VAPOR-LIQUID EQUILIBRIA CALCULATION IN GAS/LARGE ALKANE SYSTEMS USING GROUP CONTRIBUTION EQUATION OF STATE

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Introduction

Gas/alkane systems are industrially important systems. Though they are non-polar, the VLE of gas/large alkanes are rather difficult to predict accurately due to the nature of high asymmetry. In our previous work (Zhong and Masuoka, 1996), a modified MHV1 mixing rule (Michelsen, 1990) was proposed for accurate prediction of VLE of such systems, where a parameter f was introduced in the MHV1 mixing rule. The parameter f is cor-

related as a simple function of carbon number for a certain gas, and generalized correlations were developed for CO₂, CH₄ and C₂H₆, respectively. Our previous work shows that the approach gives very good accuracy for VLE of gas/large alkane systems, which is much better than the MHV1 mixing rule and a little better than the LCVm model (Boukouvalas *et al.*, 1994). In this work, the method is extended to other gases to provide additional useful relationships.

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Table 1 T_c , P_c and ω for alkanes larger than $C_{20}H_{42}$

Alkane	T_c [K]	P_c [MPa]	ω [—]
$C_{26}H_{54}^a$	817.1	0.81	1.117
$C_{28}H_{58}^b$	843.5	0.82	1.096
$C_{30}H_{62}^a$	841.3	0.66	1.275
$C_{36}H_{74}^b$	901.5	0.67	1.272
$C_{40}H_{82}^a$	882.8	0.41	1.684

^a Estimated by methods of Magoulas and Tassios (1990)^b Yau and Tsai (1993)

1. Thermodynamic Model

1.1. The SRK EOS

As in our previous work, the following SRK EOS (Soave, 1972) is used in this work:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \quad (1)$$

$$a = 0.42748 \frac{R^2 T_c^2}{P_c} \beta \quad (2)$$

$$b = 0.08664 \frac{RT_c}{P_c} \quad (3)$$

$$\beta = [1 + m(1 - T_R^{0.5})]^2 \quad (4)$$

and

$$m = 0.48508 + 1.55171\omega - 0.15613\omega^2 \quad (5)$$

where Eq. (5) was developed by Graboski and Daubert (1978), and is more accurate for large hydrocarbons. For alkanes smaller than $C_{20}H_{42}$, the T_c , P_c and ω used were taken from the property data book of Reid *et al.* (1988), and those for alkanes larger than $C_{20}H_{42}$ were taken from the paper of Yau and Tsai (1993) or estimated in this work. Data are listed in **Table 1**.

1.2. Mixing rules

1.2.1. The MHV1 mixing rule (Michelsen, 1990)

By equating the excess Gibbs free energy G^E from a cubic EOS at zero pressure to that from a G^E model, a mixing rule commonly called the MHV1 mixing rule was proposed by Michelsen (1990) as follows:

$$\frac{a_m}{b_m RT} = \sum x_i \frac{a_i}{b_i RT} + \frac{1}{q_1} [G^E / RT + \sum x_i \ln(\frac{b_m}{b_i})] \quad (6)$$

$$b_m = \sum x_i b_i \quad (7)$$

where q_1 is an EOS-dependent parameter. Holderbaum and Gmehling (1991) used a SRK EOS with the above mixing rule, called the PSRK model, to predict VLE of small molecule systems, where the original UNIFAC model (Fredenslund *et al.*, 1975) was adopted as the G^E

model. In their work, gas/alkane systems are also included, and the UNIFAC group interaction parameters for various gas/ CH_2 pairs were obtained, where the q_1 was set to -0.64663 empirically.

1.2.2. The proposed mixing rule (MR1)

The investigation of Boukouvalas *et al.* (1994) shows that the SRK EOS with the MHV1 mixing rule, the PSRK model, performs rather poorly for the prediction of VLE of gas/large alkane systems. As a result, a modified MHV1 mixing rule was proposed in our previous work to improve its accuracy as follows (Zhong and Masuoka, 1996):

$$\frac{a_m}{b_m RT} = \sum x_i \frac{a_i}{b_i RT} + \frac{1}{q_1} [G^E(1+f) / RT + \sum x_i \ln(\frac{b_m}{b_i})] \quad (8)$$

$$b_m = \sum x_i b_i \quad (7)$$

The parameter f , which accounts for an additional free volume term to the original UNIFAC model for highly asymmetric systems, was generalized as a simple function of carbon number for CO_2 , CH_4 and C_2H_6 , respectively.

