Correlation of Vapor-Liquid Equilibria Using Wilson Equation with Parameters Estimated from Solubility Parameters and Molar Volumes

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Wilson parameters were estimated from solubility parameters and molar volumes. Namely, the interaction parameters due to attractive forces were evaluated from the solubility parameters and molar volumes predicted by the group contribution method of Fedors. The vapor-liquid equilibria (VLE) of several binary systems (hydrocarbon binary mixtures, binary systems containing ethers, binary systems containing ketones, ethanol + hydrocarbon systems and water + polar molecule systems) were correlated by use of these Wilson parameters, in which the interaction parameters between unlike molecules were adopted. The interaction parameters were determined by using VLE data and the correlation of the parameters obtained was attempted with the pure component properties such as solubility parameters and normal boiling points.

Keywords: *Wilson Parameter, Solubility Parameter, Molar Volume, Vapor-Liquid Equilibrium, Binary System*

Introduction

Activity coefficients of liquid phase are very important to calculate phase equilibria such as vapor-liquid equilibria (VLE) which is the fundamental knowledge in the separation process design. To date, many equations have been proposed to give activity coefficients. Among them, the Wilson equation[1] is well known and very useful. In the application of the Wilson equation for binary systems, for example, two parameters are required which are usually determined by using VLE data. In process design, however, it is desired to obtain the two parameters with no VLE data of mixtures. In a previous paper[2], therefore, an estimation method of the Wilson parameters[1] has been proposed by using solubility parameters and molar volumes which can be obtained based on a group contribution treatment of Fedors[3].

In the present paper, the applicability of the estimation method was examined and discussed. Namely, the method was adopted to correlate VLE of several binary systems: hydrocarbon binary mixtures, binary systems containing ethers, binary systems containing ketones, ethanol + hydrocarbon systems and water + polar molecule systems. Further, it was attempted to correlate the interaction parameters between unlike molecules, which are needed in the estimation methods, with the pure component properties such as solubility parameters and normal boiling points.

1. Estimation of Wilson Parameters

The Wilson equations[1] for binary systems are given as

$$\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1+x_2}\right) \quad (1)$$

$$\ln\gamma_2 = -\ln(\Lambda_{21}x_1 + x_2) - x_1\left(\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1+x_2}\right) \quad (2)$$

where γ_1 and γ_2 denote respectively the activity coefficients of the components 1 and 2. The Wilson parameters Λ_{12} and Λ_{21} are expressed by

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left[-\frac{\lambda_{12}-\lambda_{11}}{RT}\right] \quad (3)$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\left[-\frac{\lambda_{21}-\lambda_{22}}{RT}\right] \quad (4)$$

As studied in the previous work[2], the interaction parameters λ_{11} and λ_{22} for pure components can be estimated by

$$\lambda_{11} = -(2/z) v_1 \delta_1^2 \quad (5)$$

$$\lambda_{22} = -(2/z) v_2 \delta_2^2 \quad (6)$$

where v and δ are respectively the liquid molar volume and the solubility parameter of pure components and z denotes the coordination number. Further, the interaction energy parameters between unlike molecules are approximated as follows:

$$\lambda_{12} = -(1-\varepsilon_{12})(2/z)(v_1 v_2)^{0.5} \delta_1 \delta_2 \quad (7)$$

$$\lambda_{21} = -(1-\varepsilon_{21})(2/z)(v_2 v_1)^{0.5} \delta_2 \delta_1 \quad (8)$$

where z=2 and the interaction parameters ε_{12} and ε_{21} should be evaluated by VLE data fitting.

2. Molar Volumes and Solubility Parameters

The molar volume and the solubility parameter of a pure component at a given temperature t[℃] can be obtained by using the following equations[4, 5].

$$v_t = v_{25} + \beta(t-25), \quad \beta = (v_b - v_{25})/(t_b - 25) \quad (9)$$

$$\delta_t = (v_{25}/v_t)\delta_{25} \quad (10)$$

where the liquid molar volume at the normal boiling point t_b[℃], v_b, can be estimated by using the additive method of Le Bas[6]. Further, the liquid molar volume and the solubitity parameter at 25℃, v_{25} and δ_{25}, can be predicted by Fedors method[3] based on the group-contribution treatment.

3. VLE Correlation and Discussion

At sufficiently low pressures (*i.e.*, vapor phase can be approximated as an ideal gas), VLE (x–y) of binary systems can be calculated by

$$y_1 = \gamma_1 x_1 p_1^\circ / p, \quad y_2 = \gamma_2 x_2 p_2^\circ / p \quad (11)$$

$$p = \gamma_1 x_1 p_1^\circ + \gamma_2 x_2 p_2^\circ \quad (12)$$

where x and y respectively denote the mole fractions of liquid and vapor phases. Further, p^o is the vapor pressure of a pure component, which can be calculated by Antoine equation, and p the total pressure.

The physical properties of pure components required in the present VLE correlation (v_{25}, v_b, δ_{25}, t_b and the constants of Antoine equation) are presented in **Table 1**. VLE of several binary systems containing non-polar and polar substances of which data sources are shown in the previous works[7, 8, 9] have been correlated by using these pure component properties.

3.1 Hydrocarbon Binary Systems

VLE of 18 binary systems consisting of several hydrocarbons have been correlated. The interaction parameters and the correlation performances are shown in **Table 2**. A representative x–y relation is given in **Fig. 1**. As shown in Table 2, good correlation results are obtained. The deviations Δy_1 are within the order of 2 % except cyclohexane + hexane and octane + benzene and Δt are within 0.7℃.

