l_{ij}	= binary characteristic parameter between molecules i and j ; see Eqs. (31)–(33)	[—]
M	= molar mass	[kg·mol ⁻¹]
N	= number of data	[—]
N_A	= Avogadro's number	[mol ⁻¹]
r	= displacement of a molecule from its equilibrium position in a crystal lattice	[m]
T	= absolute temperature	[K]
V	= liquid molar volume	[m ³ ·mol ⁻¹]
V_o	= solid molar volume at melting point	[m ³ ·mol ⁻¹]
V_w	= van der Waals volume	[m ³ ·mol ⁻¹]
v^*	= reduced solid molar volume at melting point; see Eq. (6)	[—]
x	= mole fraction	[—]
$x_{j(i)}$	= local mole fraction of molecule j surrounding a molecule of component i	[—]
y	= $(r/a)^2$, defined by Eq. (5)	[—]
z	= coordination number	[—]
β	= empirical parameter for polar effect; see Eqs. (9) and (10)	[—]
γ	= empirical parameter for polar effect; see Eq. (11)	[—]
ε°	= energy parameter of potential function	[J]
θ	= $(T_{c1}/V_{c1})/(T_{c2}/V_{c2})$, defined by Eq. (43)	[—]
λ	= thermal conductivity of liquid	[W·m ⁻¹ ·K ⁻¹]
ν	= frequency of molecular vibration	[s ⁻¹]
ρ	= density	[kg·m ⁻³]
σ°	= collision diameter of molecule	[m]
τ_{ij}	= $\{\varepsilon(T)_{ji} - \varepsilon(T)_{ii}\}/kT$, defined by Eq. (36)	[—]
χ	= Stiel's polar factor	[—]

ω = Pitzer's acentric factor [—]

⟨Subscripts and Superscripts⟩

c	= critical value
calcd.	= calculated
exptl.	= experimental
i, j	= components i and j
$\sim$	= mixture property
1, 2	= components 1 and 2

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HIGH-PRESSURE VAPOR-LIQUID EQUILIBRIUM CALCULATIONS BY USE OF THE CORRESPONDING-STATES PRINCIPLE

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Key Words: Vapor-Liquid Equilibrium, Hydrocarbon, Corresponding-States Principle

Prediction of vapor-liquid equilibria of asymmetric mixtures by use of the corresponding-states principle has recently been developed by a number of investigators.^{1,3,6) Joffe³⁾ and Plöcker *et al.*⁶⁾ have used the Lee-Kesler correlations⁴⁾ with the pseudocritical method. Arai *et al.*¹⁾ presented mixing rules combining functionally different equations of state on the basis of the three-parameter corresponding-states principle.}

In this work we use a one-fluid theory with new mixing rules on the basis of the corresponding-states principle to calculate the vapor-liquid equilibria for asymmetric mixtures of hydrocarbons. Data used in evaluating this calculation are taken from the literature.

1. Corresponding-States Principle with Mixing Rules

Following Van Ness,¹⁰⁾ the fugacity coefficient of component i at constant T and P is related to the mixture fugacity coefficient by

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Fig. 1. Deviations between calculated and experimental bubble pressures for the binary system methane-*n*-decane at 444.26 K⁷⁾ for different values of η .

$$\ln \phi_i = \ln \phi_M - \frac{1}{RT} \frac{\Delta h_M}{T_{CM}} \sum_{j \neq i} z_j \left(\frac{dT_{CM}}{dz_j} \right)_{z_k} + \frac{Z_M - 1}{P_{CM}} \sum_{j \neq i} z_j \left(\frac{dP_{CM}}{dz_j} \right)_{z_k} - \left(\frac{\partial \ln \phi_M}{\partial \omega_M} \right)_{T_r, P_r} \sum_{j \neq i} z_j \left(\frac{d\omega_M}{dz_j} \right)_{z_k} \quad (k \neq i, j) \quad (1)$$

where $\ln \phi_M$, $(\Delta h/RT_C)_M$ and Z_M are obtained from the Teja correlation⁹⁾:

$$g_M[T_r, P_r, \omega_M] = \sum_i^n z_i g^{(i)}[T_r, P_r, \omega_i] \quad (2)$$

To calculate $\ln \phi_M$, $(\Delta h/RT_C)_M$ and Z_M we use a one-fluid theory. The pseudocritical method, similar to that of Plöcker *et al.*,⁶⁾ is used here, and a set of mixing rules for the averaging procedure to calculating the pseudocritical constants of a mixture is proposed as follows:

$$T_{CM} v_{CM}^\eta = \sum_i \sum_j z_i z_j T_{cij} v_{cij}^\eta \quad (3)$$

$$v_{CM} = \sum_i \sum_j z_i z_j v_{cij} \quad (4)$$

$$T_{cij} v_{cij}^\eta = k_{ij} [(T_{ci} T_{cj}) (v_{ci} v_{cj})^\eta]^{1/2} \quad (5)$$

$$v_{cij} = \frac{1}{8} (v_{ci}^{1/3} + v_{cj}^{1/3})^3 \quad (6)$$

$$P_{CM} = (0.2905 - 0.085 \omega_M) RT_{CM} / v_{CM} \quad (7)$$

$$\omega_M = \sum_i z_i \omega_i \quad (8)$$

2. Calculation Procedure

The calculation procedure for vapor-liquid equilibria is similar to that of Plöcker *et al.*⁶⁾ and Arai *et al.*¹⁾

