

Correlation of Liquid–Liquid Equilibria for Alkane + Methanol + Aromatics Ternary Systems by Using Modified Wilson Equation with Parameters Estimated from Pure-Component Properties

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A useful model has been proposed to calculate liquid–liquid equilibria (LLE) of non-aqueous ternary systems, which are classified as type I (only one pair among binary systems is partially miscible), based on a modified Wilson equation. The modified Wilson equation adopted contains the interaction energy parameters of constituent binary systems and the multi-component parameter for the ternary system concerned. In this study, a simple procedure has been developed to estimate those parameters from normal boiling points and solubility parameters which can be obtained by a group-contribution method. Therefore, LLE of ternary systems can be calculated by using pure-component properties alone. The procedure has been adopted for various alkane + methanol + aromatics ternary systems and good correlation performances are obtained.

Introduction

In a series of our papers (Kobuchi *et al.*, 2011, 2012a, 2012b, 2012c, 2013a, 2013b, 2015; Kobuchi and Yonezawa, 2014a, 2014b), a simple method for estimating Wilson parameters (Wilson, 1964) from pure-component properties alone has been proposed and the method is acknowledged to be successful to calculate the vapor–liquid equilibria (VLE) of various kinds of binary mixtures and ternary mixtures. The model is termed as GC-W (Group-Contribution method based Wilson equation) and is useful to calculate VLE of mixtures. However, GC-W cannot be adopted to calculate liquid–liquid equilibria (LLE) because GC-W is based on the original Wilson equation. To calculate LLE, a modification of Wilson equation is required.

In a previous study (Kobuchi *et al.*, 2014a), two kinds of modified Wilson equations (Nishimura *et al.*, 1985; Higashiuchi *et al.*, 1987) were applied for correlation of LLE of non-aqueous ternary mixtures and their correlation performances are evaluated. It is shown that a modified Wilson equation proposed by Higashiuchi *et al.* (1987) seems to be promising. The modified Wilson equation (Higashiuchi *et al.*, 1987) contains binary interaction parameters and multi-component parameters, which are determined from

phase equilibrium data of constituent binary systems and the ternary system, and is acknowledged (Higashiuchi *et al.*, 1990b) to be superior to NRTL (Renon and Prausnitz, 1968) widely adopted for non-aqueous ternary systems such as heptane + methanol + benzene, for example. We have attempted, in the present study, to introduce the group-contribution approach to the modified Wilson equation to calculate LLE from pure-component properties alone according to a similar manner used in the development of GC-W model and its applicability has been examined to calculate LLE of various alkane + methanol + aromatics ternary mixtures. Further, its performances for LLE calculation have been evaluated in comparison with the modified UNIFAC (Dortmund) (Gmehling *et al.*, 1993; Lohmann *et al.*, 2001) widely used.

1. Modified Wilson Equation

The well-known Wilson equation (Wilson, 1964) has been modified (Higashiuchi *et al.*, 1987, 1990a, 1990b) as follows to be applicable for LLE calculation.

$$\ln \gamma_i = 1.5 \left[1 - \ln A_i - \sum_j \{ (x_j / A_j) (\Lambda_{ji} - B_{ij} + C_j) \} \right] \quad (1)$$

where A_j , B_{ij} and C_j are given by the following.

$$A_j = \sum_q \Lambda_{jq} x_q \quad (2)$$

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$$B_{ij} = \sum_q \tau_{jq} \Lambda_{jq} x_q D \quad (q=i; D=1), \quad B_{ii} = 0 \quad (3)$$

$$C_j = \sum_q \tau_{jq} \Lambda_{jq} x_q \alpha_{jq} \quad (4)$$

Further, the interaction parameters are defined as follows.

$$\Lambda_{ij} = \exp(-\alpha_{ij} \tau_{ij}), \quad \Lambda_{ii} = 1 \quad (5)$$

$$\tau_{ij} = (g_{ij} - g_{ii}) / RT = R_{ij} / RT, \quad \tau_{ii} = 0 \quad (6)$$

$$\alpha_{ij} = x_j + D \sum_k x_k \quad (k \neq i, j), \quad \alpha_{ii} = 1 \quad (7)$$

The details for derivations of Eqs. (1)–(7) and the role of parameter D have been shown in the previous study (Higashiuchi *et al.*, 1987).