3.2 Binary Systems Containing Ethers

VLE of 14 binary systems containing ethers have been correlated and the interaction parameters and the correlation performances are shown in **Table 3**. A typical illustration is given in **Fig. 2**. As shown in Table 3, good correlation results are obtained. The deviations are less than

Table 1 Physical properties of pure substances [9]

Substance	v_{25} [cm^3·mol^{-1}]	v_b [cm^3·mol^{-1}]	δ_{25} [(J·cm^{-3})$^{0.5}$]	t_b [℃]	Constants of Antoine's equation*		
					A	B	C
2–Methylbutane	115.6	118.4	14.0	27.852	5.93330	1029.602	38.856
Pentane	115.3	118.4	14.5	36.068	5.99028	1071.187	40.384
2–Methylpentane	131.7	140.6	14.4	60.271	5.99479	1152.210	44.579
3–Methylpentane	131.7	140.6	14.4	63.282	5.99139	1162.069	44.870
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
2,3–Dimethylpentane	148.1	162.8	14.4	89.783	5.98293	1240.404	51.056
Octane	163.6	185.0	15.5	125.665	6.04394	1351.938	64.030
2,2,4–Trimethylpentane	163.4	185.0	14.3	99.238	5.92751	1252.340	53.060
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
Diethyl ether	103.0	106.1	14.8	34.434	6.04920	1061.391	45.090
Methyl *t*–butyl ether	118.6	129.4	14.1	55.17	6.070343	1158.912	43.200
Ethyl *t*–butyl ether	134.7	151.6	14.6	72.71	6.073724	1206.874	49.190
t–Amyl methyl ether	134.7	151.6	14.6	86.24	6.067822	1256.258	50.100
Diisopropyl ether	135.8	151.6	14.6	68.339	5.97081	1137.408	54.634
Dibutyl ether	167.4	196.0	15.9	140.295	5.92274	1298.256	82.006
Acetone	74.0	77.6	18.6	56.067	6.25017	1214.208	43.148
Methyl ethyl ketone	93.9	96.2	18.4	79.583	6.18397	1258.940	51.425
Diethyl ketone	110.0	118.4	18.3	101.960	6.14570	1307.941	59.182
Methyl propyl ketone	110.0	118.4	18.3	102.261	6.13931	1309.629	58.585
Methyl isopropyl ketone	110.3	118.4	17.8	94.333	6.09024	1265.595	57.631
Methyl isobutyl ketone	126.4	140.6	17.8	116.183	5.81291	1176.833	80.225
Methanol	40.7	42.8	28.2	64.511	7.24693	1605.615	31.317
Ethanol	59.6	62.5	25.7	78.229	7.24222	1595.811	46.702
1–Propanol	75.7	81.4	24.2	97.153	6.87065	1438.587	74.598
2–Propanol	76.0	81.4	23.7	82.244	6.86634	1360.183	75.557
1–Butanol	91.8	103.6	23.2	117.731	6.54068	1335.028	96.496
2–Butanol	92.1	103.6	22.7	99.515	6.35079	1169.924	103.413
Water	18.1	18.8	47.9	100.001	7.06252	1650.270	46.804

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

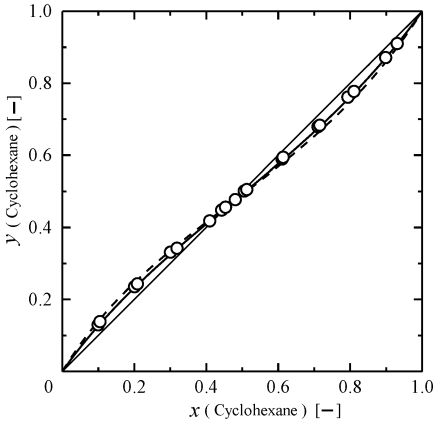

Fig. 1 Correlation of VLE for cyclohexane (1) + benzene (2) at 101.3 kPa. Experimental (○); Correlations: (——) with parameters fitted; (- - - -) with parameters by Eqs. (17) and (18)

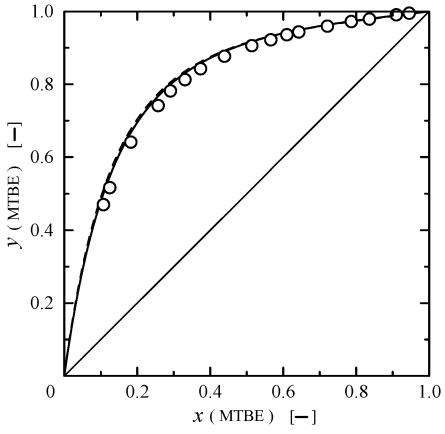

Fig. 2 Correlation of VLE for MTBE (1) +octane (2) at 101.3 kPa. Experimental (○); Correlations: (——) with parameters fitted; (- - - -) with parameters by Eqs. (21) and (22)

Table 2 Interaction parameters and correlation performances for VLE of hydrocarbon binary mixtures at 101.3 kPa

Binary system (1) + (2)	Interaction parameters		Dev.	
	ε_{21}	ε_{21}	Δy_1 *	Δt **
Hexane + Heptane[c]	0.0552	–0.0589	0.7	0.4
Heptane + Octane[d]	0.0618	–0.0595	1.7	0.2
Cyclohexane + Hexane	0.1200	–0.0551	3.2(6.6)[a]	0.3(1.0)[a]
Cyclohexane + Heptane	0.1350	–0.1200	2.1(3.2)[a]	0.3(0.2)[a]
Cyclohexane + Octane	0.1486	–0.1669	1.7(5.4)[a]	0.2(1.8)[a]
Cyclohexane + Benzene	0.0272	0.0091	0.4(2.6)[a]	0.1(0.9)[a]
Cyclohexane + Toluene	0.0729	–0.0515	1.2(2.4)[a]	0.1(0.4)[a]
Cyclohexane + Ethylbenzene	0.1095	–0.0806	2.1(1.2)[a]	0.4(1.2)[a]
Cyclohexane + *p*-Xylene	0.1100	–0.0950	1.0(2.2)[a]	0.7(1.5)[a]
Hexane + Benzene	0.0800	–0.0302	0.7(6.9)[b]	0.1(1.2)[b]
Hexane + Toluene	0.1147	–0.0915	2.0(2.1)[b]	0.4(0.4)[b]
Heptane + Benzene	0.0093	0.0418	1.9(4.8)[b]	0.1(0.8)[b]
Heptane + Toluene	0.0352	–0.0063	1.3(1.7)[b]	0.2(0.2)[b]
Heptane + Ethylbenzene	0.0696	–0.0611	1.5(1.2)[b]	0.2(0.1)[b]
Heptane + *p*-Xylene	0.0350	–0.0079	2.2(2.6)[b]	0.5(0.7)[b]
Octane + Benzene	–0.1223	0.1329	3.7(3.5)[b]	0.3(0.8)[b]
Benzene + Toluene	0.0851	–0.0884	1.5	0.4
Ethylbenzene + *p*-Xylene[e]	0.0044	–0.0044	1.1	0.1

