

SIMPLIFIED AND MODIFIED VERSIONS OF THE DDLC-EOS MODEL

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Introduction

In process design and simulation, phase equilibrium calculations usually form more than 30% of the total computation time. It is of some economical significance to shorten the calculation time of phase equilibria without sacrifice of accuracy.

In this communication, a simplified version of the DDLC-EOS unified model is proposed to correlate vapor-liquid equilibrium data of asymmetric mixtures. Reduced computation times along with results surprising similar to the original version were attained.

In addition, an additional parameter L_{ij} is proposed to modify the combining rule of the repulsive constant b in the original model. Significant improvements were achieved in correlating liquid-liquid equilibria of several highly asymmetric mixtures.

1. Simplified Version

The original model⁽⁶⁾ is expressed as follows:

$$P = RT/(v - b) - \sum x_i \sum x_j a_{ji}^0 (1 + C_{ji} E_{ji} / \sum x_k E_{ki}) \partial f(v) / \partial v \quad (1)$$

The mathematical formulation of $f(v)$ can be found in reference 6.

As stated in the previous paper,⁽⁷⁾ the departure of the nonconformal parameters E_{ji} 's from unity may be regarded as a measure of local-composition effects. Values of E_{ji} 's for both liquid and vapor phases were analyzed. For all systems investigated, it was found that values for the vapor phase, E_{ji}^v 's, were much smaller than those of the liquid phase, E_{ji}^l 's. This indicates that local-composition effects in the vapor phase are negligible in comparison with those of the liquid phase.

Thus if we assume $E_{ji}^v = E_{ij}^v = 1$, Eq. (1) for the vapor phase can be written as:

$$P = RT/(v - b) - \sum y_i \sum y_j a_{ji}^0 (1 + C_{ji}) \partial f(v) / \partial v \quad (2)$$

If we apply Eq. (1) to the liquid phase and Eq. (2) to the vapor phase, computation times are expected to be reduced.

Thirty-five binary vapor-liquid equilibrium data at 83 isothermal conditions were tested by using this simplified version. Calculated results were compared with those of the original model.⁽⁶⁾ Some arbitrarily selected examples were presented in **Table 1**. They clearly demonstrate that the fitting accuracies of this simplified version are almost the same as those of the original, while the binary interaction parameters C_{ji} obtained by both versions exhibit only a minor change in values. However, the computation time has been reduced to nearly two-third of the original one. This simplified version represents a satisfactory compromise between accuracy and speed of computation.

2. Modified Version

High-pressure liquid-liquid equilibria are greatly influenced by molecular interactions which determine the potential energy of the fluid. Most cubic equations of state endeavor to modify the mixing rule of the attractive parameter. However, less attention was paid to that of the repulsive parameter.

To improve the correlation of LLE of highly asymmetric mixtures, the following combining rule for the pair-repulsive parameter with an adjustable parameter L_{12} was adopted:

$$b_{ji} = (1 - L_{12})(b_{jj} + b_{ii})/2 \quad (3)$$

With this modification, more than 20 binary liquid-liquid equilibrium data were tested. Significant improvements have been obtained in comparison with the original model and that of Mollerup,⁽⁴⁾ as shown in **Table 2**.

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Nomenclature

a_{ji} = attractive parameter for j - i pair [J·m³·mol⁻²]

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Table 1. Correlation of binary vapor-liquid equilibria

System*	Temperature [K]	Datum point	Original				Simplified			
			C_{12}	C_{21}	AP	$\Delta y \times 100$	C_{12}	C_{21}	AP	$\Delta y \times 100$
Hydrogen Sulfide (1)	310.93	6	-0.050	0.095	0.023	0.28	-0.101	0.177	0.022	0.30
+ Toluene (2)	352.59	7	-0.203	0.379	0.055	0.34	-0.201	0.372	0.054	0.46
	394.26	8	-0.236	0.375	0.084	1.80	-0.228	0.355	0.048	2.08
Ethane (1)	298.15	4	-0.122	0.246	0.040	0.15	-0.120	0.238	0.042	0.13
+ Methanol (2)										
Ethane (1)	298.15	7	0.226	0.103	0.041	0.12	0.226	0.103	0.040	0.13
+ Acetone (2)										
Ethane (1)	298.15	10	0.266	0.041	0.056	0.19	0.265	0.043	0.056	0.21
+ Methyl acetate (2)										
Methanol (1)	423.15	14	0.043	1.109	0.027	2.21	-0.027	-0.119	0.025	2.07
+ Water	473.15	15	-0.099	-0.039	0.062	1.13	-0.043	-0.101	0.055	1.17
	523.15	10	-0.172	0.050	0.039	0.54	-0.173	0.054	0.038	0.31
Carbon dioxide (1)	298.15	13	0.279	-0.101	0.083	0.34	0.276	-0.099	0.085	0.35
+ Methanol (2)	313.15	9	0.125	0.005	0.191	0.32	0.125	0.006	0.192	0.33
Carbon dioxide (1)	298.15	11	0.359	-0.251	0.071	0.29	0.360	-0.251	0.072	0.29
+ Methyl acetate (2)										
Average					0.064	0.64			0.061	0.65

$$\Delta p = \left\{ \sum_j^m (P_{exp} - P_{cal})_j^2 / m \right\}^{0.5} \text{ [MPa]}, \quad \Delta y = \left\{ \sum_j^m (y_{1,exp} - y_{1,cal})_j^2 / m \right\}^{0.5}$$

* Data sources can be found in reference 6.

Table 2. Correlation of binary liquid-liquid equilibria

System	Temperature range [K]	Pressure range [MPa]	Datum point	Original		Modified		Mollerup ⁴⁾		Ref.
				$\Delta x_1^I \times 100$	$\Delta x_1^{II} \times 100$	$\Delta x_1^I \times 100$	$\Delta x_1^{II} \times 100$	$\Delta x_1^I \times 100$	$\Delta x_1^{II} \times 100$	
Ethane (1)	309.75–	5.251–	9	0.46	0.77	0.29	0.58	0.70	0.95	2
Nonadecane (2)	310.95	5.391								
Ethane (1) +	306.89–	4.954–	9	0.51	0.81	0.01	0.02	0.66	0.85	2
Eicosane (2)	309.78	5.287								
Ethane (1) +	302.76–	4.562–	6	0.18	0.70	0.08	0.68	0.61	0.71	1
Docosane (2)	307.11	5.009								
Ethane (1) +	267.50–	2.027–	5	1.71	0.52	0.98	0.17	2.79	2.91	3
Methanol (2)	309.57	5.176								
Carbon dioxide (1) +	234.45	1.054	17	1.29	1.89	0.81	0.45	0.92	0.70	5
Trans. Decaline (2)	313.15	8.279								
Average				0.83	0.94	0.43	0.38	1.15	1.22	

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

b	= repulsive parameter	$[\text{m}^3 \cdot \text{mol}^{-1}]$
b_{ji}	= repulsive parameter for j - i pair	$[\text{m}^3 \cdot \text{mol}^{-1}]$
C_{ji}	= binary interaction parameter	$[-]$
E_{ji}	= nonconformal parameter	$[-]$
$f(v)$	= function of volume	$[\text{mol} \cdot \text{m}^{-3}]$
x	= mole fraction of liquid phase	$[-]$
y	= mole fraction of vapor phase	$[-]$

exp = experimental

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<Superscripts>

v	= vapor phase
l	= liquid phase
o	= conformal reference state
I, II	= I and II liquid phases

<Subscripts>

i, j, k	= component
cal	= calculated