In our previous work (Zhong and Masuoka, 1996), the existing group parameters obtained by Holderbaum and Gmehling (1991) were used directly. As a result, by the introduction of a parameter in the MHV1 mixing rule, the PSRK model was extended to predict VLE of gas/large alkane systems including CO_2 , CH_4 and C_2H_6 with greatly improved accuracy. In this work, we will develop similar correlations for other three gases, C_2H_4 , CO and H_2 . In the calculation, either with the MHV1 or the MR1 mixing rule, the group parameters obtained by Holderbaum and Gmehling (1991) were used. Detailed calculation methods can be found elsewhere (Zhong and Masuoka, 1996).

2. Results

Experimental data for C_2H_4 /alkane, CO /alkane and H_2 /alkane systems were collected from the literature, and are reported in **Tables 2, 3 and 4**, respectively. The calculation results for the SRK EOS with the MHV1 mixing rule (the PSRK model), that is, the average absolute deviations (AADs) of gas mole fraction in liquid phase, are shown, respectively, in **Tables 2, 3 and 4**, as well as in **Fig. 1**. Obviously, the PSRK model gives good predictions when the carbon number of alkane is smaller than 10. However, for those carbon numbers larger than 10, the predictions become worse with increasing carbon number, which performs similarly to those for CO_2 , CH_4 and C_2H_6 systems. As a result, modification of the MHV1 mixing rule for alkanes of carbon number larger than 10 is necessary. The optimized parameters f for gas/large alkane systems obtained by fitting the experimental data are shown in **Fig. 2**. Similar to our previous treatment, the following gas-dependent generalized correlations are proposed.

Table 2 Results for C₂H₄ alkane systems

Alkane	Temp. range [K]	Press. range [MPa]	No. of data points	AAD*[%]		Data source
				MHV1	MR1	
C ₃ H ₈	200-273	0.14-3.59	34	2.8	2.8	Elshayal and Lu (1973)
C ₇ H ₁₆	216-500	0.69-9.65	86	6.5	6.5	Kay (1948)
C ₁₂ H ₂₆	283-348	0.51-9.12	58	10.2	3.0	Riberio <i>et al.</i> (1972)
C ₂₀ H ₄₂	323-423	0.49-24.40	88	20.1	4.1	de Loos <i>et al.</i> (1984)
C ₂₆ H ₅₄	348-448	0.94-30.18	117	28.4	3.7	de Loos <i>et al.</i> (1984)
C ₂₈ H ₅₈	373-573	1.01-5.06	15	39.1	2.8	Chou and Chao (1989)
C ₃₀ H ₆₂	348-448	1.43-33.42	75	30.8	4.4	de Loos <i>et al.</i> (1986)
C ₃₆ H ₇₄	373-573	1.02-5.07	15	46.4	2.3	Chou and Chao (1989)
C ₄₀ H ₈₂	373-448	1.30-40.56	90	40.0	5.8	de Loos <i>et al.</i> (1984)

$$*AAD = (100 / N) \sum |x_i^{cal.} - x_i^{exp.}| / x_i^{exp.}$$

Table 3 Results for CO/alkane systems

Alkane	Temp. range [K]	Press. range [MPa]	No. of data points	AAD [%]		Data source
				MHV1	MR1	
C ₃ H ₈	148-173	1.38-15.86	56	8.0	8.0	Trust and Kurata (1971a)
C ₈ H ₁₈	463-533	0.67-6.57	43	6.1	6.1	Connolly and Kandalic (1948)
C ₁₀ H ₂₂	311-378	2.84-6.45	18	14.2	2.6	Srivatsan <i>et al.</i> (1995)
C ₁₆ H ₃₄	301-512	3.14-5.43	44	17.4	10.5	Breman <i>et al.</i> (1994)
C ₂₀ H ₄₂	373-473	1.00-5.06	15	30.9	6.2	Huang <i>et al.</i> (1988)
C ₂₈ H ₅₈	424-520	3.07-3.77	20	47.8	10.5	Breman <i>et al.</i> (1994)
C ₃₆ H ₇₄	373-573	1.03-5.08	15	48.9	4.8	Huang <i>et al.</i> (1988)

