

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

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Abstract: A useful model, previously proposed, has been applied to calculate liquid–liquid equilibria of alkane + methanol + ether ternary systems from pure-component properties alone. Its prediction performances are evaluated in comparison with UNIFAC widely adopted. In this study, the temperature dependency of multi-component parameter in the model has been examined and discussed.

Keywords: Liquid–Liquid Equilibrium, Correlation, Modified Wilson Equation, Ternary System

Introduction

In a previous paper ¹⁾, a useful model to calculate liquid-liquid equilibria (LLE) has been proposed. The model is termed as GC-MW (Group Contribution model based Modified Wilson equation) and its successful applicability has been acknowledged in calculation of LLE for alkane + methanol + aromatics ternary systems at 25°C. As a continuation, GC-MW has been applied to predict LLE of alkane + methanol+ ether ternary systems at 20~40°C. In this study, the temperature dependency of multi-component parameter in GC-MW has been examined and its calculation performances are compared with the modified UNIFAC (Dortmund) ^{2,3)}.

1. GC-Modified Wilson Equation

LLE can be calculated by the thermodynamic equilibrium condition: $x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II}$ where γ_i means the activity coefficients of component i , and x_i denotes the mole fractions of component i in both liquid phases I and II. Therefore, LLE can be calculated by using a suitable activity coefficient equation. In this study, GC-MW has been adopted to estimate activity coefficients from pure component properties alone based on group contribution treatments.

1.1 Activity coefficients

Activity coefficients can be briefly given from GC-MW as follows ¹⁾.

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

where A_j , B_{ij} and C_j are described by

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

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

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

Further, the interaction parameters are defined as

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

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

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

1.2 Binary interaction parameters

The binary interaction energies due to attractive force g_{ij} in Eq. (6) can be estimated by Kobuchi *et al.* ¹⁾.

$$g_{ij} = - (1 - \theta_{ij}) (v_i v_j)^{0.5} \delta_i \delta_j; \quad \theta_{ii} = 0 \quad (8)$$

where the liquid molar volume v and the solubility parameters δ of pure components at a given temperature t can be calculated as follows.

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

$$\delta_i = (v_{25} / v_i) \delta_{25} \quad (10)$$

To represent LLE (mutual solubility) of partially miscible binary systems such as alkane (1) + methanol (2), the binary interaction parameters θ_{ij} between unlike molecules have been found to be dependent on temperature and they are approximated by a linear function of temperature as follows.

$$\theta_{ij} = \phi_{ij}(t - 25) + \theta_{ij}(25^\circ\text{C}): \quad \text{LLE} \quad (11)$$

where the constant $\theta_{ij}(25^\circ\text{C})$ and the coefficient ϕ_{ij} can be empirically expressed by the following equations.

$$\theta_{ij} (25^\circ\text{C}) = a_{ij} + b_{ij} t_{b,1} + c_{ij} \delta_{25,1}^2 \quad (12)$$

$$\phi_{ij} = d_{ij} + e_{ij} t_{b,1} + f_{ij} \delta_{25,1}^2 \quad (13)$$

The coefficients $a_{ij} \sim f_{ij}$ should be determined by LLE data regression.

On the other hand, the interaction parameters θ_{ij} for miscible binary mixtures such as alkane(1) + ether(3) and methanol(2) + ether(3) can be evaluated from experimental vapor-liquid equilibria (VLE) at usually 101.3 kPa and are ascertained to be independent on temperature. Therefore, they can be empirically given by

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

2. Coefficients to estimate θ

To calculate LLE of alkane(1) + methanol(2) + ether(3), θ_{ij} (LLE) for alkane(1) + methanol(2) and θ_{ij} (VLE) for alkane(1) + ether(3) and methanol(2) + ether(3) are required. The values of coefficients $a_{ij} \sim f_{ij}$ in Eqs.(12) and (13) for LLE are shown in the previous paper¹⁾. Further, θ_{ij} (VLE) for the binary systems containing ether have been determined, in this study, by using VLE data at 101.3 kPa and they are presented in **Table 1**. The calculation performances for these binary systems from the coefficients given in Table 1 are shown in **Table 2** and **Table 3**. As shown in these tables, good calculation performances can be obtained.

