π	= total pressure of the system	[mmHg]
γ	= activity coefficient	[—]
δ_{12}	= interaction parameter as defined by Eq. (3)	[cm ³ /mole]
A_{12}, A_{21}	= constants in Wilson equation	[—]
τ_{12}, τ_{21}	= constants in NRTL equation	[—]
<Subscripts>		
1	= more volatile component	
2	= less volatile component	

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APPLICATION OF THE PERTURBATION THEORY TO VAPOR-LIQUID EQUILIBRIA OF SYSTEMS CONTAINING A POLAR SUBSTANCE

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In a previous paper⁴⁾, it was shown that the perturbation theory of Barker-Henderson in conjunction with the conformal solution theory proposed by Mansoori and Leland³⁾ is applicable to the correlation of vapor-liquid equilibria of systems containing ammonia. In the present study, the perturbation theory has been further applied to systems containing a polar substance other than ammonia. The vapor-liquid equilibria of the binary system consisting of a nonpolar substance and a polar substance (acetone, ethyl ether, methyl ethyl ketone or methyl acetate) were calculated by the same procedure as reported previously.

The pair-potential energy-function used is the Lennard-Jones (12-6) type, described in the previous paper:

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

where ϵ and σ are temperature-dependent potential parameters and are defined as follows:

$$\epsilon = \epsilon^\circ \mathcal{F}^2 \quad (2)$$

$$\sigma = \sigma^\circ \mathcal{F}^{-1/6} \quad (3)$$

$$\mathcal{F} = 1 + 7Q^4/20kT\epsilon^\circ(\sigma^\circ)^{10} + 3Q^2\alpha/4\epsilon^\circ(\sigma^\circ)^8 : \quad (4)$$

for nonpolar substance

$$\mathcal{F} = 1 + \mu^4/12kT\epsilon^\circ(\sigma^\circ)^6 + \mu^2\alpha/2\epsilon^\circ(\sigma^\circ)^6 : \quad (5)$$

for polar substance

where α , μ and Q are polarizability, dipole moment, and quadrupole moment, respectively. These parameters were determined by using vapor pressure data and saturated P - V - T relation for pure substances^{1,7)}. The values of these parameters for nonpolar substances are given in Table 1, where α is arbitrarily assumed to be zero. Figure 1 shows the vapor pressures and saturated volumes for methane calculated with two different sets of parameters. The pair-potential energy function containing the quadrupole moment seems to improve the calculated results. As shown in Fig. 2, the following linear relations were obtained between the reduced potential parameters and the acentric factor:

$$\epsilon^\circ/kT_c = 0.734 - 0.396\omega \quad (6)$$

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(a) vapor pressure for methane (b) saturated volume for methane
Solid line: calculated with $\epsilon^\circ/k=139.4$ [K], $\sigma^\circ=3.742$ [Å]
 $Q=2.177 \times 10^{-26}$ [erg $^{1/2}$ cm $^{5/2}$]
Broken line: calculated with $\epsilon^\circ/k=150.0$ [K], $\sigma^\circ=3.742$ [Å]
 $Q=0$ [erg $^{1/2}$ cm $^{5/2}$]

Fig. 1 The calculated and observed vapor pressure and saturated volume for methane

Fig. 2 Correlation of potential parameters

Table 1 Potential parameters for nonpolar and polar substances

(a) nonpolar substances

Substance	ω	ϵ°/k [K]	σ° [Å]	$Q \times 10^{26}$ [erg $^{1/2}$ ·cm $^{5/2}$]	α [Å 3]
Methane	0.013	139.4	3.742	2.177	—
Ethylene	0.089	197.6	4.125	3.948	—
Ethane	0.105	211.3	4.298	4.630	—
Propylene	0.143	247.0	4.567	6.253	—
Propane	0.152	249.1	4.778	7.082	—
n-Butane	0.201	278.3	5.208	9.837	—
n-Pentane	0.252	300.6	5.596	12.82	—
n-Hexane	0.290	311.0	5.885	15.69	—
Nitrogen	0.040	90.90	3.610	1.745	—
Carbon monoxide	0.041	95.65	3.614	1.823	—
Carbon dioxide	0.225	196.2	3.744	3.711	—

(b) polar substances

Substance	ω	ϵ°/k [K]	σ° [Å]	$\mu \times 10^{18}$ [erg $^{1/2}$ ·cm $^{3/2}$]	α [Å 3]
Acetone	0.318	313.0	4.932	2.822	5.354
Methyl ethyl ketone	0.337	352.0	5.390	3.180	7.578
Ethyl ether	0.230	299.2	5.348	3.008	4.313
Methyl acetate	0.339	345.0	4.789	2.581	5.510

$$\sigma^\circ/(V_c/N_A)^{1/3}=0.678+0.0762\omega \quad (7)$$

$$Q^k/kT_c\epsilon^\circ(\sigma^\circ)^{10}=0.0693+1.062\omega \quad (8)$$

The values of four parameters for polar substances are also given in Table 1. For polar substances, however, these values could not be correlated with a characteristic parameter such as the acentric factor.