2. Phase Equilibrium Calculations

2.1 LLE calculation

LLE between phase I (upper) and phase II (lower) can be expressed as follows based on the thermodynamic equilibrium condition.

$$\gamma_i^I x_i^I = \gamma_i^{II} x_i^{II} \quad (8)$$

Adopting to Eq. (8), LLE ($x_i^I - x_i^{II}$) can be calculated from activity coefficients given by Eq. (1).

2.2 VLE calculation

At sufficiently low pressures (i.e. when vapor phase can be approximated as an ideal gas), VLE ($x-y$) of binary mixtures can be calculated as follows.

$$py_i = \gamma_i x_i p^\circ \quad (9)$$

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

3. Model Parameters

To obtain activity coefficients from Eq. (1), the interaction energies g_{ij} in Eq. (6) and the multi-component parameter D in Eq. (7) are required.

3.1 Interaction energies

According to the previous study (Kobuchi *et al.*, 2013b), the interaction energies due to attractive force g_{ij} between molecules i and j can be estimated by

$$g_{ij} = -(1 - \theta_{ij})(v_i v_j)^{0.5} \delta_i \delta_j, \quad \theta_{ii} = 0 \quad (10)$$

Further, the molar volume v_t and the solubility parameter δ_t of pure components at given temperature t can be calculated as follows.

$$v_t = v_{25} + \beta(t - 25), \quad \beta = (v_b - v_{25}) / (t_b - 25) \quad (11)$$

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

where the molar volume v_{25} and the solubility parameter δ_{25} at 25°C can be calculated from the group-contribution treatment of Fedors (1974) and the molar volume v_b at the normal boiling point t_b from the additive method of Le Bas (1915). To predict v_b , Tyn and Calus method (Tyn and Calus, 1975) seems to give better results. However, we need reliable critical molar volumes, which are sometimes difficult to be obtained especially for large molecules, to adopt the model of Tyn and Calus. Therefore, the model of Le Bas based on a simple additive treatment is used in the present study. The interaction parameter θ_{ij} in Eq. (10) can be evaluated from the following empirical equations which have been found, from trial and error examination, to be most effective to evaluate the contributions of pure-component properties to mixture properties.

$$\theta_{ij} = a_{ij} + b_{ij} t_{b,i} + c_{ij} t_{b,j} + d_{ij} \delta_{25,i}^2 + e_{ij} \delta_{25,j}^2 \quad (13)$$

$$\theta_{ji} = a_{ji} + b_{ji} t_{b,i} + c_{ji} t_{b,j} + d_{ji} \delta_{25,i}^2 + e_{ji} \delta_{25,j}^2 \quad (14)$$

where t_b may show the contribution from molecular structure and δ_{25}^2 from polarity, and the coefficients $a_{ij} - e_{ij}$ and $a_{ji} - e_{ji}$ should be evaluated from phase equilibrium experimental data such as VLE data. These values of coefficients have been usually evaluated by using constant-pressure VLE data at 101.3 kPa. The coefficients obtained can be adopted to other conditions such as 25°C because they are insensitive to temperature in calculation of VLE as ascertained in the previous studies (Kobuchi and Yonezawa, 2014a, 2014b).

3.2 Multi-component parameter

According to the previous paper (Kobuchi *et al.*, 2014b), the multi-component parameter D contained in Eq. (7) can be expressed by the following equation which is similar to Eqs. (13) and (14).

$$D = a_0 + \sum_i b_i t_{b,i} + \sum_i c_i \delta_{25,i}^2 \quad (15)$$

The coefficients in Eq. (15) required should be obtained from LLE data of multi-component systems considered.

4. LLE of Ternary Systems

In the present study, typical non-aqueous mixtures: alkane (1)+methanol (2)+aromatics (3) systems have been considered. These ternary systems are classified as type I ternary systems which contain one partially miscible binary system (Treybal, 1963). For the ternary systems mentioned above, (1)+(2) binary system is partially miscible and (1)+(3) and (2)+(3) binary systems are generally miscible near room temperature.

