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AN EXPONENT-TYPE MIXING RULE FOR ENERGY PARAMETERS

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Introduction

A mixing rule for parameters such as constants appearing in equations of state is needed to calculate the mixture properties. Usually, a quadratic form (so called as conventional mixing rule) is adopted as a mixing rule for energy parameters. However, the quadratic form sometimes fails to represent quantitatively the phase behavior of an asymmetric mixture⁴⁾. Therefore, several models based on local mole fraction concept⁶⁾ and others^{1, 14)} have been proposed. In this study, an exponent-type mixing rule which

is rather simple is proposed and several applications are presented.

1. Exponent-Type Mixing Rule

An exponent-type mixing rule proposed in this study for the energy parameter contained in an equation of state is given by the following equation.

$$a_m = \sum_i \sum_j x_i^{\alpha_{ij}} x_j^{\alpha_{ji}} a_{ij} \quad (1)$$

When $\alpha_{ij} = 1$ and $\alpha_{ji} = 1$, Eq. (1) becomes the

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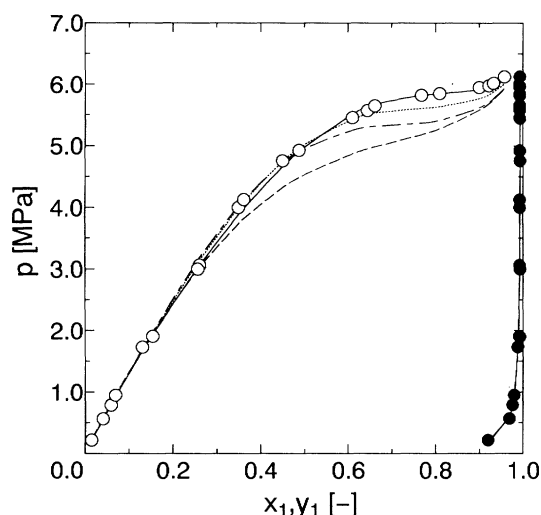


Fig. 1 Correlation results of carbon dioxide(1)-methanol(2) system at 298.2 K

- (○) experimental data in liquid phase^{8,11)}
- (●) experimental data in vapor phase^{8,11)}
- (----) conventional mixing rule ($k_{12}=0.026$);
- (-•-) modified conventional mixing rule ($m_{12}=0.032$, $n_{12}=-0.013$);
- (-----) exponent type mixing rule ($\alpha_{21}=1.017$, $k_{12}=0.020$);
- (——) exponent type mixing rule ($\alpha_{21}=1.034$, $k_{12}=-0.026$, $l_{12}=-0.034$);

quadratic expression usually applied. The present form, Eq. (1), is suggested by the studies of Hálá³⁾ and Kumagai *et al.*⁹⁾ for electrolyte solution. As x_i and x_j (mole fraction) are smaller than unity,

$$x_i^{\alpha_{ij}} > x_i \quad (\alpha_{ij} < 1) \quad (2a)$$

$$x_i^{\alpha_{ij}} < x_i \quad (\alpha_{ij} > 1) \quad (2b)$$

This may express that the contact probability of molecule i with molecule j can be adjusted by introducing the exponent α_{ij} . This means that non-randomness in the mixture can be evaluated empirically.

For a binary mixture, the following expressions are valid.

$$\alpha_{11} = 1 \quad (3a)$$

$$\alpha_{22} = 1 \quad (3b)$$

2. Application to Equation of State

To examine the applicability of Eq. (1), the calculation of vapor-liquid equilibria (VLE) was attempted. Eq. (1) was applied to an equation of state (EOS) of the following form proposed by one of the present authors⁷⁾.

$$p = \frac{RT}{v-b} - \frac{a}{v^2 - c(v-b)} \quad (4)$$

This equation of state (IML) contains three constants a , b and c and can give better correlation performance, espe-

Table 1. Correlation results using exponent-type mixing rule and IML equation of state