Application of the Barker-Henderson perturbation theory to the mixture was performed in conjunction with the conformal solution theory of Mansoori and Leland. According to the conformal solution theory, the intermolecular potential parameters of the hypothetical pure substance, which possesses the same properties as the mixture, are given by the following mixing rules:

Fig. 3 Vapor-liquid equilibria for the carbon dioxide-acetone system

$$\left. \begin{aligned} \bar{\sigma}^3 &= \left[\sum_{i=1}^m \sum_{j=1}^m x_i x_j \sigma_{ij}^3 \epsilon_{ij} \right]^2 / \sum_{i=1}^m \sum_{j=1}^m x_i x_j \sigma_{ij}^3 \epsilon_{ij}^2 \\ \bar{\epsilon} &= \left[\sum_{i=1}^m \sum_{j=1}^m x_i x_j \sigma_{ij}^3 \epsilon_{ij} \right] / \bar{\sigma}^3 \\ \sigma_{ij} &= (\sigma_{ii} + \sigma_{jj}) / 2 \\ \epsilon_{ij} &= (1 - k_{ij}) \sqrt{\epsilon_{ii} \epsilon_{jj}} \end{aligned} \right\} \quad (9)$$

where k_{ij} is a binary-interaction parameter which is generally determined experimentally.

By using the above mixing rules, vapor-liquid equilibria were calculated for nine binary systems containing a polar substance using the same procedure as described in the previous paper. Comparisons of calculated and experimental vapor-liquid equilibria for three binary systems are shown in Figs. 3 to 5. While the dew-point line is not so sensitive to the binary interaction parameter, k_{12} , the introduction of k_{12} can effectively correct the bubble-point line. As

Fig. 4 Vapor-liquid equilibria for the ethane-ethyl ether system

Fig. 5 Solubility of ethylene in acetone

Table 2 Values of k_{12} for binary mixture containing polar substance

System (1)-(2)	Temp. [°C]	k_{12}
ethylene-acetone	-45.0 ⁽⁷⁾	-0.15
	-25.0 ⁽⁷⁾	-0.13
	0.0 ⁽⁹⁾	-0.09
ethylene-methyl ethyl ketone ⁽⁹⁾	0.0	-0.14
ethylene-methyl acetate ⁽⁹⁾	0.0	-0.11
ethane-acetone ⁽⁶⁾	25.0	-0.04
ethane-methyl acetate ⁽⁶⁾	25.0	-0.01
ethane-ethyl ether ⁽⁶⁾	25.0	-0.04
carbon dioxide-acetone ⁽²⁾	25.0	-0.09
	40.0	-0.07
carbon dioxide-methyl acetate ⁽⁵⁾	25.0	-0.12
	40.0	-0.10
carbon dioxide-ethyl ether ⁽⁵⁾	25.0	-0.01
	40.0	0.01

shown in Table 2, and Figs. 3 to 5, k_{12} is temperature-dependent, and it seems that the higher the temperature, the larger the k_{12} value needed. Figure 3 also shows that the calculated results tend to be poor near the critical temperature of solute gas. This may be ascribed to the fact that the equation of state used here for the pure substances is poor in the critical region.

In summary, the perturbation theory of Barker-Henderson in conjunction with the conformal solution theory was found to be useful for correlating vapor-liquid equilibria of systems containing polar substances, except in the critical region.

Nomenclature

k	= Boltzmann constant	[erg/K]
k_{ij}	= binary interaction parameter	[—]
N_A	= Avogadro's number	[1/mol]
Q	= quadrupole moment	[erg ^{1/2} ·cm ^{5/2}]
r	= intermolecular distance	[Å]
T	= temperature	[K]
$u(r)$	= pair-potential energy-function	[erg]
x	= mole fraction	[—]
V	= molar volume	[cm ³ /mol]
α	= polarizability	[Å ³]
ϵ	= well depth in potential function	[erg]
μ	= dipole moment	[erg ^{1/2} ·cm ^{3/2}]
σ	= collision diameter	[Å]
ω	= Pitzer's acentric factor	[—]

<Superscripts and subscripts>

i, j	= component i and j
c	= critical property
—	= hypothetical pure substance
$\circ$	= pure substance property

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