4.1 Alkane (1)+methanol (2) binary systems

Alkane (1)+methanol (2) binary systems, such as heptane+methanol, are partially miscible in general near room temperature and show UCST (upper critical solu-

Table 1 Coefficients of Eqs. (17) and (18) for alkane (1)+methanol (2) binary systems

Coefficient	a_{ij}	b_{ij}	c_{ij}	d_{ij}	e_{ij}	f_{ij}
12	0.5291	-2.647×10^{-3}	-3.741×10^{-4}	0.006475	-5.167×10^{-6}	-2.119×10^{-5}
21	-0.2054	1.850×10^{-3}	9.555×10^{-4}	-0.008868	6.039×10^{-6}	2.750×10^{-5}

Table 2 Correlation performances for LLE of alkane (1)+methanol (2) binary systems^a

Alkane (1)	t [°C]	N	$\phi_{12} \times 10^3$	$\phi_{21} \times 10^3$	θ_{12} (25°C)	θ_{21} (25°C)	Dev. [%] ^b
Heptane	25–50	6	1.071	-1.920	0.1821	0.1974	2.4
Octane	25–60	8	0.735	-1.502	0.1066	0.2566	2.5
2,2,4-Trimethylpentane	25–40	4	1.629	-2.645	0.1899	0.1736	0.6
Nonane	25–60	8	0.539	-1.265	0.0389	0.3061	1.7
Decane	25–60	8	0.285	-0.951	-0.0252	0.3553	0.9

^a The values of ϕ_{ij} and θ_{ij} (25°C) presented are obtained from Eqs. (17) and (18) with the coefficients given in Table 1.

^b Dev. [%] = $100 \left\{ \sum_{i=1}^2 \sum_{p=1}^2 \sum_{t=1}^N (x_{ipt}^{\text{calc}} - x_{ipt}^{\text{exp}})^2 / 4N \right\}^{0.5}$ where x_{ipt}^{calc} and x_{ipt}^{exp} are respectively the calculated and experimental mole fractions of component i in phase p at tie-line t , and N denotes the number of tie-line data.

tion temperature). Reliable mutual solubility data have been reported by Higashiuchi *et al.* (1987, 1990a) in the temperature range of 25–60°C. Adopting these mutual solubility data ($x_1^I - x_1^{II}$), the binary interaction parameters θ_{ij} have been evaluated. It has been shown that θ_{ij} depends on temperature. Therefore, θ_{ij} has been approximated by a linear function of temperature as follows.

$$\theta_{ij} = \phi_{ij}(t - 25) + \theta_{ij}(25^\circ\text{C}) \quad (16)$$

where the coefficient ϕ_{ij} and θ_{ij} (25°C) can be expressed by the following equations.

$$\theta_{ij}(25^\circ\text{C}) = a_{ij} + b_{ij}t_{b,1} + c_{ij}\delta_{25,1}^2 \quad (17)$$

$$\phi_{ij} = d_{ij} + e_{ij}t_{b,1} + f_{ij}\delta_{25,1}^2 \quad (18)$$

In alkane (1)+methanol (2) binary systems, the component (2) is fixed. Therefore, the terms of $t_{b,2}$ and $\delta_{25,2}^2$ can be included in the constant terms a_{ij} and d_{ij} . The values of coefficients of Eqs. (17) and (18) obtained by data regression are presented in **Table 1** and correlation performances in **Table 2**. The physical properties of pure-components needed t_b , v_{25} and δ_{25} can be cited from the previous paper (Kobuchi *et al.*, 2010). Further, a typical illustration is given in **Figure 1**. As presented in Table 2 and Figure 1, good correlation performances are obtained. It should be noted that LLE (mutual solubilities) can be correlated by using t_b , v_{25} and δ_{25} of pure-component properties alone through Eqs. (16)–(18).

4.2 Alkane (1)+aromatics (3) binary systems

Alkane (1)+aromatics (3) binary systems, such as heptane+benzene, are miscible at atmospheric pressure. The coefficients of Eqs. (13) and (14) for alkane (1)+aromatics (3) binary systems have been determined by data fitting using VLE data at atmospheric pressure from Eqs. (1) and (9). The coefficients obtained are listed in **Table 3** and its correlation performances are given in **Table 4**. Further, a

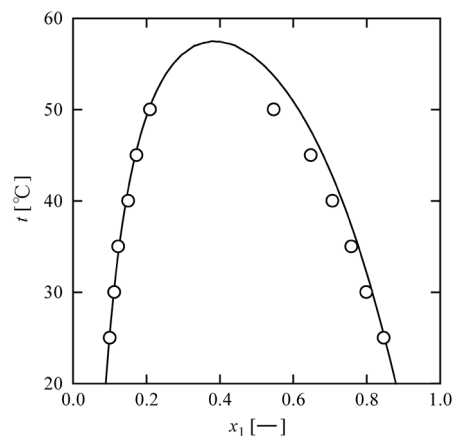


Fig. 1 Mutual solubilities of heptane (1)+methanol (2). Experimental, Higashiuchi *et al.* 1987: (O). Calculation: (—)

graphical comparison is shown in **Figure 2**. As shown in Table 4 and Figure 2, good correlation performances are obtained from the physical properties of pure-components t_b , v_{25} and δ_{25} and the constants of Antoine's equation which can be cited from the previous paper (Kobuchi *et al.*, 2010).