3. Results and Discussion

The mixing rules proposed in this work are similar

Table 1. Binary parameter k_{ij} for binary vapor-liquid equilibria

System	Temperature range [K]	Max. pressure [atm]	Set of eqs.*	k_{ij}
Methane-ethane	130-200	51	a-b	1.049
Methane-propane	130-214	64	a-b	1.113
Methane- <i>n</i> -butane	166-283	113	a-b	1.185
Methane-isobutane	311-378	109	a-b	1.160
Methane- <i>n</i> -pentane	311-444	167	a-b	1.267
Methane- <i>n</i> -hexane	323-423	160	a-b	1.315
Methane- <i>n</i> -octane	298-423	70	a-b	1.448
Methane- <i>n</i> -decane	378-511	336	a-b	1.567
Methane- <i>n</i> -hexadecane	462-623	249	a-b	1.870
Methane-toluene	222-255	136	a-b	1.335
Methane-diphenylmethane	462-623	250	a-b	1.652
Ethane-propane	200-255	15	b-b	1.020
Ethane- <i>n</i> -pentane	278-411	67	b-b	1.072
Ethane- <i>n</i> -octane	313-373	52	b-b	1.170
Propane- <i>n</i> -butane	363-393	40	b-b	1.002
Propane- <i>n</i> -pentane	344-444	44	b-b	1.020
Propane- <i>n</i> -hexane	363-453	48	b-b	1.040
Propane- <i>n</i> -heptane	363-473	48	b-b	1.070
Propane- <i>n</i> -decane	278-511	70	b-b	1.153
<i>n</i> -Butane- <i>n</i> -decane	311-511	49	b-b	1.090
Ethylene-propylene	263-293	52	a-b	1.015
Ethylene-1-butene	273-293	54	a-b	1.037

* a: Bender's equation of state.²⁾

b: Generalized Benedict-Webb-Rubin equation of state.⁵⁾

Fig. 2. Correlation of binary parameters k_{ij} for hydrocarbon-hydrocarbon systems.

to those presented by a number of authors.^{1,3,4,6)} From the computed results it can be found that the exponent η appearing in Eqs. (3) and (5) is of no importance for slightly asymmetric mixtures, that is, the calculated deviations of bubble pressure and vapor composition change slightly as the values of η change from zero to unity. However, for strongly asymmetric mixtures the exponent η becomes significant, as shown in Fig. 1. We have determined η empirically by a systematic study of numerous asymmetric mixtures of hydrocarbons. The calculated results show that the best value of η changes somewhat from one system to another, and good agreement with experiment is obtained by setting $\eta=0.35$ for all

Table 2. Comparison of experimental and calculated vapor-liquid equilibria using different methods

System	No. of data points	DEVP* [%]				DEVY** [%]			
		A	B	C	D	A	B	C	D
Methane-ethane	104	0.9	1.0	1.0	1.1	0.6	0.7	0.7	0.8
Methane- <i>n</i> -hexane	61	2.6	5.0	2.8	3.3	1.7	1.5	1.5	1.4
Methane- <i>n</i> -octane	42	7.4	7.7	4.8	4.7	0.4	0.4	0.4	0.4
Methane- <i>n</i> -decane	104	10.7	17.8	3.2	3.5	3.0	2.0	0.9	1.0
Methane-toluene	34	8.8	2.8	2.6	3.0	0.1	0.1	0.1	0.1
Ethane- <i>n</i> -octane	45	2.9	5.1	2.7	2.3	0.7	0.7	0.7	0.7
Propane- <i>n</i> -heptane	31	1.6	1.7	1.5	1.4	2.4	1.8	2.0	2.2
Propane- <i>n</i> -decane	50	3.7	5.1	2.1	3.4	1.1	0.9	0.8	0.5
<i>n</i> -Butane- <i>n</i> -decane	59	1.6	1.7	1.7	2.6	0.8	0.5	0.6	0.8
Ethylene-propylene	40	0.8	0.8	0.8	0.9	0.7	0.7	0.7	0.8
Grand average		4.1	4.9	2.3	2.6	1.2	0.9	0.8	0.9

$$* \text{ DEVP} = \frac{1}{n} \sum_i \left| \frac{P_{i\text{calc.}} - P_{i\text{exp.}}}{P_{i\text{exp.}}} \right| \cdot 100\% \quad ** \text{ DEVY} = \frac{1}{n} \sum_i \left| \frac{y_{i\text{calc.}} - y_{i\text{exp.}}}{y_{i\text{exp.}}} \right| \cdot 100\%$$

A: Plöcker *et al.* method.⁶⁾ (Set of equations used are Lee-Kesler correlations.⁴⁾)

B: Arai *et al.* method.¹⁾ (Set of equations used are the same as that used in Method C.)