3. LLE of alkane(1) + methanol(2) + ether(3)

To calculate LLE of alkane(1) + methanol(2) + ether(3), the binary parameters θ_{ij} (LLE) and θ_{ij} (VLE) are needed and they are determined as mentioned above. Further, the multi-component parameter D in Eq. (7) is required. It can be empirically expressed by

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

where the coefficients a_0 , b_i and c_i should be

determined by using experimental LLE data of the multi-component mixtures. Those coefficients for alkane(1) + methanol(2) + ether(3) have been evaluated by using LLE data at 25°C by Higashiuchi *et al.*^{4, 5)} and they are presented in **Table 4** and its correlation performances are given in **Table 5**. Further, correlation performances at other temperatures are also shown in the table. The correlation performances by UNIFAC^{2, 3)} are included in Table 5 for comparison. And, typical illustrations are shown in **Figure 1** and **Figure 2**. As shown in Table 4 and these figures, good correlation performances are obtained. It should be noted that correlated results in Table 4 for LLE at 20, 30 and 40°C are obtained by using Eq. (15) with the coefficients determined from LLE data at 25°C. Namely, the multi-component parameter D may be almost insensitive to temperature.

Conclusion

A useful model GC-MW based on a modified Wilson equation¹⁾ has been successfully applied to calculate LLE of alkane + methanol + ether ternary systems at 20~40°C. It is noted that the parameters needed in calculation can be estimated from the knowledges of molecular structures and the normal boiling points and solubility parameters obtained from the group-contribution treatments. The correlation performances of GC-MW have been acknowledged to be comparable or slightly better in comparison with the modified UNIFAC (Dortmund)^{2, 3)} widely used. Further application of GC-MW to other mixtures still remains in the future work.

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	[-]

Table 1 Coefficients of Eq. (14) for binary systems containing ether^a

Binary system (i) + (j)	a_{ij}	b_{ij}	c_{ij}	d_{ij}	e_{ij}
	a_{ji}	b_{ji}	c_{ji}	d_{ji}	e_{ji}
Alkane + ether	-0.2645	2.550×10^{-3}	-2.551×10^{-3}	2.815×10^{-3}	-1.714×10^{-3}
	0.4530	-2.549×10^{-3}	2.110×10^{-3}	-2.669×10^{-3}	8.878×10^{-4}
Alcohol ^b + ether	0.9922	-3.167×10^{-3}	2.813×10^{-3}	5.223×10^{-4}	2.664×10^{-3}
	0.6265	6.565×10^{-4}	-2.442×10^{-3}	-2.656×10^{-4}	-3.609×10^{-4}

^a VLE data at 101.3kPa have been adopted of which data sources are given in previous papers^{6, 7)}.

^b Alcohol contains methanol.

Table 2 Correlation performances for VLE of alkane (1) + ether (3) binary systems at 101.3 kPa^a

Binary system (1) + (3)	N	Eqs. (14) ^b		Dev. ^c	
		θ_{13}	θ_{31}	$\Delta y_1[-]$	$\Delta t [^\circ\text{C}]$
2-Methylbutane + diethyl ether	19	0.0329	0.0134	0.0056	0.30
Pentane + diethyl ether	12	-0.0125	0.0434	0.0083	0.29
2-Methylpenane + methyl <i>t</i> -butyl ether	23	-0.0733	0.0930	0.0015	0.22
3-Methylpenane + methyl <i>t</i> -butyl ether	21	-0.0810	0.0994	0.0042	0.26
2,3-Dimethylpenane + methyl <i>t</i> -butyl ether	20	-0.1486	0.1553	0.0044	0.23
Octane + methyl <i>t</i> -butyl ether	17	-0.2965	0.2606	0.0182	1.38
2,2,4-Trimethylpenane + methyl <i>t</i> -butyl ether ether	22	-0.1678	0.1727	0.0176	1.13
2-Methylpentane + ethyl <i>t</i> -butyl ether	20	0.0118	0.0100	0.0114	0.50
2-Methylpenane + <i>t</i> -amyl methyl ether	18	0.0463	-0.0245	0.0081	0.28
3-Methylpenane + <i>t</i> -amyl methyl ether	22	0.0386	-0.0181	0.0048	0.23
2,3-Dimethylpenane + <i>t</i> -amyl methyl ether	21	-0.0290	0.0378	0.0062	0.34
2,3-Dimethylpenane + diisopropyl ether	22	-0.0746	0.0834	0.0152	0.73
			Avg.	0.0088	0.49

^a VLE data at 101.3kPa have been adopted of which data sources are given in a previous paper ⁶⁾.

^b The interaction parameters θ_{13} and θ_{31} are obtained by Eqs. (14) with the coefficients given in Table 1.