4.3 Methanol (2)+aromatics (3) binary systems

Methanol (2)+aromatics (3) binary systems, methanol+benzene for example, are miscible at atmospheric pressure. The coefficients of Eqs. (13) and (14) for alcohol (2)+aromatics (3) binary systems have been determined by using VLE data at atmospheric pressure and are presented in **Table 5**. In this case, alcohols contain methanol. The correlation performances obtained are shown in **Table 6** and a typical illustration is given in **Figure 3**. As presented in Table 5 and Figure 3, correlation performances seem to be suitable.

Table 3 Coefficients of Eqs. (13) and (14) for alkane (1)+aromatics (3) binary systems

Binary system (1)+(3)	a_{13}	b_{13}	c_{13}	d_{13}	e_{13}
	a_{31}	b_{31}	c_{31}	d_{31}	e_{31}
Alkane+aromatics	1.7800	-2.488×10^{-3}	1.167×10^{-3}	-1.058×10^{-3}	-3.911×10^{-3}
	-0.9053	2.496×10^{-3}	-1.857×10^{-3}	7.907×10^{-4}	1.887×10^{-3}

Table 4 Correlation performances for VLE of alkane (1)+aromatics (3) binary systems at 101.3 kPa

Binary system (1)+(3)	Ref.	N	Eqs. (13) and (14) ^a		Devs. ^b	
			θ_{13}	θ_{31}	Δy_1 [—]	Δt [°C]
Hexane+benzene	c	34	0.0852	-0.0400	0.0049	0.4
Hexane+toluene	d	16	0.1355	-0.1037	0.0070	0.2
Hexane+ <i>p</i> -xylene	e	13	0.1825	-0.1623	0.0284	1.7
Heptane+benzene	f	20	0.0018	0.0413	0.0049	0.2
Heptane+toluene	e	13	0.0521	-0.0225	0.0033	0.5
Heptane+ethylbenzene	c	29	0.1111	-0.0840	0.0041	0.1
Heptane+ <i>p</i> -xylene	e	24	0.0991	-0.0810	0.0158	0.1
Octane+benzene	g	20	-0.0757	0.1165	0.0054	0.8
Octane+toluene	e	26	-0.0254	0.0528	0.0030	0.2
Octane+ethylbenzene	h	20	0.0336	-0.0087	0.0034	0.1
Octane+ <i>p</i> -xylene	g	24	0.0216	-0.0058	0.0082	0.7
2,2,4-Trimethylpentane+benzene	g	24	0.0279	0.0223	0.0041	0.2
2,2,4-Trimethylpentane+toluene	i	11	0.0782	-0.0415	0.0018	0.6

^aThe binary interaction parameters θ_{13} and θ_{31} are obtained by Eqs. (13) and (14) with the coefficients given in Table 3.

^b Δy_1 [—] = $\frac{1}{N} \sum_{i=1}^N |y_{1,calc} - y_{1,exp}|$, Δt [°C] = $\frac{1}{N} \sum_{i=1}^N |t_{calc} - t_{exp}|$ where N = number of data points.

^cMyers (1955). ^dKlon-Palczewska *et al.* (1980). ^eMichishita *et al.* (1971). ^fMaczyński *et al.* (1997). ^gSieg (1950). ^hYang and Van Winkle (1955).

ⁱThornton and Garner (1951).

Table 5 Coefficients of Eqs. (13) and (14) for alcohol (2)+aromatics (3) binary systems

Binary system (2)+(3)	a_{23}	b_{23}	c_{23}	d_{23}	e_{23}
	a_{32}	b_{32}	c_{32}	d_{32}	e_{32}
Alcohol+aromatics	0.0397	-1.871×10^{-3}	1.693×10^{-3}	7.089×10^{-4}	-1.360×10^{-3}
	-0.2517	1.169×10^{-3}	-1.348×10^{-3}	-1.912×10^{-4}	1.602×10^{-3}

