

Measurement and correlation of the isobaric vapor-liquid equilibrium for mixtures of alcohol+ketone systems at atmospheric pressure

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Abstract– Vapor-liquid equilibrium (VLE) for binary mixtures composed of ethanol+methyl isobutyl ketone, 1-butanol+methyl ethyl ketone, and 1-butanol+methyl propyl ketone systems was measured using a circulation type equilibrium apparatus at atmospheric pressure. The measured data and literature data for alcohol and ketone systems have been correlated by the UNIversal Quasi-Chemical (UNIQUAC) model with two binary interaction parameters and the non-random lattice fluid equation of state with hydrogen bonding equation of state (NLF-HB EoS) using a single binary interaction parameter. For the NLF-HB EoS calculations, the numbers of proton acceptor for ketones were adjusted between 0 and 1. The calculation results with the NLF-HB EoS are better than those with the UNIQUAC model.

Key words: Alcohol, Ketone, Vapor-liquid Equilibrium, Hydrogen Bonding

INTRODUCTION

The vapor-liquid equilibrium (VLE) for mixtures composed of an alcohol and a ketone shows strong non-ideality such as exhibiting an azeotrope or immiscibility due to differences in the polarity of the molecules. An alcohol contains both a proton donor and a proton acceptor, whereas a ketone only contains a proton acceptor. The local composition concept [1] has been used for the calculation for such systems, but the complex nature of hydrogen bonding makes it difficult to generalize the model without relying on experimental VLE data.

The non-random lattice fluid equation of state with hydrogen bonding equation of state (NLF-HB EoS) [2,3] was originally developed for the interpretation of hydrogen-bonded molecules using Veytsman statistics [4], and proved to be applicable for diverse types of molecules and various process conditions such as supercritical VLE [2], hydrate forming systems [5], water [6], polymers [2] and amino acids [7]. Previous researches on hydrogen bonding EoS [2,7] mainly focused on the formation of hydrogen bonding with the same type of molecules. For better understanding of hydrogen bonding phenomena, interaction between different types of molecules must be explored as well.

For the understanding of the complex hydrogen bonding between different types of molecules, an appropriate amount of phase equilibrium data is necessary. Although some experimental data have been published [8-13] for 1-alcohols and linear ketones, equilibrium data for 1-alcohols+branched ketones are still insufficient. In this work, binary VLE for ethanol+methyl isobutyl ketone, 1-butanol+methyl ethyl ketone, and 1-butanol+methyl propyl ketone were selected and phase equilibrium data were measured using a circulation type phase equilibrium measurement apparatus at atmospheric pressure. The measured data and literature data were correlated with

the UNIQUAC [1] excess Gibbs energy model and the NLF-HB EoS [2,3]. Steric hindrance effects of hydrogen bonding have been analyzed by adjusting the number of proton acceptor for ketones using NLF-HB EoS.

EXPERIMENTAL

1. Chemicals

The chemicals used in this study - ethanol, 1-butanol, methyl ethyl ketone (MEK), methyl propyl ketone (MPK), and methyl isobutyl ketone (MIBK) - were supplied by Sigma-Aldrich, Inc. and minimum mass fraction purities were 99.5%, 99.4%, 99.0%, 99.0%, and 99.5%, respectively. These materials were used without further purification. For the verification of purity of chemicals, the normal boiling points and the densities were measured and reported in Table 1 together with reliable literature values [14]. Densities were measured using an Anton Paar density meter (DMA 5000) with uncertainties of $\pm 0.00001 \text{ g/cm}^3$. The boiling points of the samples were measured using the VLE measurement apparatus described in next section. As shown in Table 1, the measured values are in good agreement within uncertainties of the measurements.

