{12} = a + b \times 10^{-3} t \text{ [}^\circ\text{C]}, \quad \text{DDLC-SRK: } C_{12} = c + d \times 10^{-3} t \text{ [}^\circ\text{C]}, \quad C_{21} = e + f \times 10^{-3} t \text{ [}^\circ\text{C]}$$

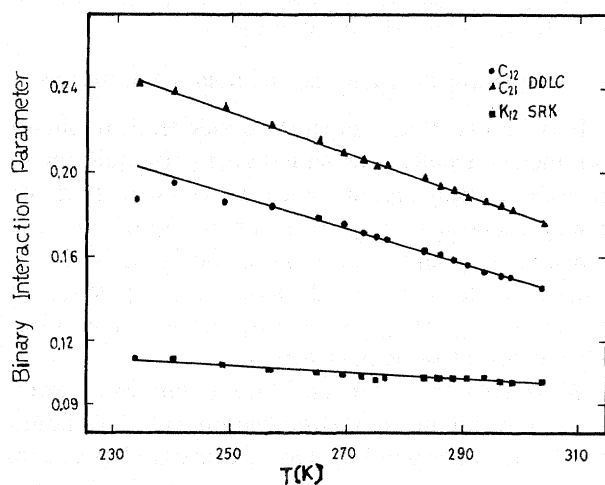


Fig. 1. Temperature-Dependence of Binary Interaction Parameters for the Carbon Dioxide-Nonylbenzene System

For the DDLC-EOS model:

$$C_{12} = c + dT$$

$$C_{21} = e + fT$$

If we incorporate this temperature dependence of binary parameters into the regression procedure, much better agreement of calculated results with experimental values are achieved in comparison with the SRK equation of state with temperature-dependent parameters.

4. Calculated Results

4.1 Binary liquid-liquid equilibria

The 25 binary systems tested in this investigation

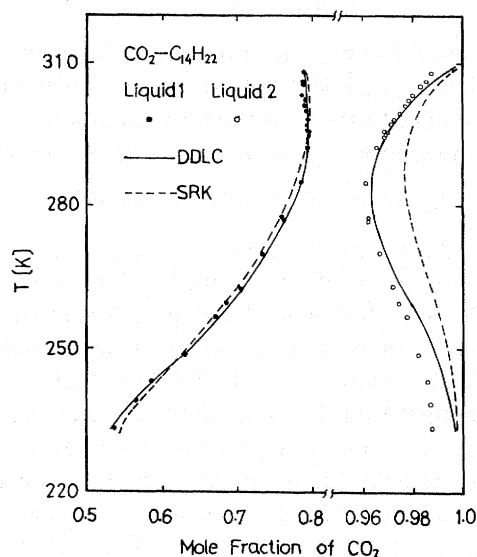


Fig. 2. Liquid-Liquid Equilibria of the Carbon Dioxide-Octylbenzene System

may be classified into four groups: carbon dioxide-alkane, carbon dioxide-alkylbenzene, ethane-alkane and others. Critical constants of alkylbenzenes were taken from the API Technical Data Book.¹⁾ Some of their acentric factors were estimated by the Edminster method.²⁾ The critical properties and acentric factors of all other compounds were obtained from Reid *et al.*¹⁵⁾

Other typical examples are presented in **Table 1**. From a total of 331 datum points, the average standard deviations of the proposed model are

Table 2. Correlation of ternary liquid-liquid equilibria for alcohol aqueous mixtures

System	Temperature Range [K]	Pressure Range [MPa]	SRK		DDLC-SRK		Ref.
			$\overline{\Delta x^I} \times 100$	$\overline{\Delta x^{II}} \times 100$	$\overline{\Delta x^I} \times 100$	$\overline{\Delta x^{II}} \times 100$	
Carbon dioxide (1) + Ethanol (2) + Water (3)	304.2 308.2	6.78–6.99 10.08	Nonconvergence		0.37 0.11	2.96 1.35	18
1,1-DFE (1) + Ethanol (2) + Water (3)	323.2 323.2 323.2	1.32 6.08 10.13	1.05 1.09 1.09	8.88 8.81 8.82	1.17 1.18 1.19	0.87 0.89 0.89	13
1,1-DFE (1) + <i>n</i> -Propanol (2) + Water (3)	323.2 323.2	1.32 6.08	15.83 19.26	3.54 3.83	1.41 1.88	0.84 1.09	13
1,1-DFE (1) + <i>n</i> -Butanol (2) + Water (3)	323.2	1.32	1.56	0.48	0.90	0.35	13
1,1-DFE (1) + <i>n</i> -Pentanol (2) + water (3)	323.2 323.2	1.32 6.08	2.46 0.57	0.85 0.49	0.69 0.56	0.27 0.28	13
Average*			5.36	4.46	1.12	0.69	

* System No. 1 was excluded. $\overline{\Delta x^I} = (\Delta x_1^I + \Delta x_2^I + \Delta x_3^I)/3$, $\overline{\Delta x^{II}} = (\Delta x_1^{II} + \Delta x_2^{II} + \Delta x_3^{II})/3$,
 $\Delta x_i^I = \left\{ \sum_j^m (x_{i,exp}^I - x_{i,cal}^I)^2 / m \right\}^{0.5}$, $\Delta x_i^{II} = \left\{ \sum_j^m (x_{i,exp}^{II} - x_{i,cal}^{II})^2 / m \right\}^{0.5}$.