$^{*}\Delta y_1[\%] = \frac{100}{N}\sum^{N}\frac{|y_{1,\mathrm{calc}} - y_{1,\mathrm{exp}}|}{y_{1,\mathrm{exp}}}$, $^{**}\Delta t[^{\circ}\mathrm{C}] = \frac{1}{N}\sum^{N}|t_{\mathrm{calc}} - t_{\mathrm{exp}}|$, N = number of data points

[a] values in parentheses are obtained by Eqs. (17) and (18), [b] values in parentheses are obtained by Eqs. (19) and (20)

[c] at 101.0kPa, [d] at 94.0kPa, [e] at 100.65kPa

Table 3 Interaction parameters and correlation performances for VLE of binary systems containing ethers at 101.3 kPa

Binary system (1)+(2)	Interaction parameters		Dev.	
	ε_{12}	ε_{21}	Δy_1 *	Δt **
Diethyl ether + 2–Methylbutane	0.0196	0.0040	0.1(2.2)[a]	0.1(0.3)[a]
Diethyl ether + Pentane	0.0714	–0.0431	3.2(3.7)[a]	0.1(0.2)[a]
Methyl *t*–butyl ether + 2–Methylpentane	0.0895	–0.0723	0.4(0.5)[a]	0.1(0.2)[a]
Methyl *t*–butyl ether + 3–Methylpentane	0.0975	–0.0830	0.4(0.4)[a]	0.1(0.1)[a]
Methyl *t*–butyl ether + 2,3–Dimethylpentane	0.1011	–0.0652	0.4(2.2)[a]	0.2(0.6)[a]
Methyl *t*–butyl ether + Octane	0.2302	–0.2619	2.2(2.7)[a]	0.8(1.3)[a]
Methyl *t*–butyl ether + 2,2,4–Trimethylpentane	0.2055	–0.2209	1.3(1.6)[a]	0.4(0.5)[a]
Methyl *t*–butyl ether + Methanol	0.1246	–0.0085	3.1	0.3
Ethyl *t*–butyl ether + 2–Methylpentane	0.0000	0.0132	0.3(1.1)[a]	0.1(0.2)[a]
Ethyl *t*–butyl ether + Ethanol	0.1551	–0.0407	1.2	0.1
t–Amyl methyl ether + 2–Methylpentane	–0.0254	0.0388	1.3(2.5)[a]	0.1(0.3)[a]
t–Amyl methyl ether + 3–Methylpentane	0.0172	0.0000	0.3(1.8)[a]	0.1(0.3)[a]
t–Amyl methyl ether + 2,3–Dimethylpentane	0.0211	0.0000	0.4(0.2)[a]	0.1(0.1)[a]
Diisopropyl ether + 2,3–Dimethylpentane	0.1124	–0.0958	0.6(0.7)[a]	0.1(0.1)[a]

$^{*}\Delta y_1[\%] = \frac{100}{N}\sum^{N}\frac{|y_{1,\mathrm{calc}} - y_{1,\mathrm{exp}}|}{y_{1,\mathrm{exp}}}$, $^{**}\Delta t[^{\circ}\mathrm{C}] = \frac{1}{N}\sum^{N}|t_{\mathrm{calc}} - t_{\mathrm{exp}}|$, N = number of data points

[a] values in parentheses are obtained by Eqs. (21) and (22)

Table 4 Interaction parameters and correlation performances for VLE of binary systems containing ketones at 101.3 kPa

Binary system (1)+(2)	Interaction parameters		Dev.	
	ε_{12}	ε_{21}	Δy_1 *	Δt **
Acetone + Hexane	0.2149	–0.0077	1.3	0.2
Acetone + Benzene	0.1704	–0.1399	0.2(0.8) [a]	0.1(0.4) [a]
Acetone + Dibutyl ether	0.2834	–0.2342	0.6	1.0
Acetone + Methanol	0.0863	–0.0370	0.8(1.4) [b]	0.1(0.1) [b]
Acetone + Ethanol	0.1901	–0.1757	2.4(2.7) [b]	0.3(0.4) [b]
Methyl ethyl ketone + Heptane	0.1389	–0.0039	0.9	0.3
Methyl ethyl ketone + Cyclohexane	0.0338	0.0907	2.6(2.1) [a]	0.3(0.3) [a]
Methyl ethyl ketone + Benzene	0.0378	–0.0107	0.4(7.3) [a]	0.1(1.5) [a]
Methyl ethyl ketone + Toluene	0.0434	–0.0036	2.0(2.0) [a]	0.3(0.4) [a]
Methyl ethyl ketone + Ethanol	0.0783	–0.0239	1.0(3.1) [b]	0.1(0.7) [b]
Methyl ethyl ketone + 1–Propanol	0.1574	–0.1376	0.8(1.0) [b]	0.1(0.2) [b]
Methyl ethyl ketone + 2–Propanol	0.1264	–0.1008	0.5(1.8) [b]	0.1(0.6) [b]
Diethyl ketone + 2–Propanol	0.0521	–0.0179	1.2(2.0) [b]	0.4(0.2) [b]
Diethyl ketone + 1–Butanol	0.1315	–0.1156	2.2(3.0) [b]	0.6(0.4) [b]
Methyl propyl ketone + 2–Propanol	0.0478	–0.0140	2.1(2.5) [b]	0.1(0.3) [b]
Methyl isopropyl ketone + Octane	0.1418	–0.0481	0.9	0.2
Methyl isopropyl ketone + Cyclohexane	0.0307	0.0683	0.4(3.5) [a]	0.1(0.7) [a]
Methyl isobutyl ketone + Cyclohexane	–0.0026	0.0905	5.0(8.1) [a]	0.8(1.5) [a]
Methyl isobutyl ketone + 2–Propanol	0.0220	0.0178	2.8(2.5) [b]	0.2(0.3) [b]
Methyl isobutyl ketone + 1–Butanol	0.0864	–0.0624	0.6(0.5) [b]	0.3(0.5) [b]
Methyl isobutyl ketone + 2–Butanol	0.0710	–0.0494	0.8(2.0) [b]	0.4(0.1) [b]