Table 4 Results for H₂ alkane systems

Alkane	Temp. range [K]	Press. range [MPa]	No. of data points	AAD [%]		Data source
				MHV1	MR1	
C ₃ H ₈	173-348	1.38-20.68	46	6.4	6.4	Trust and Kurata (1971b)
C ₄ H ₁₀	328-394	2.78-16.88	60	5.9	5.9	Klink <i>et al.</i> (1975)
C ₅ H ₁₂	308-453	2.86-14.08	78	9.5	9.5	Connolly and Kandalic (1986)
C ₆ H ₁₄	298-373	1.14-9.81	24	10.4	10.4	Brunner (1985)
C ₇ H ₁₆	424-499	2.53-81.04	29	5.6	5.6	Peter and Reinhartz (1960)
C ₈ H ₁₈	463-543	1.01-15.04	50	8.9	8.9	Connolly and Kandalic (1989)
C ₁₆ H ₃₄	301-508	3.85-6.60	44	34.6	14.5	Breman <i>et al.</i> (1994)
C ₂₀ H ₄₂	373-573	0.99-5.08	15	38.8	10.3	Huang <i>et al.</i> (1988)
C ₂₈ H ₅₈	373-573	4.14-5.07	15	50.5	10.7	Breman <i>et al.</i> (1994)
C ₃₆ H ₇₄	373-573	1.02-5.07	15	56.2	9.6	Huang <i>et al.</i> (1988)

For C₂H₄/alkane systems

$$f = 0.187381n - 0.2218 \quad (n \geq 10) \quad (9)$$

$$f = 0 \quad (n < 10) \quad (10)$$

For CO/alkane systems

$$f = 0.13681n - 0.1128 \quad (n \geq 10) \quad (11)$$

$$f = 0 \quad (n < 10) \quad (10)$$

For H₂/alkane systems

$$f = 0.115481n + 0.0006 \quad (n \geq 10) \quad (12)$$

$$f = 0 \quad (n < 10) \quad (10)$$

where n is carbon number. The calculation results of the SRK EOS with the MR1 mixing rule and Eqs.(9)-(12) are shown in Tables 2-4 and also in Fig. 1. Obviously, the MR1 mixing rule gives satisfactory calculations for large alkane systems, which is much better than that of the MHV1 mixing rule. As gas-dependent generalized cor-

Fig. 1 Calculated results of gas mole fraction in liquid phase

Fig. 2 Optimized parameter f versus carbon number

relations were proposed and the existing group parameters of the PSRK model can be used directly, the MR1 mixing rule is convenient for practical use.

The experimental and calculated solubilities of C_2H_4 , CO and H_2 in $C_{36}H_{74}$ at 473.15 K are shown, as examples, in Figs. 3, 4 and 5, respectively. From the figures, the great improvement of the MR1 mixing rule over the MHV1 mixing rule can be seen clearly.

Conclusion

The MR1 mixing rule proposed in our previous work is extended to other gases, C_2H_4 , CO, and H_2 , in this work. Generalized correlations for the parameter in the MR1 mixing rule are proposed for them as done before for CO_2 , CH_4 and C_2H_6 . The SRK EOS with the MR1 mixing rule and the generalized correlations gives satisfactory accuracy for the calculation of VLE of these gases and large alkane systems. By this method, the existing PSRK group parameters can be used directly with greatly improved accuracy for gas/large alkane systems.

Nomenclature

a	= co-energy parameter in SRK EOS	[Pa.m ⁶ /mol ²]
b	= co-volume parameter in SRK EOS	[m ³ /mol]
f	= correction parameter in Eq. (8)	[-]
G^E	= excess Gibbs free energy	[Pa.m ³ /mol]

Fig. 3 Experimental and calculated pressure versus liquid mole fraction of C_2H_4 for $C_2H_4 + C_{36}H_{74}$ at 473 K

Fig. 4 Experimental and calculated pressure versus liquid mole fraction of CO for $CO + C_{36}H_{74}$ at 473 K

Fig. 5 Experimental and calculated pressure versus liquid mole fraction of H_2 for $H_2 + C_{36}H_{74}$ at 473 K

m	= parameter in Eq. (4)	[-]
n	= carbon number of alkane	[-]
N	= number of data points	[-]
P	= pressure	[Pa]
q_1	= parameter in Eqs. (6) and (8)	[-]
R	= gas constant	[Pa.m ³ /mol.K]
T	= temperature	[K]

v	= molar volume	[m ³ /mol]
x	= mole fraction	—
β	= parameter in Eq. (2)	—
ω	= acentric factor	—
< Subscript >		
c	= critical property	—
i	= component i	—
m	= mixture	—
R	= reduced property	—
< Superscript >		
cal.	= calculated value	—
exp.	= experimental value	—

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