Table 1. Comparison of measured normal boiling point and density data with literature values at 298.15 K for the pure components used in this study

Chemical	Normal boiling point T_b /K		Density ρ /g cm^{-3}	
	Experimental	Literature [14]	Experimental	Literature [14]
Ethanol	351.6	351.4	0.7851	0.7849
1-Butanol	391.0	390.9	0.8058	0.8058
MEK	352.6	352.7	0.7997	0.7994
MPK	375.4	375.4	0.8016	0.8020
MIBK	389.1	389.6	0.7958	0.7962

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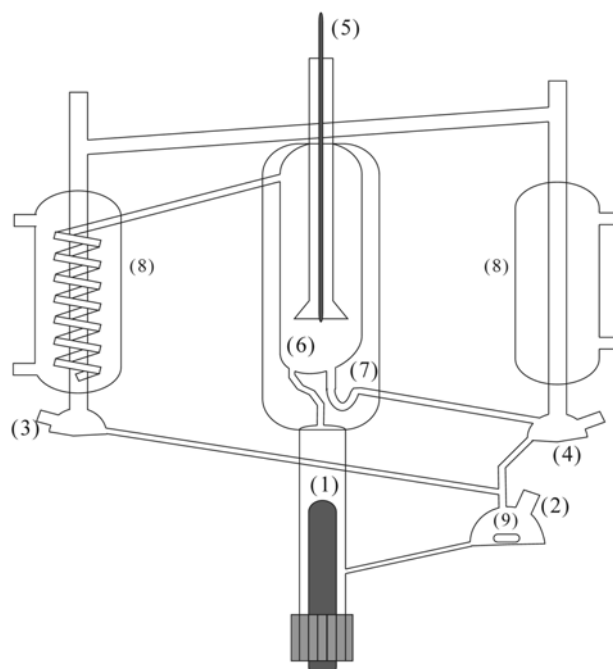


Fig. 1. Schematic diagram of low pressure vapor-liquid equilibrium apparatus used in this study.

- | | |
|-------------------------------|---------------------|
| 1. Heating bulb | 6. Equilibrium cell |
| 2. Feeding port | 7. Vacuum column |
| 3. Vapor phase sampling port | 8. Condenser |
| 4. Liquid phase sampling port | 9. Magnetic bar |
| 5. RTD sensor PT-100 | |

2. Apparatus and Procedure

A schematic diagram of the apparatus used in this experimental work is shown in Fig. 1. The equilibrium still was made of Pyrex and surrounded with vacuum column. A heating coil (1) is installed in lower part of the still and the amount of applied heat was controlled with a voltage regulator. The equilibrium temperature in the still was measured with platinum resistance temperature detector PT-100 (5) to an uncertainty of ± 0.1 K. Vaporized samples are collected and re-circulated to still using a condenser (8). The liquefied vapor (3) and liquid (4) samples were taken using a syringe and analyzed by gas chromatography (7890A series, Agilent Inc.). The gas chromatograph was equipped with a flame ionization detector (FID) and a HP-INNOWax column (length 30 m, inside diameter 0.32 mm, film thickness 0.5 μm). The temperature of injector and detector was kept at 453.2 K.

3. Procedure

Before the measurements, the apparatus was cleaned using acetone and evacuated at least 6 hours with a vacuum pump. For each measurement, an appropriate feed composition was estimated and a liquid mixture was prepared according to the composition. Then the liquid mixture of about 110 ml composed of an alcohol and a ketone was fed to the feeding port (2) and was heated using the heating bulb (1). The evaporated vapor went up to the equilibrium cell (6) and vapor and liquid phases were separated. The separated vapor went through a condenser (8) and was collected in the vapor phase sampling port (3). Also, the separated liquid went through a U-tube (7) and was collected in the liquid phase sampling port (4). The U-

tube was used to prevent overflowing of the vapor phase to the liquid sampling port. The overflowed liquid in the sampling ports went back to feeding port (2) and re-circulated to the still. In the feeding port, a magnetic bar (9) was installed to help mixing. After the equilibrium period (2-3 hours), the vapor and liquid phases were taken with a syringe and the compositions were analyzed by gas chromatography. The samples were analyzed five times for each measurement and the mean value was taken as the final composition. The uncertainties of vapor and liquid mole fractions were estimated as ± 0.0020 and ± 0.0002 , respectively. The pressure in the experimental apparatus was maintained with a pressure regulator within 101.3 ± 0.1 kPa.