^c VLE have been calculated from $py_i = x_i \gamma_i p_i^\circ$ and

$$\Delta y_1[-] = \frac{1}{N} \sum |y_{1,\text{calc}} - y_{1,\text{exp}}|, \Delta t [^\circ\text{C}] = \frac{1}{N} \sum |t_{\text{calc}} - t_{\text{exp}}| \quad \text{where } N = \text{number of data points.}$$

Table 3 Correlation performances for VLE of alcohol (2) + ether (3) binary systems at 101.3 kPa^a

Binary system (2) + (3)	N	Eqs. (14) ^b		Dev. ^c	
		θ_{23}	θ_{32}	$\Delta y_2[-]$	$\Delta t [^\circ\text{C}]$
Methanol + diethyl ether	14	-0.1008	0.2945	0.0174	0.73
Methanol + methyl <i>t</i> -butyl ether	28	-0.0963	0.2512	0.0085	0.34
Methanol + ethyl <i>t</i> -butyl ether	30	-0.0088	0.2031	0.0276	0.69
Methanol + <i>t</i> -amyl methyl ether	17	0.0293	0.1701	0.0019	0.20
Ethanol + methyl <i>t</i> -butyl ether	54	-0.2102	0.2960	0.0146	0.99
Ethanol + dipropyl ether	15	-0.0019	0.1961	0.0225	0.91
Ethanol + diisopropyl ether	14	-0.1349	0.2586	0.0145	0.80
Ethanol + ethyl <i>t</i> -butyl ether	28	-0.1226	0.2479	0.0114	0.92
<i>i</i> -Propanol + diisopropyl ether	14	-0.2339	0.2909	0.0103	1.00
2-Propanol + diisopropyl ether	29	-0.1992	0.2875	0.0244	0.80
1-Butanol + methyl <i>t</i> -butyl ether	19	-0.3991	0.3544	0.0188	2.49
1-Butanol + dibutyl ether	19	-0.0158	0.1270	0.0256	0.97
1-Butanol + <i>t</i> -amyl methyl ether	18	-0.2735	0.2733	0.0043	0.51
1-Pentanol + diisopropyl ether	20	-0.2741	0.2775	0.0187	1.30
			Avg.	0.0158	0.90

^a VLE data at 101.3 kPa have been adopted of which data sources are given in a previous papers ⁷⁾.

^b The interaction parameters θ_{23} and θ_{32} are obtained by Eqs. (14) with the coefficients given in Table 1.

^c VLE have been calculated from $py_i = x_i \gamma_i p_i^\circ$ and

$$\Delta y_2[-] = \frac{1}{N} \sum |y_{2,\text{calc}} - y_{2,\text{exp}}|, \Delta t [^\circ\text{C}] = \frac{1}{N} \sum |t_{\text{calc}} - t_{\text{exp}}| \quad \text{where } N = \text{number of data points.}$$

Table 4 Coefficients of Eq. (15) for alkane (1) + methanol (2) + ether (3) ternary systems at 25°C

Ternary system (1)+(2)+(3) ^a	a_0	b_1	b_3	c_1	c_3
Alkane + methanol + ether	-4.2823	0.008253	0.001905	0.0	0.01593

^a LLE data at 25°C have been cited from Higashiuchi *et al.*^{4,5)}.

Table 5 Correlation performances for LLE of alkane (1) + methanol (2) + ether (3) ternary systems^a