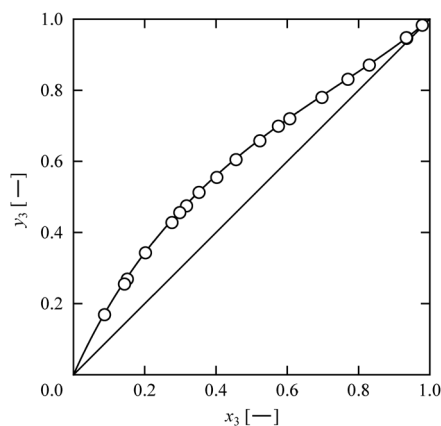


Fig. 2 VLE of heptane (1)+benzene (3) at 101.3 kPa. Experimental, Maczyński *et al.* 1997: (O). Calculation: (—)

4.4 Alkane (1)+methanol (2)+aromatics (3) ternary systems

LLE of alkane (1)+methanol (2)+aromatics (3) ternary systems reported by Higashiuchi *et al.* (1987, 1990a) have been examined. The interaction parameters of constituent binary systems can be estimated based on the procedures mentioned above. For partially miscible binary systems, Eqs. (16)–(18) can be adopted. Further, Eqs. (13) and (14) are used for miscible binary systems. By using the binary interaction parameters θ_{ij} and θ_{ji} estimated, the multi-component parameters D in Eq. (7) have been optimized to fit experimental LLE of ternary systems at 25°C. Then, the optimized values D_{opt} have been approximated by Eq. (15). In this case, methanol (2) is fixed and, therefore, the terms of $t_{b,2}$ and $\delta_{25,2}$ can be included in the coefficient a_0 . The coefficients thus obtained are listed in **Table 7**. Further, the correlation per-

Table 6 Correlation performances for VLE of alcohol (2)+aromatics (3) binary systems at 101.3 kPa

Binary system (2)+(3)	Ref.	N	Eqs. (13) and (14) ^a		Devs. ^b	
			θ_{23}	θ_{32}	Δy_2 [—]	Δt [°C]
Methanol+benzene	c	18	0.1377	0.1299	0.012	0.5
Ethanol+benzene	d	14	0.0165	0.1717	0.021	0.9
1-Propanol+benzene	e	50	−0.0720	0.2081	0.019	0.5
2-Propanol+benzene	f	29	−0.0611	0.1953	0.013	0.6
2-Butanol+benzene	g	16	−0.1263	0.2244	0.010	0.2
2-Methylpropan-1-ol+benzene	h	10	−0.1420	0.2342	0.014	0.6
<i>t</i> -Pentanol+benzene	i	15	−0.1655	0.2366	0.018	1.4
Methanol+toluene	j	14	0.1945	0.0827	0.012	0.8
2-Propanol+toluene	k	35	−0.0043	0.1481	0.010	0.6
1-Butanol+toluene	l	16	−0.0873	0.1941	0.011	0.3
2-Methylpropan-1-ol+toluene	m	18	−0.0852	0.1870	0.023	1.1
1-Pentanol+toluene	n	13	−0.1511	0.2248	0.012	0.4
1-Butanol+ <i>o</i> -xylene	o	30	−0.0250	0.1426	0.008	0.8
Methanol+ <i>m</i> -xylene	p	11	0.2477	0.0384	0.012	0.9
Methanol+ <i>p</i> -xylene	p	11	0.2465	0.0394	0.011	0.9
Ethanol+ <i>p</i> -xylene	q	11	0.1253	0.0812	0.009	0.6
1-Propanol+ <i>p</i> -xylene	q	23	0.0368	0.1176	0.009	0.7
2-Propanol+ <i>p</i> -xylene	k	36	0.0477	0.1048	0.014	0.7
1-Butanol+ <i>p</i> -xylene	r	15	−0.0353	0.1508	0.004	0.4
1-Pentanol+ <i>p</i> -xylene	r	17	−0.0991	0.1814	0.007	0.4
Ethanol+ethylbenzene	q	15	0.1267	0.0782	0.004	0.6
1-Propanol+ethylbenzene	s	13	0.0382	0.1146	0.010	0.6
2-Propanol+ethylbenzene	k	33	0.0491	0.1018	0.008	0.5
1-Pentanol+ethylbenzene	t	16	−0.0977	0.1784	0.008	0.6

^aThe binary interaction parameters θ_{23} and θ_{32} are obtained by Eqs. (13) and (14) with the coefficients given in Table 5.

^b $\Delta y [-] = \frac{1}{N} \sum |y_{2,calc} - y_{2,exp}|$, $\Delta t [^{\circ}C] = \frac{1}{N} \sum |t_{calc} - t_{exp}|$ where N = number of data points.