$^{*}\Delta y_1[\%] = \frac{100}{N}\sum^{N}\frac{\left|y_{1,\mathrm{calc}} - y_{1,\mathrm{exp}}\right|}{y_{1,\mathrm{exp}}}$, $^{**}\Delta t[^{\circ}\mathrm{C}] = \frac{1}{N}\sum^{N}\left|t_{\mathrm{calc}} - t_{\mathrm{exp}}\right|$, N = number of data points

[a] values in parentheses are obtained by Eqs. (23) and (24), [b] values in parentheses are obtained by Eqs. (25) and (26)

2 % and 0.5℃ respectively for Δy_1 and Δt except diethyl ether + pentane, methyl *t*-butyl ether + octane and methyl *t*-butyl ether + methanol among 14 binary systems studied here.

3.3 Binary Systems Containing Ketones

VLE of 21 binary systems containing ketones have been correlated and the interaction parameters and the correlation performances are given in **Table 4**. A graphic representation is given in **Fig. 3**. As seen in Table 4, good results are obtained for VLE correlation. Δy_1 are within the order of 2 % and Δt are almost within 0.5℃ except methyl isobutyl ketone + cyclohexane.

3.4 Ethanol + Hydrocarbon Systems

VLE of 6 ethanol + hydrocarbon binary systems have been correlated. The interaction parameters determined and the correlation performances are presented in **Table 5** and a typical *x*-*y* relation is given in **Fig. 4**. As shown in Table 5, good correlation results are obtained for every hydrocarbon mixture. Δy_1 and Δt are respectively within 2 % and within 0.8℃.

3.5 Binary Systems Containing Water

VLE of 5 binary systems containing water have been correlated and the interaction parameters and the correlation performances are presented in **Table 6**. In **Fig. 5**, a typical correlation result is illustrated. As presented in Table 6, good VLE correlation results are obtained. The deviations Δy_1 and Δt are respectively within 1.5 % and 0.1℃ for all 5 systems.

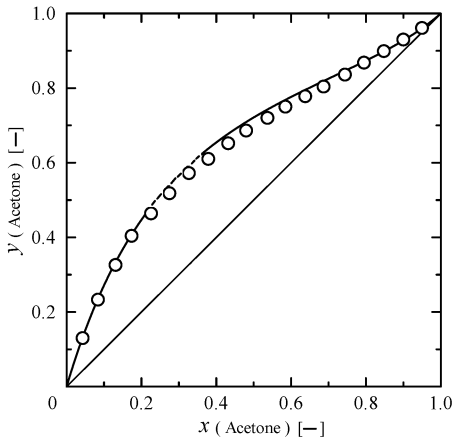

Fig. 3 Correlation of VLE for acetone (1) + ethanol (2) at 101.3 kPa. Experimental (○); Correlations: (——) with parameters fitted; (- - - -) with parameters by Eqs. (25) and (26)

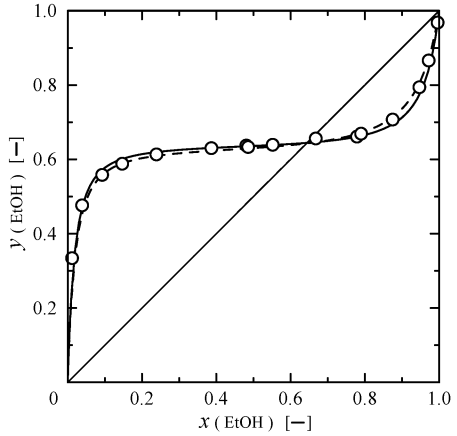

Fig. 4 Correlation of VLE for ethanol (1) + heptane (2) at 101.3 kPa. Experimental (○); Correlations: (——) with parameters fitted; (- - - -) with parameters by Eqs. (27) and (28)

Table 5 Correlation performances for VLE of ethanol (1) + hydrocarbon (2) binary systems at 101.3 kPa

Binary system (1) + (2)	Interaction parameters		Dev.	
	ε_{12}	ε_{21}	Δy_1^{*}	Δt^{**}
Ethanol + Hexane	0.0965	0.1923	1.5 (2.4) [a]	0.1 (0.5) [a]
Ethanol + Heptane	0.1707	0.1618	2.0 (2.3) [a]	0.8 (0.5) [a]
Ethanol + Octane	0.2268	0.0575	0.6 (1.0) [a]	0.1 (0.4) [a]
Ethanol + Cyclohexane	0.1068	0.1652	1.0 (0.9) [a]	0.3 (0.5) [a]
Ethanol + Benzene	0.0388	0.1329	1.8 (1.6) [a]	0.4 (0.4) [a]
Ethanol + Toluene [b]	0.0991	0.0752	1.6 (1.9) [a]	0.2 (0.2) [a]