THEORY

In this study, UNIQUAC [1] excess Gibbs energy model and NLF-HB EoS [2,3] are used to correlate the experimental and literature data. The expression of activity coefficient for UNIQUAC model is:

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + \Phi_i \left(l_i - \frac{r_i}{r_j} \right) - q_i \ln (\theta_i + \theta_j \tau_{ji}) + \theta_j q_j \left(\frac{\tau_{ji}}{\theta_i + \theta_j \tau_{ji}} - \frac{\tau_{ji}}{\theta_j + \theta_i \tau_{ij}} \right) \quad (1)$$

where,

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad (2)$$

$$\Phi_i = \frac{x_i r_i}{x_i r_i + x_j r_j} \quad (3)$$

Table 2. Pure component parameters for UNIQUAC model

Components	r_i	q_i
Ethanol	2.1055	1.972
1-Propanol	2.7799	2.512
1-Butanol	3.4543	3.052
Acetone	2.5735	2.336
MEK	3.2479	2.876
MPK	3.9223	3.416
MIBK	4.5959	3.952

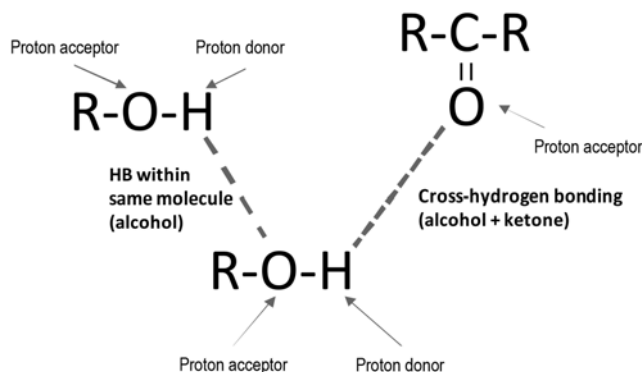


Fig. 2. Hydrogen bonds between alcohols and ketones.

Table 3. Pure component parameters for NLF-HB EoS

Component	r_a	r_b	r_c	ε_a	ε_b	ε_c	T range/K	
							T_1	T_2
Ethanol	5.334	3.317E-04	3.932E-03	102.8	1.565E-02	-4.016E-02	320	400
1-Propanol	6.876	9.474E-05	4.522E-03	104.2	4.451E-03	-8.879E-02	320	400
1-Butanol	8.472	2.701E-05	5.181E-03	105.9	6.639E-03	-9.349E-02	320	400
Acetone	6.953	2.838E-03	5.253E-03	124.7	-5.533E-02	-1.048E-01	320	400
MEK	8.442	2.767E-03	6.475E-03	112.0	-3.270E-02	-9.163E-02	350	392
MPK	9.992	1.627E-03	6.960E-03	116.4	-1.026E-02	-8.140E-02	375	392
MIBK	11.59	3.754E-04	7.109E-03	111.3	4.697E-03	-7.847E-02	350	390

$$\theta_i = \frac{x_i q_i}{x_i q_i + x_j q_j} \quad (4)$$

$$\ln \tau_{ij} = \frac{\Delta u_{ij}}{RT}, \quad \ln \tau_{ji} = \frac{\Delta u_{ji}}{RT} \quad (5)$$