^cNagata (1969). ^dEllis (1952). ^eGmehling and Onken (1977). ^fHiaki *et al.* (1994). ^gGovindaswamy *et al.* (1977). ^hNataraj and Rao (1967). ⁱSabarathinam and Andiappan (1981). ^jLu (1957). ^kDe Alfonso *et al.* (1983). ^lSeetharamaswamy *et al.* (1969). ^mKireev *et al.* (1952). ⁿSadler *et al.* (1971). ^oJimenez Esteller *et al.* (1997). ^pBudantseva *et al.* (1975). ^qGalska-Krajewska (1966). ^rGalska-Krajewska (1967). ^sEllis and Froome (1954). ^tLisicki and Galska-Krajewska (1966).

Table 7 Coefficients of Eq. (15) for alkane (1)+methanol (2)+aromatics (3) ternary systems at 25°C

Ternary system (1)+(2)+(3)	a_0	b_1	b_3	c_1	c_3
Alkane+methanol+aromatics	−155.9963	3.737×10^{-3}	5.557×10^{-2}	1.334×10^{-5}	4.284×10^{-1}

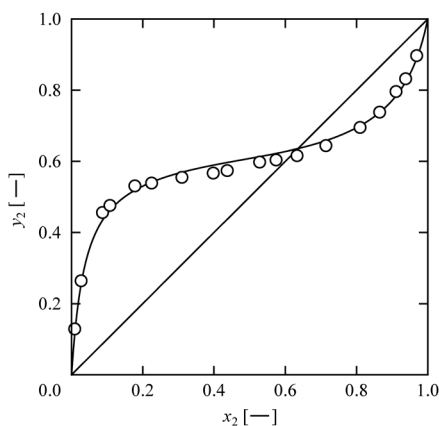


Fig. 3 VLE of methanol (2)+benzene (3) at 101.3 kPa. Experimental, Nagata, 1969: (O). Calculation: (—)

formances for LLE of ternary systems obtained by Eq. (15) with the coefficients shown in Table 7 are presented in **Table 8** with good results. The ternary systems adopted to determine the coefficients in Table 7 are Nos. 1–8 given in Table 8. A typical graphical presentation is shown in **Figure 4(a)**. For comparison, the LLE calculated by modified UNIFAC (Gmehling *et al.*, 1993; Lohmann *et al.*, 2001) are also presented in **Figure 4(b)**. It is shown that LLE calculated from the present approach seems to be better than the modified UNIFAC (Dortmund). For the ternary systems Nos. 9–18, the constituent binary systems which show VLE have not been included in Tables 4 and 6 because VLE data are not available in the literature. Namely, VLE data of those binary systems have not been used to determine the coefficients of Eqs. (13) and (14). Therefore, it is interesting to examine whether Eqs. (13) and (14) with the coefficients given in

Table 8 Correlation performances for LLE of alkane (1)+methanol (2)+aromatics (3) ternary systems at 25°C

Ternary system (1)+(2)+(3)	Binary interaction parameters estimated						N	Eq. (15) ^a	Dev. ^b [%]
	θ_{12}	θ_{21}	θ_{13}	θ_{31}	θ_{23}	θ_{32}		D	
1 Heptane+methanol+benzene	0.1821	0.1974	0.0018	0.0413	0.1377	0.1299	8	0.239	1.6
2 Heptane+methanol+toluene	0.1821	0.1974	0.0521	-0.0230	0.1945	0.0827	7	0.329	1.9
3 Heptane+methanol+p-xylene	0.1821	0.1974	0.0991	-0.0810	0.2465	0.0394	6	0.272	2.2
4 Octane+methanol+benzene	0.1066	0.2566	-0.0757	0.1165	0.1377	0.1299	6	0.341	3.8
5 Octane+methanol+toluene	0.1066	0.2566	-0.0254	0.0528	0.1945	0.0827	7	0.431	1.4
6 Octane+methanol+p-xylene	0.1066	0.2566	0.0216	-0.0060	0.2465	0.0394	7	0.374	3.0
7 2,2,4-Trimethylpentane+methanol+benzene	0.1899	0.1736	0.0279	0.0223	0.1377	0.1299	6	0.242	0.8
8 2,2,4-Trimethylpentane+methanol+toluene	0.1899	0.1736	0.0782	-0.0420	0.1945	0.0827	6	0.332	2.1
9 2,2,4-Trimethylpentane+methanol+p-xylene	0.1899	0.1736	0.1251	-0.1000	0.2465	0.0394	6	0.275	2.2
10 Nonane+methanol+benzene	0.0389	0.3061	-0.1415	0.1817	0.1377	0.1299	8	0.435	5.2
11 Nonane+methanol+toluene	0.0389	0.3061	-0.0912	0.1180	0.1945	0.0827	7	0.525	4.3
12 Nonane+methanol+p-xylene	0.0389	0.3061	-0.0433	0.0594	0.2465	0.0394	7	0.468	4.8
13 2-Methyloctane+methanol+benzene	0.0622	0.2834	-0.1130	0.1557	0.1377	0.1299	6	0.407	2.9
14 2-Methyloctane+methanol+toluene	0.0622	0.2834	-0.0627	0.0919	0.1945	0.0827	7	0.497	4.2
15 2-Methyloctane+methanol+p-xylene	0.0622	0.2834	-0.0158	0.0334	0.2465	0.0394	8	0.440	2.7
16 Decane+methanol+benzene	-0.0252	0.3553	-0.2062	0.2449	0.1377	0.1299	8	0.522	6.3
17 Decane+methanol+toluene	-0.0252	0.3553	-0.1559	0.1811	0.1945	0.0827	7	0.612	13.8
18 Decane+methanol+p-xylene	-0.0252	0.3553	-0.1089	0.1226	0.2465	0.0394	7	0.555	4.8