$^{*}\Delta y_1[\%] = \frac{100}{N}\sum^{N}\frac{|y_{1,\mathrm{calc}} - y_{1,\mathrm{exp}}|}{y_{1,\mathrm{exp}}}$, $^{**}\Delta t[^{\circ}\mathrm{C}] = \frac{1}{N}\sum^{N}|t_{\mathrm{calc}} - t_{\mathrm{exp}}|$, N = number of data points

[a] values in parentheses are obtained by Eqs. (27) and (28), [b] at 100.8kPa

Table 6 Interaction parameters and correlation performances for VLE of binary systems containing water at 101.3 kPa

Binary system (1)+(2)	Interaction parameters		Dev.	
	ε_{12}	ε_{21}	Δy_1^{*}	Δt^{**}
Water + Acetone	–0.0963	0.2711	1.3	0.1
Water + Methanol	–0.0959	0.1512	1.3 (2.1) [a]	0.1 (0.2) [a]
Water + Ethanol	0.0640	0.0841	1.1 (5.7) [a]	0.1 (0.8) [a]
Water + 1-Propanol	0.1492	0.1442	1.3 (1.4) [a]	0.1 (0.3) [a]
Water + 2-Propanol	0.1207	0.1169	1.3 (2.1) [a]	0.1 (0.3) [a]

$^{*}\Delta y_1[\%] = \frac{100}{N}\sum^{N}\frac{|y_{1,\mathrm{calc}} - y_{1,\mathrm{exp}}|}{y_{1,\mathrm{exp}}}$, $^{**}\Delta t[^{\circ}\mathrm{C}] = \frac{1}{N}\sum^{N}|t_{\mathrm{calc}} - t_{\mathrm{exp}}|$, N = number of data points

[a] values in parentheses are obtained by Eqs. (29) and (30)

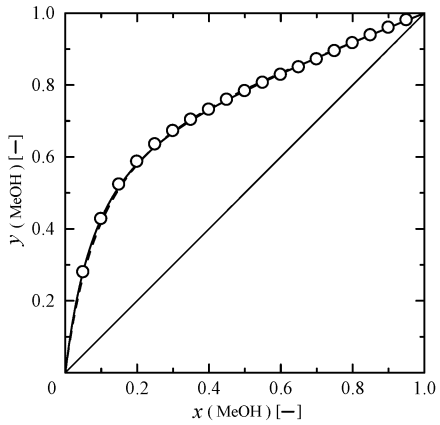

Fig. 5 Correlation of VLE for water (1) + methanol (2) at 101.3 kPa. Experimental (○); Correlations: (———) with parameters fitted; (- - - - -) with parameters by Eqs. (29) and (30)

4. Binary Interaction Parameters

To estimate the Wilson parameters, it is required to correlate the binary interaction parameters ε_{12} and ε_{21} with the pure component properties. In this study, from various attempts, the following equations were adopted to correlated the interaction parameters ε_{12} and ε_{21}.

$$\varepsilon_{12} = a_{12} + b_{12} t_{b,1} + c_{12} t_{b,2} + d_{12} \delta_{25,1}{}^2 + e_{12} \delta_{25,2}{}^2 \quad (13)$$

$$\varepsilon_{21} = a_{21} + b_{21} t_{b,1} + c_{21} t_{b,2} + d_{21} \delta_{25,1}{}^2 + e_{21} \delta_{25,2}{}^2 \quad (14)$$

where t_b and δ are respectively the normal boiling point and the solubility parameter of the each pure component. When the component (1) is fixed, for example ethanol (1) + hydrocarbon (2), the following reduced relations can be used because $t_{b,1}$ and $\delta_{25,1}$ are the constant values.

$$\varepsilon_{12} = a_{12}^{\circ} + b_{12}^{\circ} t_{b,2} + c_{12}^{\circ} \delta_{25,2}{}^2 \quad (15)$$

$$\varepsilon_{21} = a_{21}^{\circ} + b_{21}^{\circ} t_{b,2} + c_{21}^{\circ} \delta_{25,2}{}^2 \quad (16)$$

Further, if $t_{b,2}$ or $\delta_{25,2}{}^2$ is relatively insensitive to ε_{12} and ε_{21}, b_{12}° and b_{21}° or c_{12}° and c_{21}° may be zero.

4.1 Hydrocarbon Binary Mixtures

For cyclohexane (1) + paraffinic or aromatic hydrocarbon (2) seven binary systems, the interaction parameters can be correlated by

$$\varepsilon_{12} = 0.1807 + 1.08 \times 10^{-3} t_{b,2} - 6.53 \times 10^{-4} \delta_{25,2}{}^2 \quad (17)$$

$$\varepsilon_{21} = -0.1174 - 1.82 \times 10^{-3} t_{b,2} + 7.86 \times 10^{-4} \delta_{25,2}{}^2 \quad (18)$$

As shown in **Fig. 6**, a fairly good correlation can be obtained. VLE correlation results with Eqs. (17) and (18) are given in Table 2 and Fig.1. As shown in Table 2, good correlation results are obtained except hexane (2) and octane (2).

For other paraffinic (1) + aromatic (2) seven hydrocarbon binary systems, the following relations can be derived based on the data regression.

$$\varepsilon_{12} = 15.2407 + 1.65 \times 10^{-2} t_{b,1} - 2.07 \times 10^{-5} t_{b,2} - 6.36 \times 10^{-2} \delta_{25,1}{}^2 - 6.40 \times 10^{-3} \delta_{25,2}{}^2 \quad (19)$$

$$\varepsilon_{21} = -6.1894 - 9.94 \times 10^{-4} t_{b,1} - 8.26 \times 10^{-5} t_{b,2} + 1.28 \times 10^{-2} \delta_{25,1}{}^2 + 9.51 \times 10^{-3} \delta_{25,2}{}^2 \quad (20)$$

A fairly good results can be given as shown in Table 2 except hexane(1) + benzene (2) and heptane (1) + benzene (2) binary systems.

