An Extended Regular Solution Model with Local Volume Fraction

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The regular solution model (the Hildebrand-Scatchard equation) coupled with the Flory-Huggins equation has been extended by using the local volume fraction proposed by Wilson so that it can be applied to polar mixtures. From the extended regular solution model, activity coefficient equations can be derived. Pair energy parameters required to evaluate local volume fractions can be estimated by solubility parameters and molar volumes predicted from the molecular structures of constituent pure components by using additive methods. The applicability of the present regular solution model is examined by correlating vapor-liquid equilibria of several ethanol + hydrocarbon binary systems, and it is found that the proposed model can be adopted for polar mixtures.

Keywords: *Regular Solution, Local Volume Fraction, Activity Coefficient, Vapor-Liquid Equilibrium, Ethanol, Hydrocarbon*

Introduction

The Hildebrand-Scatchard equation based on the regular solution model (RSM) seems to be a promising equation to give liquid phase activity coefficients using physical properties (*i.e.,* solubility parameters and liquid molar volumes) of constituent pure components[1)]. However, the application is limited to non-polar or slightly polar mixtures. Therefore, in a previous study[2)], the solution model has been extended so that it can be applied to polar mixtures by introducing an exponent-type mixing rule and a composition-dependent interaction parameter between unlike molecules. This model is termed here as RSM-α (see Appendix). The extended regular solution model can be successfully adopted to polar mixtures such as ethanol + hydrocarbon mixtures using the exponent parameter α which represents the non-randomness in molecular mixing and other two interaction parameters. As a continuation, in this study, an another extended regular solution model is proposed by using the local volume fraction given by Wilson [3)] to express the non-randomness in molecular mixing. The applicability of the proposed regular solution model is examined by correlating the vapor-liquid equilibria (VLE) of several ethanol + hydrocarbon binary systems studied in the previous work[2)].

1. An Extended Regular Solution Model

The molar excess Gibbs energy based on the regular solution model[1)] with the local volume fractions is proposed as

$$g^{\mathrm{E}} = \left(\sum_i x_i v_i\right)\left(\frac{1}{2}\sum_i\sum_j A_{ij}\phi_i^{\mathrm{L}}\phi_j^{\mathrm{L}}\right) + RT\sum_i x_i \ln\frac{\phi_i^{\mathrm{L}}}{x_i} \qquad (1)$$

where the Flory-Huggins equation is added as a size-effect term and $A_{ij}=A_{ji}$ and $A_{ii}=A_{jj}=\cdots=0$. Eq.(1) is termed here as RSM-L. In the original form, the local volume fraction ϕ_i^{L} should be replaced by the usual volume fraction ϕ_i. When the first term of right hand side of Eq.(1), that is the energy of mixing term, is omitted it becomes the well-known Wilson equation[3)]. In this study, Wilson equation is considered to be an excess entropy expression[4)]. The coefficient A_{ij} is expressed in terms of solubility parameters[1)] as follows:

$$A_{ij} = \left(\delta_i - \delta_j\right)^2 + 2l_{ij}\delta_i\delta_j \qquad (2)$$

According to Adachi and Sugie[5)], the interaction parameter l_{ij} for mixtures is given by

$$l_{ij} = m_{ij} + n_{ij}\left(x_i - x_j\right) \quad (3)$$

Based on the standard thermodynamic procedure, the activity coefficients of a binary mixture can be derived from Eq.(1) as follows:

$$\begin{aligned}\ln\gamma_1 &= \ln\gamma_1\left(A_{12}\right) + \ln\gamma_1\left(n_{12}\right) + \ln\gamma_1(\mathrm{W}) \\ &= \frac{A_{12}}{RT}\left\{ v_1\left(1 + \frac{x_2}{x_1}\frac{\phi_1{}^{\mathrm{L}}}{\phi_1}\Lambda_{12}\right) - v_2\frac{\phi_2{}^{\mathrm{L}}}{\phi_2}\Lambda_{21}\right\}\phi_1{}^{\mathrm{L}}\phi_2{}^{\mathrm{L}} \\ &\quad + 4n_{12}\left\{\left(x_1v_1 + x_2v_2\right)\delta_1\delta_2 / RT\right\}x_2\,\phi_1{}^{\mathrm{L}}\phi_2{}^{\mathrm{L}} \qquad (4) \\ &\quad - \ln\left(x_1 + \Lambda_{12}x_2\right) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)\end{aligned}$$