^a Multi-component parameters obtained by Eqs. (15) with the coefficients given in Table 7.

^b Dev. [%] = $100 \left\{ \sum_{i=1}^3 \sum_{p=1}^2 \sum_{t=1}^N (x_{ipt}^{\text{calc}} - x_{ipt}^{\text{exp}})^2 / 6N \right\}^{0.5}$ where x_{ipt}^{calc} and x_{ipt}^{exp} are respectively the calculated and experimental mole fractions of component i in phase p at tie-line t , and N denotes the number of tie-line data. In the present calculations, an algorithm (Higashiuchi, 1991, Higashiuchi *et al.*, 1983) with K -value ($K_i = x_i^{\text{II}}/x_i^{\text{I}}$) has been adopted and x_3^{II} is given from experimental data at 25°C under atmospheric pressure.

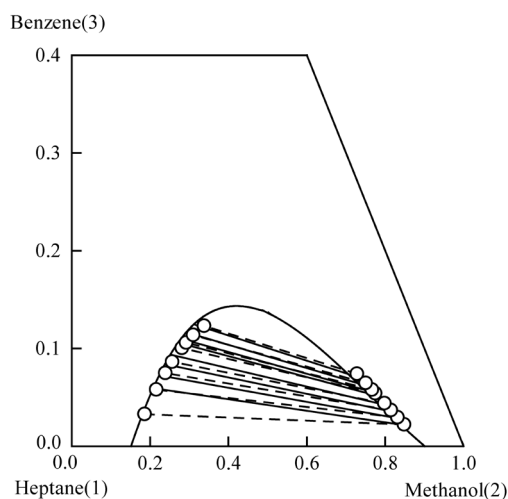


Fig. 4(a) LLE of heptane (1)+methanol (2)+benzene (3) at 25°C. Experimental, Higashiuchi *et al.* 1987: (O---O). Calculation: present (—)

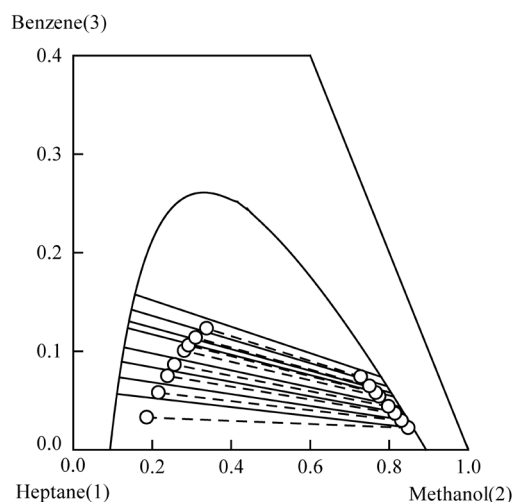


Fig. 4(b) LLE of heptane (1)+methanol (2)+benzene (3) at 25°C. Experimental, Higashiuchi *et al.* 1987: (O---O). Calculation: modified UNIFAC (—)

Tables 3 and 5 can be extensively applied to the LLE correlations of the systems Nos. 9–18. As presented in Table 8, it is noted that LLE of those ternary systems can be calculated with good performances from the pure-component properties t_b and δ_{25} through Eqs. (13) and (14). A typical illustration is presented in **Figure 5(a)**. It is noted that correlation performances of the present model seem to be better than those of the modified UNIFAC (Dortmund) as shown in **Figures 5(a) and 5(b)**.