4.2 Ether + Paraffinic Hydrocarbon Systems

For ether + paraffinic hydrocarbon various binary systems, the following equations can be obtained.

$$\varepsilon_{12} = 0.3419 - 2.64 \times 10^{-3} t_{b,1} + 2.18 \times 10^{-3} t_{b,2} - 1.46 \times 10^{-3} \delta_{25,1}{}^2 + 2.17 \times 10^{-4} \delta_{25,2}{}^2 \quad (21)$$

$$\varepsilon_{21} = -0.1808 + 2.73 \times 10^{-3} t_{b,1} - 2.42 \times 10^{-3} t_{b,2} + 1.58 \times 10^{-3} \delta_{25,1}{}^2 - 9.98 \times 10^{-4} \delta_{25,2}{}^2 \quad (22)$$

As shown in **Fig. 7**, good linear relations can be obtained. As presented in Table 3 and Fig. 2, good VLE correlation performances are given. However, it is hard

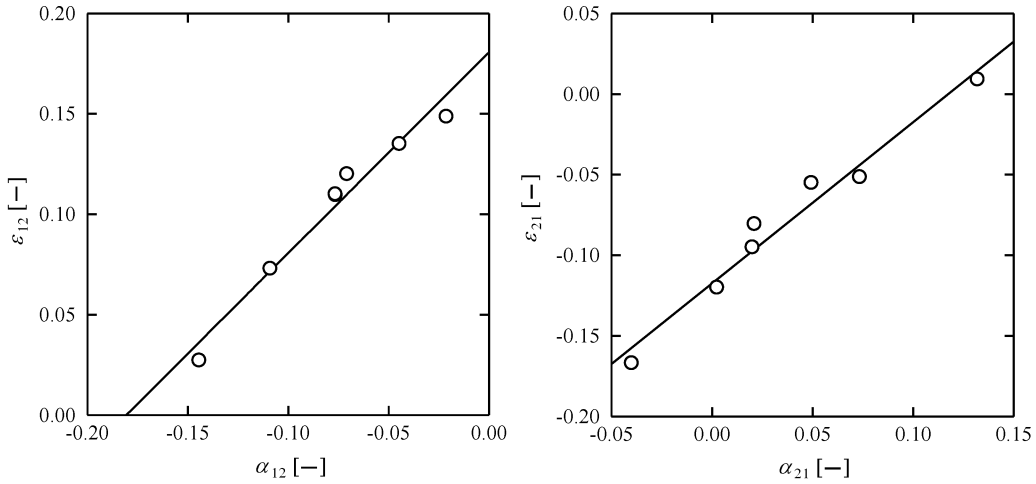

Fig. 6 Relationships between ε_{12}, ε_{21} and α_{12}, α_{21} for cyclohexane (1) + paraffinic or aromatic hydrocarbon (2) systems; $\alpha_{12}=1.08\times10^{-3}\,t_{b,2}-6.53\times10^{-4}\,\delta_{25,2}{}^2$ and $\alpha_{21}=-1.82\times10^{-3}\,t_{b,2}+7.86\times10^{-4}\delta_{25,2}{}^2$

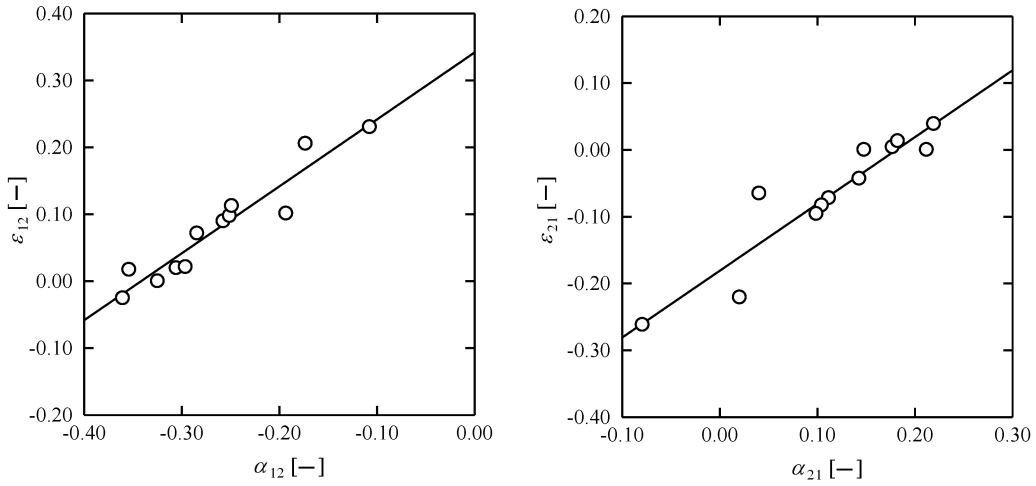

Fig. 7 Relationships between ε_{12}, ε_{21} and α_{12}, α_{21} for ether (1) + paraffinic hydrocarbon (2) systems; $\alpha_{12}=-2.64\times10^{-3}\,t_{b,1}+2.18\times10^{-3}\,t_{b,2}-1.46\times10^{-3}\delta_{25,1}{}^2+2.17\times10^{-4}\delta_{25,2}{}^2$ and $\alpha_{21}=2.73\times10^{-3}\,t_{b,1}-2.42\times10^{-3}\,t_{b,2}+1.58\times10^{-3}\,\delta_{25,1}{}^2-9.98\times10^{-4}\,\delta_{25,2}{}^2$

to include methanol and ethanol (alcohols) in the present correlations; Eqs. (21) and (22).