Ternary system (1)+(2)+(3)	t [°C]	Binary interaction parameters calculated ^b						N	Eq.(15) ^c		Dev.[%] ^d	
		θ_{12}	θ_{21}	θ_{13}	θ_{31}	θ_{23}	θ_{32}		D	GC-MW	UNIFAC ^e	
Heptane+methanol+diethyl ether	25	0.1821	0.1974	-0.2072	0.1934	-0.1008	0.2945	5	0.0849	3.3	5.0	
Octane+methanol+diethyl ether	25	0.1066	0.2566	-0.2925	0.2591	-0.1008	0.2945	6	0.3097	2.4	4.7	
Heptane+methanol+methyl <i>t</i> -butyl ether	25	0.1821	0.1974	-0.2112	0.1945	-0.0963	0.2512	5	-0.1979	2.0	9.0	
Octane+methanol+ methyl <i>t</i> -butyl ether	25	0.1066	0.2566	-0.2965	0.2602	-0.0963	0.2512	6	0.0270	1.9	4.3	
Heptane+methanol+diisopropyl ether	25	0.1821	0.1974	-0.1373	0.1227	-0.0211	0.2138	6	0.0558	0.9	5.5	
Octane+methanol+diisopropyl ether	25	0.1066	0.2566	-0.2226	0.1883	-0.0211	0.2138	7	0.2806	4.4	4.6	
Heptane+methanol+methyl <i>t</i> -butyl ether	20	0.1768	0.2070	-0.2112	0.1945	-0.0963	0.2512	15	-0.1979	2.6	6.6	
Heptane+methanol+methyl <i>t</i> -butyl ether	30	0.1875	0.1878	-0.2112	0.1945	-0.0963	0.2512	8	-0.1979	2.6	6.3	
Heptane+methanol+methyl <i>t</i> -butyl ether	40	0.1982	0.1686	-0.2112	0.1945	-0.0963	0.2512	8	-0.1979	4.9	7.7	
Octane+methanol+methyl <i>t</i> -butyl ether	20	0.1029	0.2642	-0.2965	0.2602	-0.0963	0.2512	13	0.0270	4.0	7.8	
Octane+methanol+methyl <i>t</i> -butyl ether	30	0.1103	0.2491	-0.2965	0.2602	-0.0963	0.2512	7	0.0270	3.3	6.5	
Octane+methanol+methyl <i>t</i> -butyl ether	40	0.1176	0.2341	-0.2965	0.2602	-0.0963	0.2512	7	0.0270	4.4	9.2	
<i>i</i> -Octane+methanol+methyl <i>t</i> -butyl ether	20	0.1818	0.1868	-0.1678	0.1727	-0.0963	0.2512	14	-0.1911	4.6	14.9	
<i>i</i> -Octane+methanol+methyl <i>t</i> -butyl ether	30	0.1981	0.1604	-0.1678	0.1727	-0.0963	0.2512	8	-0.1911	5.6	17.9	

^a LLE data have been cited from Higashiuchi *et al.*^{4,5)} and Watanabe *et al.*⁸⁾.

^b Estimated from Eqs. (11) and (14) with the coefficients shown in the previous paper¹⁾ and Table 1.

^c Multi-component parameters obtained by Eq. (15) with the coefficients given in Table 4.

^d 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 with K -value ($K_i = x_i^{\text{II}} / x_i^{\text{I}}$) has been adopted and x_i^{II} is given from experimental data under atmospheric pressure.

^e UNIFAC parameters have been cited from Gmehling *et al.*²⁾ and Lohmann *et al.*³⁾.

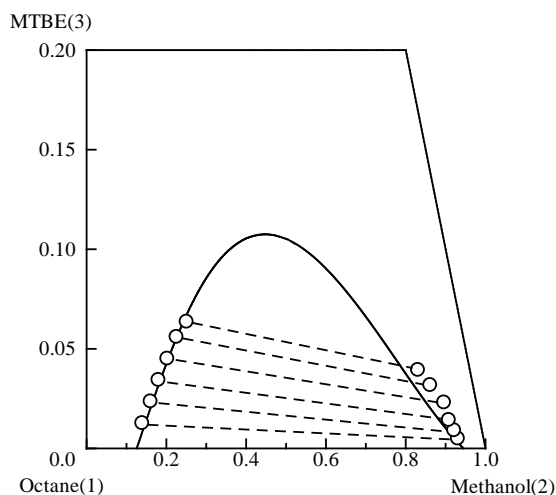


Figure 1 LLE of octane (1) + methanol (2) + MTBE (3) at 25°C; Exp.: (○); GC-MW: (—)

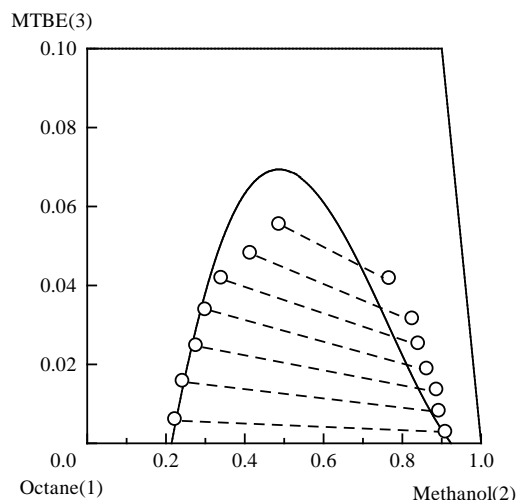


Figure 2 LLE of octane (1) + methanol (2) + MTBE (3) at 40°C; Exp.: (○); GC-MW: (—)

y	= mole fraction of vapor phase	[-]
γ	= liquid-phase activity coefficient	[-]
δ	= solubility parameter	$[(\text{J} \cdot \text{cm}^{-3})^{0.5}]$
θ	= interaction parameter between unlike molecules	[-]
A	= 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 and 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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