Pure component parameters for UNIQUAC equations for alcohols and ketones used in this study are listed in Table 2. For the calculation of saturated vapor pressure, the coefficients of vapor pressure equation in the CRC Handbook of Thermophysical and Thermochemical Data [14] were used. The NLF EoS was extended for the hydrogen-bonded system [2,3] using Veytsman statistics [4]. The equation of state can be written as:

$$\frac{PV_H}{RT} = \frac{z}{2} \ln \left[1 + \left(\frac{q_M}{r_M} - 1 \right) \rho \right] - \ln(1 - \rho) + \rho \frac{l_M}{r_M} - \frac{z\beta}{2} \varepsilon_M \theta^2 - v_{HB} \rho \quad (6)$$

where,

$$r_M = \sum_{i=1}^c x_i r_i, \quad q_M = \sum_{i=1}^c x_i q_i \quad (7)$$

Table 4. Isobaric vapor-liquid equilibrium data for ethanol (1)+1-butanol (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
351.6	1.0000	1.0000		
351.8	0.9797	0.9948	1.0019	1.2947
352.3	0.9446	0.9864	1.0103	1.2111
354.3	0.8671	0.9687	0.9999	1.0569
356.4	0.7918	0.9452	0.9857	1.0707
360.8	0.6256	0.8817	0.9866	1.0514
361.2	0.6188	0.8734	0.9736	1.0854
361.8	0.6003	0.8611	0.9679	1.1056
362.0	0.5644	0.8565	1.0165	1.0387
363.6	0.5314	0.8348	0.9927	1.0359
367.0	0.4381	0.7760	0.9911	1.0108
369.6	0.3766	0.7097	0.9629	1.0571
373.2	0.2908	0.6119	0.9509	1.0699
376.2	0.2262	0.5426	0.9807	1.0241
377.2	0.2060	0.5017	0.9637	1.0447
383.2	0.1037	0.3265	1.0283	0.9923
385.8	0.0664	0.2244	1.0189	0.9956
389.1	0.0000	0.0000		

$$v_{HB} = \frac{\sum_k \sum_l N_{kl}^{HB}}{\sum_i N_i r_i} \quad (8)$$

$$\varepsilon_M = \frac{1}{\theta^2} \left[\sum \sum \theta_i \theta_j \varepsilon_{ij} + \left(\frac{\beta}{2} \right) \sum \sum \sum \theta_i \theta_j \theta_k \varepsilon_{ij} (\varepsilon_{ij} + 3 \varepsilon_{kl} - 2 \varepsilon_{ik} - 2 \varepsilon_{jk}) \right] \quad (9)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii} \varepsilon_{jj}} (1 - \lambda_{ij}) \quad (10)$$

Detailed derivations of the chemical potential and other properties are described in the previous publications [2,3,7].

For binary systems composed of alcohols and ketones, hydrogen bonds can be formed and these bonds make the VLE behavior much more complex than other systems. The alcohols contain both a proton donor and an acceptor, whereas ketones only contain a proton acceptor. Fig. 2 schematically shows the behavior of hydrogen bonding for a mixture composed of alcohols and ketones.

There are two types of hydrogen bond formation depending on the nature of molecular sites: (1) alcohol (-H atom)+alcohol (-O atom) and (2) alcohol (-H atom)+ketone (=O atom). The energies of hydrogen bonding for alcohols are reported [3], but the cross hydrogen bonding energies have not been reported yet. In this study, it is assumed that the ketone+alcohol hydrogen bonding energies

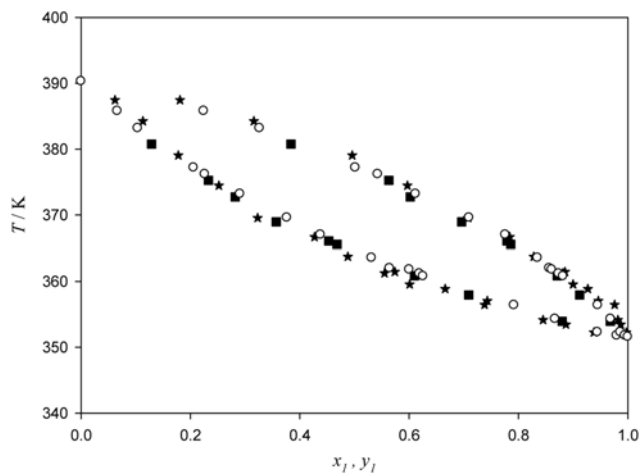


Fig. 3. Comparison of the VLE measurement results for ethanol (1)+1-butanol (2) system with the literature data at 101.3 kPa; ○, this work; ■ [15], ★ [16], literature data.