System	Temp.(K)	α_{21}	k_{12}	l_{12}	Δp [%]*	$\Delta y \times 10^3$ **	Ref.
CO ₂ (1)-Methanol(2)	298.2	1.034	-0.026	-0.034	1.17	0.918	8),11)
CO ₂ (1)-Ethanol(2)	304.4	1.025	0.000	-0.057	0.578	0.440	15)
Methanol(1)-Water(2)	373.2	0.987	0.010	0.091	0.707	6.87	2)
	423.2	1.018	-0.118	-0.042	0.626	9.53	2)
	473.2	1.025	-0.119	-0.052	0.536	7.17	2)
	523.2	1.006	-0.006	0.064	0.430	4.48	2)
Acetone(1)-Water(2)	373.2	1.011	0.034	0.209	1.85	4.94	2)
	423.2	1.028	0.012	0.171	0.665	6.52	2)
	473.2	1.017	0.091	0.228	0.783	4.19	2)
	523.2	1.045	-0.001	0.126	0.368	2.90	2)
H ₂ (1)-NH ₃ (2)	311.0	0.730	0.753	0.199	8.33	7.11	12)
	377.6	1.189	0.357	-0.007	3.09	8.61	12)
N ₂ (1)-NH ₃ (2)	311.0	1.012	0.376	0.082	1.35	7.47	13)
	377.6	1.015	-0.115	-0.245	0.437	1.42	13)
Ar(1)-NH ₃ (2)	298.2	1.075	0.273	-0.014	2.11	8.05	10)
	323.2	1.008	0.338	0.037	3.86	14.8	10)
	373.2	1.006	0.073	-0.187	0.543	15.6	10)
Toluene(1)-H ₂ S(2)	311.0	1.041	0.115	0.099	6.03	1.41	5)
	352.6	1.016	-0.060	-0.037	0.335	5.61	5)
	394.3	1.014	-0.028	0.002	1.30	16.5	5)
	477.6	1.053	0.049	0.114	0.904	20.2	5)
Heptane(1)-H ₂ S(2)	311.0	1.010	0.079	0.015	4.41	4.84	5)
	352.6	0.990	-0.041	-0.079	1.58	4.34	5)
	394.3	1.109	0.117	0.135	2.83	14.7	5)
	477.6	1.129	0.167	0.244	1.64	18.2	5)

$$* \Delta p = \frac{1}{N} \sum \left| \frac{p_{\text{exp}} - p_{\text{calc.}}}{p_{\text{calc.}}} \right| \times 100$$

$$** \Delta y = \frac{1}{N} \sum |y_{1,\text{exp.}} - y_{1,\text{calc.}}|$$

N : number of data

cially for polar systems. The following mixing rules for the constant b_m are used.

$$b_m = \sum_i \sum_j x_i x_j b_{ij} \quad (5)$$

$$b_{ij} = (1 - l_{ij})(b_{ii} + b_{jj}) / 2 \quad (6)$$

For the constant c_m , the same mixing rules as Eqs. (5) and (6) are adopted.

3. VLE Calculation

3.1 Characteristics of a_m

We first applied the exponent-type mixing rule to VLE data^{8, 11)} of the binary system CO₂(1)-methanol(2) at 298.2K, which is well known as a typical asymmetric mixture. The exponent α_{12} was assumed to be unity because non-randomness around non-polar molecules is not so significant. In the present calculation for binary systems, T and x_1 were fixed by using the experimental data.

For a binary system, a_{12} is given by the conventional mixing rule ($\alpha_{12} = \alpha_{21} = 1$ in Eq.(1)) as follows.

$$a_{12} = (1 - k_{12})\sqrt{a_{11}a_{22}} \quad (7)$$

Adachi *et al.*¹⁾ empirically expressed k_{12} as a function of composition for polar systems.

$$k_{12} = m_{12} + n_{12}(x_1 - x_2) \quad (8)$$

To examine clearly the contribution of these mixing

rules to a_m , the interaction parameter l_{12} for molecular sizes was set at zero. As shown in **Fig. 1**, the conventional mixing rule shows a large discrepancy in the liquid phase in the high pressure region. The modified conventional mixing rule proposed by Adachi *et al.* can improve the correlation performance. However, the discrepancy in the high pressure region still remains. On the other hand, the exponent-type mixing rule can be applied with good results up to the critical range.

3.2 VLE of several polar systems

The authors attempted to introduce l_{12} to provide better correlation. As shown in Fig. 1, for example, the correlation performance can be improved.

To examine the usefulness of the present mixing rule, VLE of several polar systems were additionally correlated and the results are shown in **Table 1**. As shown in this table, the exponent-type mixing rule seems to be useful to correlate VLE of asymmetric mixtures.

Conclusion

An exponent-type mixing rule is proposed for evaluating energy parameters and an example applied to equation of state is presented. By using the present expression, VLE of several asymmetric mixtures can be correlated with good accuracy. It may be noted that an exponent-type mixing rule is simple and useful to evaluate the energy parameter of asymmetric mixtures.

Nomenclature

a	= parameter of EOS	[Pa·m ⁶ ·mol ⁻²]
b, c	= parameters of EOS	[m ³ ·mol ⁻¹]
k, l	= characteristic parameters	[-]

m, n	= parameters in Eq.(8)	[-]
p	= pressure	[Pa]
R	= gas constant	[Pa·m ³ ·K ⁻¹ ·mol ⁻¹]
T	= temperature	[K]
v	= molar volume	[m ³ ·mol ⁻¹]
x	= mole fraction in liquid phase	[-]
y	= mole fraction in vapor phase	[-]
α	= exponent in Eq.(1)	[-]

<Subscripts>

i, j	= components i and j
m	= mixture property
1	= component 1
2	= component 2

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