$$\begin{aligned}\ln\gamma_2 &= \ln\gamma_2\left(A_{12}\right) + \ln\gamma_2\left(n_{12}\right) + \ln\gamma_2(\mathrm{W}) \\ &= \frac{A_{12}}{RT}\left\{ v_2\left(1 + \frac{x_1}{x_2}\frac{\phi_2{}^{\mathrm{L}}}{\phi_2}\Lambda_{21}\right) - v_1\frac{\phi_1{}^{\mathrm{L}}}{\phi_1}\Lambda_{12}\right\}\phi_1{}^{\mathrm{L}}\phi_2{}^{\mathrm{L}} \\ &\quad - 4n_{12}\left\{\left(x_1v_1 + x_2v_2\right)\delta_1\delta_2 / RT\right\}x_1\,\phi_1{}^{\mathrm{L}}\phi_2{}^{\mathrm{L}} \qquad (5) \\ &\quad - \ln\left(\Lambda_{21}x_1 + x_2\right) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)\end{aligned}$$

where the local volume fraction ϕ^{L} and the volume fraction ϕ are defined as

$$\phi_1{}^{\mathrm{L}} = \frac{x_1}{x_1 + x_2\Lambda_{12}}, \quad \phi_2{}^{\mathrm{L}} = \frac{x_2}{x_2 + x_1\Lambda_{21}} \quad (6)$$

$$\phi_1 = \frac{x_1v_1}{x_1v_1 + x_2v_2}, \quad \phi_2 = \frac{x_2v_2}{x_1v_1 + x_2v_2} \quad (7)$$

where A_{12} and the Wilson parameters are given by

$$A_{12} = \left(\delta_1 - \delta_2\right)^2 + 2l_{12}\delta_1\delta_1, \quad l_{12} = m_{12} + n_{12}\left(x_1 - x_2\right) \quad (8)$$

$$\Lambda_{12} = \frac{v_2}{v_1}\exp\left[-\frac{\lambda_{12} - \lambda_{11}}{RT}\right], \quad \Lambda_{21} = \frac{v_1}{v_2}\exp\left[-\frac{\lambda_{21} - \lambda_{22}}{RT}\right] \quad (9)$$

2. Pair Energy Parameters and Solubility Parameters

To apply Eqs.(4) and (5), the pair energy parameters λ are required to evaluate the Wilson parameters Λ_{12} and Λ_{21}. The definition of solubility parameter is $\delta = \left(-E/v\right)^{0.5}$ where E is the cohesive energy due to molecular attraction force. In this study λ is approximated as $(2/z)E$, according to Wong and Eckert(6), where usually $-E$ is given by $\Delta H^{\mathrm{V}} - RT$ 1) and z is the co-ordination number. Then, the pair energy parameters λ can be obtained as follows:

$$\lambda_{11} = -(2/z)v_1\delta_1{}^2, \quad \lambda_{22} = -(2/z)v_2\delta_2{}^2 \quad (10)$$

Further, for the unlike pair, the following geometric mean is adopted.

$$\begin{aligned}\lambda_{12} = \lambda_{21} &= -\left(1 - \varepsilon_{12}\right)\left(\lambda_{11}\lambda_{22}\right)^{0.5} \\ &= -\left(1 - \varepsilon_{12}\right)(2/z)\left(v_1v_2\right)^{0.5}\delta_1\delta_2\end{aligned} \quad (11)$$

where ε_{12} is an interaction parameter.

The solubility parameters and the liquid molar volumes at a given temperature t needed in the above calculation can be obtained as follows(7, 8):

$$\delta_t = \frac{v_{25}}{v_t}\delta_{25} \quad (12)$$

and

$$v_t = v_{25} + \beta(t - 25), \quad \beta = \frac{v_{\mathrm{b}} - v_{25}}{t_{\mathrm{b}} - 25} \quad (13)$$

where v_{b} is the liquid molar volume at the normal boiling point t_{b}[℃], which can be estimated by using the additive method of Le Bas(9) except small molecules such as methanol and ethanol(7). The solubility parameters at 25℃(δ_{25}) and the liquid molar volumes at 25℃(v_{25}) can be predicted by Fedors method(10) based on the group-contribution method.