4.3 Binary Systems Containing Ketones

The interaction parameters ε_{12} and ε_{21} of ketones + cyclohexane or aromatic hydrocarbon binary systems can be expressed by

$$\varepsilon_{12}=1.1806-3.60\times10^{-3}\,t_{b,1}-8.74\times10^{-4}\,t_{b,2}-2.55\times10^{-3}\delta_{25,1}{}^2+3.14\times10^{-4}\,\delta_{25,2}{}^2 \quad (23)$$

$$\varepsilon_{21}=-1.0989+3.38\times10^{-3}\,t_{b,1}+1.29\times10^{-3}t_{b,2}+3.62\times10^{-3}\delta_{25,1}{}^2-1.55\times10^{-3}\delta_{25,2}{}^2 \quad (24)$$

The correlation results obtained are presented in Table 4. As shown in this table, fairly good results can be obtained except methyl ethyl ketone + benzene and methyl isobutyl ketone + cyclohexane.

For ketone + alcohol binary mixtures, the following correlation equations are obtained as shown in **Fig. 8**.

$$\varepsilon_{12}=1.1034-4.32\times10^{-3}\,t_{b,1}+1.88\times10^{-3}\,t_{b,2}-1.51\times10^{-3}\,\delta_{25,1}{}^2-4.66\times10^{-4}\delta_{25,2}{}^2 \quad (25)$$

$$\varepsilon_{21}=-1.3730+5.17\times10^{-3}\,t_{b,1}-2.29\times10^{-3}\,t_{b,2}+1.96\times10^{-3}\delta_{25,1}{}^2+6.50\times10^{-4}\,\delta_{25,2}{}^2 \quad (26)$$

As given in Table 4 and Fig. 3 (the solid and dotted lines are almost overlapped), fairly good VLE calculations can be performed.

4.4 Ethanol + Hydrocarbon Systems

For ethanol (1) + hydrocarbon (2) binary systems, ε_{12} and ε_{21}, can be expressed as

$$\varepsilon_{12} = 0.1137 + 2.31\times10^{-3} t_{b,2} - 7.48\times10^{-4}\delta_{25,2}{}^2 \quad (27)$$

$$\varepsilon_{21} = 0.4269 - 2.20\times10^{-3} t_{b,2} - 3.21\times10^{-4}\delta_{25,2}{}^2 \quad (28)$$

As illustrated in **Fig. 9**, fairly good linear relations are expressed. The VLE correlation performances are presented in Table 5 and Fig. 4 with good results. In the previous study[2], on the other hand, the interaction parameters have been correlated by $\varepsilon_{12} = (5.0 \times 10^{-4})\,\Delta\delta^2 - 0.086$ and $\varepsilon_{21} = (6.0 \times 10^{-4})\,\Delta\delta^2 - 0.079$ with good results except ethanol (1) + octane (2) where $\Delta\delta^2$ is defined as $|\delta_1{}^2 - \delta_2{}^2|$ at 25℃. It is found that the present correlation using Eqs. (27) and (28) can give better performances for VLE correlation than the previous correlation[2] using $\Delta\delta^2$. For example, Δy_1 and Δt of ethanol + octane are respectively 4.1 % and 2.1 ℃ by the previous correlation[2].

4.5 Water + Alcohol Systems

The interaction parameters of water (1) alcohol (2) binary systems can be regressed by

$$\varepsilon_{12} = 0.2944 + 2.83\times10^{-3} t_{b,2} - 7.12\times10^{-4}\delta_{25,2}{}^2 \quad (29)$$

$$\varepsilon_{21} = -0.2090 + 1.84\times10^{-3} t_{b,2} + 2.84\times10^{-4}\delta_{25,2}{}^2 \quad (30)$$

As presented in **Fig. 10**, good linear correlations can be obtained. The correlation performances for VLE of water (1) + alcohol (2) binary systems are given in Table 6 and Fig. 5 with fairly good results except water + ethanol.

Conclusion

An estimation method for Wilson parameters by using solubility parameters and molar volumes was adopted to correlate VLE of several binary systems such as hydrocarbon binary mixtures, binary systems containing ethers, binary systems containing ketones, ethanol + hydrocarbon systems and water + polar molecule systems. In the present correlation, the interaction parameters between unlike molecules were used. By adjusting the interaction parameters, VLE of every binary system consisting of non-polar and polar molecules have been correlated with good performances. It is found that the interaction parameters required can be related to the pure component properties such as the normal boiling point and the solubility parameter. Namely, the interaction parameters ε_{12} and ε_{21} of various binary systems; cyclohexane + paraffinic or aromatic hydrocarbons, paraffinic and aromatic hydrocarbon binary systems, ether + paraffinic hydrocarbons, ketone + cyclohexane or aromatic hydrocarbons, ketone+alcohols, ethanol + hydrocarbons and water + alcohols can be well correlated with t_b and $\delta_{25}{}^2$ of pure components. For these binary mixtures, VLE may be predicted from the pure component properties alone.