Table 3. Correlation of vapor-liquid-liquid equilibria for several binary asymmetric mixtures

No.	System	Temperature Range [K]	Pressure Range [MPa]	SRK				DDLC-SRK				Ref.
				ΔP	Δx_1^I	Δx_1^{II}	Δy_1	ΔP	Δx_1^I	Δx_1^{II}	Δy_1	
1	Ethane (1) + Methanol (2)	267.15–308.41	2.03–5.07	0.376	15.16	10.38	0.54	0.064	0.64	1.45	1.49	9
2	Ethane (1) + Eicosane (2)	307.16–309.56	4.98–5.26	0.012	0.29	0.66	0.06	0.005	0.53	0.92	0.10	7
3	Methane (1) + <i>n</i> -Hexane (2)	186.23–193.15	3.85–4.77	0.065	1.48	2.73	0.02	0.065	0.83	2.65	0.02	8
4	Hydrogen sulfide (1) + Water (2)	312.04–371.87	2.76–8.62	0.0711	2.98	0.96	0.75	0.038	0.53	1.25	0.52	16
5	Carbon dioxide (1) + Water (2)	298.15	6.41	0.078	1.38	0.95	0.03	0.016	0.13	0.32	0.03	12
Average				0.120	4.26	3.14	0.28	0.038	0.53	1.32	0.43	

$\Delta P = \left\{ \sum_j^m (P_{exp} - P_{cal})_j^2 / m \right\}^{0.5}$, $\Delta y_1 = \left\{ \sum_j^m (y_{1,exp} - y_{1,cal})_j^2 / m \right\}^{0.5}$, Δx_1^I and Δx_1^{II} same as Table 1.

$\overline{\Delta x_1^I} = 0.79$ and $\overline{\Delta x_1^{II}} = 0.80$, while those of the SRK equation are $\overline{\Delta x_1^I} = 0.84$ and $\overline{\Delta x_1^{II}} = 1.77$ for the ten systems of carbon dioxide–alkane. For the five systems of carbon dioxide–alkylbenzene, those of the proposed model are $\overline{\Delta x_1^I} = 0.49$ and $\overline{\Delta x_1^{II}} = 0.78$, better than the $\overline{\Delta x_1^I} = 0.64$ and $\overline{\Delta x_1^{II}} = 1.21$ of the SRK equation. However, no improvements were obtained for the five systems of ethane–alkane. Comparisons of calculated

results with experimental values for the carbon dioxide–octylbenzene system⁴⁾ are shown in **Fig. 2**.

4.2 Ternary liquid-liquid equilibria

Five ternary liquid-liquid equilibrium data for alcohols and water were selected for testing. Results are summarized in **Table 2**. It is clear that the calculated results of the proposed model are much better in agreement with the experimental values than those of the conventional method.

4.3 Binary vapor-liquid-liquid equilibria

Five binary vapor-liquid-liquid equilibrium data of mixtures containing heavy hydrocarbon and associated substance were correlated by the proposed model and the SRK equation. Results are shown in Table 3. Significant improvements were also obtained by the proposed model except for the vapor-phase compositions, which were worse than those obtained by the SRK equation. However, most are within the limit of experimental uncertainty.

Conclusions

The proposed DDLC-EOS unified model is capable of correlating multiphase equilibria with a better result than that of the conventional cubic equation of state, especially for polar and nonpolar asymmetric mixtures.

The temperature-dependence of the binary interaction parameters for this model seems to have a semi-theoretical basis which needs further investigation.

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Nomenclature

a_{ji}	= attractive parameter for j - i pair	$[\text{J} \cdot \text{m}^3 \cdot \text{mol}^{-2}]$
b	= repulsive parameter	$[\text{m}^3 \cdot \text{mol}^{-1}]$
C_{ji}	= binary interaction parameter	$[-]$
E_{ji}	= nonconformal parameter	$[-]$
f_i	= fugacity of component i	$[\text{MPa}]$
m	= number of datum point	$[-]$
P	= pressure	$[\text{MPa}]$
R	= gas constant	$[\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]$
T	= absolute temperature	$[\text{K}]$
v	= molar volume	$[\text{m}^3 \cdot \text{mol}^{-1}]$
x	= mole fraction of liquid phase	$[-]$
Z	= compressibility factor	$[-]$
z	= coordination number	$[-]$
α_i	= correction factor for a_{ei}	$[-]$
ϕ_i	= fugacity coefficient of component i	$[-]$

<Superscripts>

I, II	= liquid phases I and II
v	= vapor phase

o = conformal reference state

<Subscripts>

i, j, k	= component
c	= critical value
cal	= calculated
exp	= experimental

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