3. VLE Correlation and Discussion

For comparison of the present model (RSM-L) with the previous one (RSM-α(2)), VLE of the same ethanol + hydrocarbon binary systems have been correlated. At sufficiently low pressures, VLE (x-y) of binary mixtures can be calculated by

$$y_1 = \gamma_1 x_1 p_1^\circ / p \quad , \quad y_2 = \gamma_2 x_2 p_2^\circ / p \tag{14}$$

$$p = \gamma_1 x_1 p_1^\circ + \gamma_2 x_2 p_2^\circ \tag{15}$$

where x and y denote mole fractions of liquid and vapor phases, respectively. And p° is the vapor pressure given by the Antoine's equation for a pure component and p is the total pressure. Therefore VLE can be calculated by using the activity coefficients γ_1 and γ_2 obtained from Eqs.(4) and (5). The physical properties of pure substances (v_{25}, δ_{25}, t_b, v_b and the constants of Antoine's equation) are shown in **Table 1**. The correlation performances for VLE and the parameters required are summarized in **Table 2**, and typical graphical representations are shown in **Figures 1-3** for C_6 hydrocarbons.

As shown in Table 2 and Figures 1 and 2, the correlation performance of RSM-L is almost the same as the previous model RSM-α for cyclohexane and aromatics. The co-ordination number z optimized is 10 as usually expected[6)].

The contribution of interaction parameter n_{12}, which represents the composition dependence of the interaction parameter l_{12}, is found to be very small. Therefore, the parameter is let be n_{12}=0. On the other hand, for paraffin systems, the correlation performance is poor and the co-ordination number should be z=4 to obtain better correlation results. Even though z=4 , the correlation performance of RSM-L is slightly inferior to RSM-α as shown in Table 2. It is noted that the contribution of $\ln\gamma_i$(W), that is the excess entropy term, is positive for paraffins though $\ln\gamma_i$(W) for cyclohexane and aromatics is negative.

The contributions of excess entropy term to activity coefficients, as shown in Eqs. (4) and (5), are $\ln\gamma_i$(W) given by the Wilson

Table 1 Physical properties of pure substances

Substance	v_{25} [2)] [cm^3 · mol^{-1}]	v_b [2)] [cm^3 · mol^{-1}]	δ_{25} [2)] [(J·m^{-3})$^{0.5}$]	t_b [11)] [℃]	Constants of Antoine's equation[*, 11)] A	B	C
Hexane	131.4	140.6	14.9	68.740	6.01098	1176.102	48.251
Heptane	147.5	162.8	15.2	98.423	6.02701	1267.592	56.354
Octane	163.6	185.0	15.5	125.665	6.04394	1351.938	64.030
Cyclohexane	112.6	118.2	16.5	80.731	6.00569	1223.273	48.061
Benzene	90.4	96.0	18.8	80.090	6.01905	1204.637	53.081
Toluene	104.9	118.2	18.7	110.622	6.08436	1347.620	53.363
Ethanol	59.6	62.5	25.7	78.229	7.24222	1595.811	46.702

$* \log p^\circ[\text{kPa}] = A - B/(T[\text{K}] - C)$

Table 2 Correlation performances for VLE at 101.3 kPa of ethanol (1) + hydrocarbon (2) binary systems and interaction parameters

Hydrocarbon (2) [a]	RSM–L (n_{12} = 0)					RSM–α[b]	
	z	m_{12}	ε_{12}	Δy_1*	Δt**	Δy_1*	Δt**
Hexane	4	–0.1603	0.1989	1.4	0.4	1.5	0.2
Heptane	4	–0.1549	0.3751	2.9	0.7	1.0	0.8
Octane	4	–0.1442	0.4144	2.2	0.8	0.2	0.3
Cyclohexane	10	0.1670	–0.2532	1.0	1.0	1.3	0.7
Benzene	10	0.1193	–0.1898	1.5	0.5	1.9	0.7
Toluene [c]	10	0.2046	–0.2639	1.4	0.8	0.9	0.7

$*\Delta y_1[\%] = (100/N)\times\sum^N \left[\,|y_{1,\text{calc}} - y_{1,\text{exp}}|/y_{1,\text{exp}}\right]$, $**\Delta t[℃] = (1/N)\times\sum^N |t_{\text{calc}} - t_{\text{exp}}|$, N = number of data points

[a] VLE data sources are shown in the previous paper[2)]; [b] Three model parameters α_{12}, m_{12} and n_{12} are adopted[2)]; [c] Total pressure is 100.8 kPa

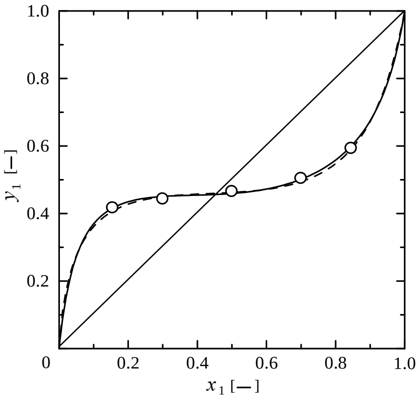

Fig. 1 Correlation of vapor-liquid equilibria of ethanol (1) + cyclohexane (2) binary system at 101.3 kPa. Experimental: (○); Correlations : (——)RSM-L; (- - -)RSM-α (α_{12} = 0.915, m_{12}= − 0.0112, n_{12} = −0.0241)