Nomenclature

p	= total pressure	[Pa]
p°	= vapor pressure of pure component	[Pa]
R	= gas constant	[J·mol^{-1}·K^{-1}]
T	= absolute temperature	[K]
t	= temperature	[℃]
v	= liquid molar volume	[cm^3·mol^{-1}]
x	= mole fraction of liquid phase	[–]
y	= mole fraction of vapor phase	[–]
z	= co-ordination number	[–]
γ	= liquid phase activity coefficient	[–]
Λ	= Wilson parameter	[–]
δ	= solubility parameter	[(J·cm^{-3})$^{0.5}$]
ε	= interaction parameter between unlike molecules	[–]
λ	= interaction energy due to attractive force	[J·mol^{-1}]

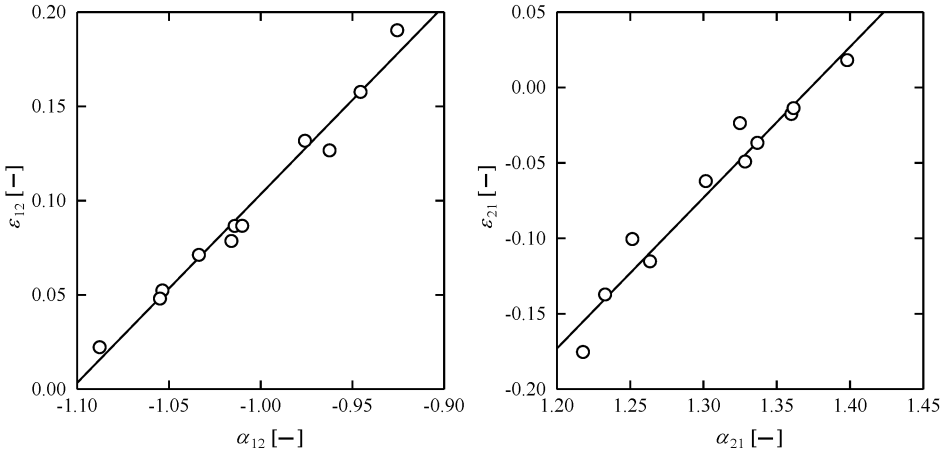

Fig. 8 Relationships between ε_{12}, ε_{21} and α_{12}, α_{21} for ketone (1) + alcohol (2) systems; $\alpha_{12} = -4.32\times10^{-3}\, t_{b,1} + 1.88\times10^{-3}\, t_{b,2} - 1.51\times10^{-3}\, \delta_{25,1}{}^2 - 4.66\times10^{-4}\, \delta_{25,2}{}^2$ and $\alpha_{21} = 5.17\times10^{-3}\, t_{b,1} - 2.29\times10^{-3}\, t_{b,2} + 1.96\times10^{-3}\, \delta_{25,1}{}^2 + 6.50\times10^{-4}\, \delta_{25,2}{}^2$

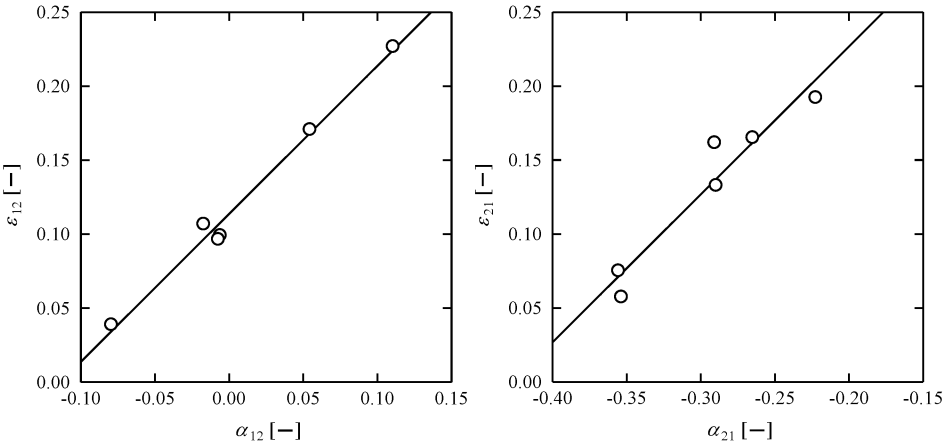

Fig. 9 Relationships between ε_{12}, ε_{21} and α_{12}, α_{21} for ethanol (1) + hydrocarbon (2) systems; $\alpha_{12} = 2.31\times10^{-3}\, t_{b,2} - 7.48\times10^{-4}\, \delta_{25,2}{}^2$ and $\alpha_{21} = -2.20\times10^{-3}\, t_{b,2} - 3.21\times10^{-4}\delta_{25,2}{}^2$

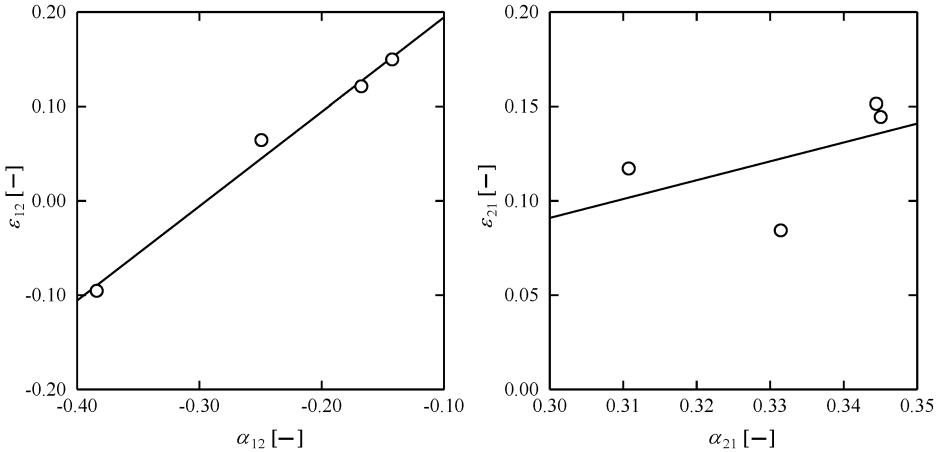

Fig. 10 Relationships between ε_{12}, ε_{21} and α_{12}, α_{21} for water (1) + alcohol (2) systems; $\alpha_{12} = 2.83\times10^{-3}\, t_{b,2} - 7.12\times10^{-4}\delta_{25,2}{}^2$ and $\alpha_{21} = 1.84\times10^{-3}\, t_{b,2} + 2.84\times10^{-4}\delta_{25,2}{}^2$

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

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