Conclusion

A useful model based on a modified Wilson equation has been proposed for calculating LLE of ternary systems. The model contains the interaction parameters of constituent binary systems and the multi-component parameter which are required to obtain LLE by calculation. The interaction parameters and the multi-component parameter can be estimated from the pure-component

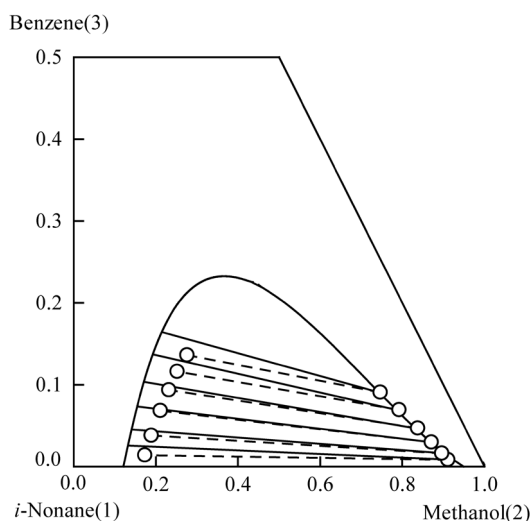


Fig. 5(a) LLE of 2-methyloctane (1)+methanol (2)+benzene (3) at 25°C. Experimental, Higashiuchi *et al.* 1990a: (O---O). Calculation: present (—)

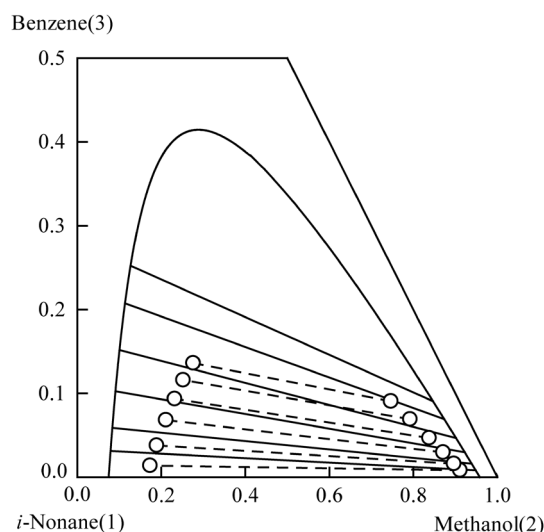


Fig. 5(b) LLE of 2-methyloctane (1)+methanol (2)+benzene (3) at 25°C. Experimental, Higashiuchi *et al.* 1990a: (O---O). Calculation: modified UNIFAC (—)

properties alone. The applicability of the present model has been ascertained for non-aqueous ternary systems: alkane+methanol+aromatics. It should be noted that LLE of alkane+methanol+aromatics ternary mixtures can be calculated from the normal boiling point, the solubility parameter and the molar volume which can be obtained from group-contribution methods. The correlation performances are acknowledged to be superior or comparable to UNIFAC (Dortmund) widely adopted.

The present model is termed herein as GC-MW (Group-Contribution method based Modified Wilson equation). Further applications of GC-MW to other ternary systems and quaternary systems still remain in the future work and the temperature dependence of multi-component parameter D should be examined and discussed.

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Nomenclature

D	= multi-component parameter	[—]
g	= interaction energy due to attractive force	[J·mol ⁻¹]
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	[°C]
v	= liquid molar volume	[cm ³ ·mol ⁻¹]
x	= mole fraction of liquid phase	[—]
y	= mole fraction of vapor phase	[—]
γ	= liquid-phase activity coefficient	[—]
δ	= solubility parameter	[(J·cm ⁻³) ^{0.5}]
θ	= interaction parameter between unlike molecules	[—]
Λ	= Wilson parameter	[—]

Subscripts

b	= normal boiling point
$calc$	= calculated value
exp	= experimental data
i, j	= components i and j
1, 2, 3	= component 1, 2, 3
25	= standard temperature (25°C)

Superscripts

I	= phase I (upper alkane-rich phase)
II	= phase II (lower methanol-rich phase)

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