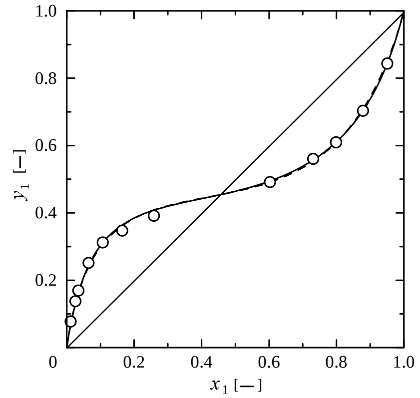

Fig. 2 Correlation of vapor-liquid equilibria of ethanol (1) + benzene (2) binary system at 101.3 kPa. Experimental: (○); Correlations : (——)RSM-L; (- - -)RSM-α (α_{12} = 0.962, m_{12}= 0.0156, n_{12} = −0.0218)

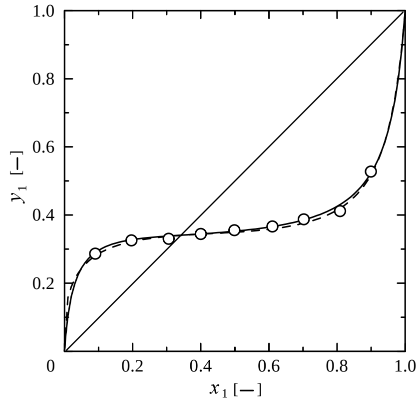

Fig. 3 Correlation of vapor-liquid equilibria of ethanol (1) + hexane (2) binary system at 101.3 kPa. Experimental: (○); Correlations : (——)RSM-L; (- - -)RSM-α (α_{12} = 0.827, m_{12}= − 0.0722, n_{12} = −0.0189)

equation. By fitting the present model (RSM-L) to experimental VLE data, it is found that lnγ_i(W)>0 for ethanol(1) + paraffin(2) binary systems while lnγ_i(W)<0 for the other three binary systems as mentioned above. This fact of lnγ_i(W)>0 means the molar excess entropy is s^E<0. On the other hand, lnγ_i(W)<0 indicates s^E>0. If the Flory-Huggins(FH) equation is adopted to give the excess entropy, as studied in the previous work (RSM-α), s^E(FH)>0 and lnγ_i(FH)<0 for any binary system.

The molar excess entropy s^E of ethanol(1) + hydrocarbon(2) mixtures is discussed here using the informations available in the literature. For ethanol(1) + heptane(2), s^E at 20, 40 and 60℃ are presented (Fig.4 in ref.) 12). This result shows s^E<0 though slightly s^E>0 near x_1=0. And, for ethanol(1) + toluene(2), s^E at −100 to 35℃ are reported (Fig.3 in ref.) 13). It is represented s^E<0 while slightly s^E>0 at 35℃ near x_1=0. These results s^E<0 support ln γ_i(W)>0. It is noted, however, that the temperatures (boiling points at 101.3 kPa for ethanol(1) + heptane(2) and at 100.8 kPa for ethanol(1) + toluene(2), see Table 1) much differ from those at which s^E reported in the literature cited because s^E markedly depends on temperature. Therefore, the evaluation of s^E discussed here may be obscure in rigorous sense.

Conclusions

An extended regular solution model (RSM-L) has been developed by adopting the local volume fraction of Wilson3). The activity coefficient equations derived from RSM-L can be adopted to correlate vapor-liquid equilibria of polar mixtures such as ethanol(1) + hydrocarbon(2). However, it is noted that the correlation performance of RSM-L is slightly inferior to the previous model RSM-α for paraffins. The applicability and physical meanings of interaction parameters of RSM-L should be further examined and discussed by adopting vapor-liquid equilibrium data of other polar mixtures.