C: This work. (Set of equations used are shown in Table 1.)

D: This work. (Set of equations used are Soave R-K equation.⁸⁾)

binary systems studied in this work.

Vapor-liquid equilibrium calculations are performed for 22 binary hydrocarbon-hydrocarbon systems. The obtained best values of k_{ij} are listed in Table 1. Figure 2 shows k_{ij} as a function of the dimensionless group $(T_{ci}v_{ci})/(T_{cj}v_{cj})$ and the correlation can be approximately expressed by

$$k_{i,j} = 0.945989 + 0.042214 \left(\frac{T_{ci}v_{ci}}{T_{cj}v_{cj}} \right) - 0.000467 \left(\frac{T_{ci}v_{ci}}{T_{cj}v_{cj}} \right)^2 \quad (9)$$

Equation (9) can be used to estimate k_{ij} value of other hydrocarbon-hydrocarbon systems where insufficient experimental information is at hand.

Table 2 compares the deviations in calculated and experimental bubble pressure and vapor composition between those obtained by Plöcker *et al.*⁶⁾ and Arai *et al.*¹⁾ and those obtained from the methods proposed here by using the BWR type equation and Soave-RK equation. It can be seen that the calculated results do not differ appreciably for symmetric and slightly asymmetric systems. However, for strongly asymmetric systems, both methods proposed here are superior.

Vapor-liquid equilibria for the ternary system can be calculated by using binary parameters listed in Table 1. Figure 3 compares calculated K values of the strongly asymmetric system methane-propane-*n*-decane with experimental data. The calculated K values of methane and propane agree very well with experimental data, and the calculated K values of *n*-decane also agree well with experimental data except for the high-pressure region.

Fig. 3. Calculated K values for the ternary system methane-propane-*n*-decane; comparison with experimental data of Wiese *et al.*¹¹⁾

Nomenclature

g	= thermodynamic property	[—]
Δh	= molar residual enthalpy	[atm · l/mol]
K	= vaporization equilibrium ratio	[—]
k_{ij}	= binary parameter for the i - j mixture	[—]
P	= pressure	[atm]
R	= gas constant	[atm · l/mol · K]
T	= temperature	[K]
v	= molar volume	[l/mol]
Z	= compressibility factor	[—]
z	= mole fraction	[—]
η	= universal exponent in the mixing rule	[—]

ϕ = fugacity coefficient [—]
 ω = acentric factor [—]

<Subscripts>

CM = pseudocritical property
 c = critical property
 M = mixture property
 r = reduced property
 i, j, k = component i, j, k

<Superscript>

(i) = component i

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LYSIS RATES OF FIBRIN CLOT BY PLASMIN

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Key Words: Medical Chemical Engineering, Biochemical Engineering, Enzyme Reaction, Adsorption, Fibrinolysis, Plasmin

Introduction

Under normal conditions a homeostatic balance between blood coagulation and fibrinolysis maintains fluidity in the vascular system. The conversion of fibrinogen to fibrin by thrombin makes a thrombus, as shown in Fig. 1. In the fibrinolytic system fibrin is hydrolyzed by the proteolytic enzyme plasmin, which is activated from plasminogen by plasmin activators. Therapeutic enhancement of the fibrinolytic system by these activators, such as urokinase and streptokinase, has been attempted for treatment of many pathological disorders caused by enhanced coagulability. Recent biochemical studies¹⁾ of the plasminogen molecule elucidated that plasmin and plasminogen have the lysine-binding site and interact with fibrin and antiplasmin through it. The enzymatic lysis mechanism of solids such as fibrin is still uncertain. So it is interesting to study the effect of the interaction between plasmin or plasminogen and fibrin on the lysis rate. The present work was undertaken to measure the rates of fibrinolysis by plasmin and plasminogen-urokinase and to study the mechanism of fibrinolysis.

Materials and Methods

Bovine serum fibrinogen (Nakarai Chemicals Co.) was made plasminogen-free by a lysine-Sepharose 4B affinity column. Plasminogen and plasmin, which had the lysine-binding site, in bovine fibrinogen were selectively adsorbed in this column. The fibrinogen was fluoro-labelled by fluorescamine.

Bovine thrombin (587 NIH units/mg-protein, Sigma Chemicals Co.) was used to clot fibrinogen. Porcine plasmin and plasminogen (2.7 and 1.7 units/mg-protein, respectively, Sigma Chemicals Co.) were used and their activities were assayed by hydrolysis of casein. One unit is defined as $\Delta A_{280\text{ nm}}^{1\text{ cm}} = 1.0$ for perchloric acid soluble products in 20 min at pH 7.5 and 37°C. Plasminogen was activated by use of urokinase (Green Cross Co.).

Fig. 1. Scheme of fibrinolysis.