Nomenclature

A = interaction term $[\mathrm{J \cdot cm^{-3}}]$
g = molar Gibbs energy $[\mathrm{J \cdot mol^{-1}}]$
l = interaction parameter between unlike molecules [–]
m = interaction parameter between unlike molecules [–]
n = interaction parameter between unlike molecules [–]
p = total pressure [Pa]
p^{o} = vapor pressure of pure component [Pa]
R = gas constant $[\mathrm{J \cdot mol^{-1} \cdot K^{-1}}]$
s = molar entropy $[\mathrm{J \cdot mol^{-1} \cdot K^{-1}}]$
T = absolute temperature [K]
t = temperature [℃]
v = liquid molar volume $[\mathrm{cm^{3} \cdot mol^{-1}}]$
x = mole fraction of liquid phase [–]
y = mole fraction of vapor phase [–]
z = co-ordination number [–]

γ = liquid phase activity coefficient [–]
δ = solubility parameter $[(\mathrm{J \cdot cm^{-3}})^{0.5}]$
ε = interaction parameter between unlike molecules [–]
λ = interaction energy due to attractive force $[\mathrm{J \cdot mol^{-1}}]$
ϕ = volume fraction [–]

<Subscript>
b = normal boiling point
calc = calculated value
exp = experimental data
i = component i
j = component j
1 = component 1 (ethanol)
2 = component 2 (hydrocarbon)
25 = standard temperature (25℃)

<Superscript>
E = excess property
L = local quantity

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Appendix: RSM-α

The molar excess Gibbs energy of RSM-α is expressed by

$$g^{\mathrm{E}} = \left(\sum_i x_i v_i\right)\left(\frac{1}{2}\sum_i \sum_j A_{ij}\phi_i^{\alpha_{ij}}\phi_j^{\alpha_{ji}}\right) + RT\sum_i x_i \ln\frac{\phi_i}{x_i} \quad \text{(A1)}$$

The activity coefficients derived for a binary system are given as follows.

$$\begin{aligned}\ln\gamma_1 &= \ln\gamma_1(A_{12}) + \ln\gamma_1(n_{12}) + \ln\gamma_1(\mathrm{FH})\\ &= \frac{A_{12}}{RT}\left\{(1-\alpha_{21})v_1 + \alpha_{12}\frac{x_2}{x_1}v_2\right\}\phi_1^{\alpha_{12}}\phi_2^{\alpha_{21}}\\ &\quad + 4n_{12}\{(x_1v_1 + x_2v_2)\delta_1\delta_2/RT\}x_2\phi_1^{\alpha_{12}}\phi_2^{\alpha_{21}}\\ &\quad + \ln\frac{\phi_1}{x_1} + 1 - \frac{\phi_1}{x_1}\end{aligned} \quad \text{(A2)}$$

$$\begin{aligned}\ln\gamma_2 &= \ln\gamma_2(A_{12}) + \ln\gamma_2(n_{12}) + \ln\gamma_2(\mathrm{FH})\\ &= \frac{A_{12}}{RT}\left\{\alpha_{21}\frac{x_1}{x_2}v_1 + (1-\alpha_{12})v_2\right\}\phi_1^{\alpha_{12}}\phi_2^{\alpha_{21}}\\ &\quad - 4n_{12}\{(x_1v_1 + x_2v_2)\delta_1\delta_2/RT\}x_1\phi_1^{\alpha_{12}}\phi_2^{\alpha_{21}}\\ &\quad + \ln\frac{\phi_2}{x_2} + 1 - \frac{\phi_2}{x_2}\end{aligned} \quad \text{(A3)}$$

where the exponent α_{21} is treated as $\alpha_{21}=1$ and the other details should be refered to the previous paper2). The proposed model (RSM-α) is found to be useful to correlate VLE of ethanol(1) + hydrocarbon(2) binary systems and it is noticed that at infinite dilution condition14) :

$$\alpha_{12} < 1 : \ln\gamma_1^{\infty}\ (x_1 = 0) = +\infty \quad \text{(A4)}$$

$$\alpha_{12} = 1 : \ln\gamma_1^{\infty}\ (x_1 = 0) = \frac{A_{12}v_1}{RT} + \ln\left(\frac{v_1}{v_2}\right) + 1 - \frac{v_1}{v_2} \quad \text{(A5)}$$

$$\alpha_{12} > 1 : \ln\gamma_1^{\infty}\ (x_1 = 0) = \ln\left(\frac{v_1}{v_2}\right) + 1 - \frac{v_1}{v_2} \quad \text{(A6)}$$

For ethanol(1) + hydrocarbon(2) binary systems, for example ethanol(1) + hexane(2), $\alpha_{12}=0.827$ ($\alpha_{12}<1$) and Eq. (A2) is found to be effective to represent the behavior of $\ln\gamma_1$ curve (rapid increase) near $x_1=0$ though Eq.(A2) may be inadequate to be adopted at infinite dilution condition because of the fact of Eq. (A4). It is noted with interest, based on an associated solution model15), that the infinite dilution activity coefficient of a dimerizing component (all molecules are dimerized) in a non dimerizing inert solvent becomes to be infinite (+∞).

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