are the same as the energy for alcohol+alcohol hydrogen bond. The reported internal energy and entropy of hydrogen bonding for alcohols are as follows:

$$U_{HB}/\text{J}\cdot\text{mol}^{-1} = -25100 \quad (11)$$

$$S_{HB}/\text{J}\cdot\text{mol}^{-1}\text{K}^{-1} = -26.5 \quad (12)$$

Table 5. Isobaric vapor-liquid equilibrium data for ethanol (1)+MIBK at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
351.6	1.0000	1.0000		
352.0	0.9128	0.9486	1.0155	2.0212
353.6	0.7890	0.8866	1.0335	1.7350
355.9	0.6423	0.8235	1.0782	1.4603
357.0	0.5579	0.7912	1.1438	1.3420
359.8	0.4388	0.7360	1.2218	1.2125
364.0	0.2987	0.6547	1.3666	1.0944
365.5	0.2632	0.6183	1.3915	1.0961
369.0	0.2116	0.5464	1.3692	1.0952
373.6	0.1337	0.4335	1.4552	1.0620
380.7	0.0631	0.2516	1.4208	1.0412
389.1	0.0000	0.0000		

Table 6. Isobaric vapor-liquid equilibrium data for 1-butanol (1)+MEK at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
391.0	1.0000	1.0000		
388.0	0.9507	0.8639	1.0032	1.0346
385.1	0.9163	0.7624	1.0230	1.1428
378.8	0.8254	0.5558	1.0553	1.2030
375.2	0.7437	0.4252	1.0330	1.1637
372.0	0.6779	0.3362	1.0222	1.1667
369.1	0.6045	0.2849	1.0985	1.1115
366.1	0.4821	0.2169	1.1920	1.0117
363.0	0.4108	0.1611	1.1937	1.0445
360.2	0.2901	0.1151	1.3720	0.9951
356.0	0.1415	0.0569	1.6873	0.9968
352.6	0.0000	0.0000		

Table 7. Isobaric vapor-liquid equilibrium data for 1-butanol (1)+MPK (2) at 101.3 kPa

T/K	x_1	y_1	g_1	g_2
390.7	1.0000	1.0000		
389.9	0.9690	0.9358	0.9982	1.4093
387.2	0.8596	0.7532	1.0007	1.2785
386.8	0.8448	0.7377	1.0084	1.2387
385.8	0.7896	0.6686	1.0162	1.1844
384.3	0.7205	0.5910	1.0425	1.1448
383.4	0.6672	0.5324	1.0496	1.1247
382.5	0.6189	0.4833	1.0643	1.1121
381.1	0.5019	0.3779	1.0886	1.0652
379.4	0.3586	0.2723	1.1780	1.0148
378.3	0.3109	0.2389	1.2430	1.0178
377.7	0.2510	0.1940	1.2824	1.0083
376.2	0.1279	0.1029	1.4244	1.0072
375.4	0.0000	0.0000		

Although the assumption that the hydrogen bond energies are the same for alcohol+alcohol and alcohol+ketone seems reasonable as it is the interaction between the same kind of atoms, ketones normally have two bulky alkyl groups near the proton accepting oxygen atom, whereas alcohols have only one alkyl group near the oxygen atom. To account for such steric hindrances of hydrogen bond formation, the number of proton acceptors for ketones was adjusted between 0 and 1 depending on the size and configuration

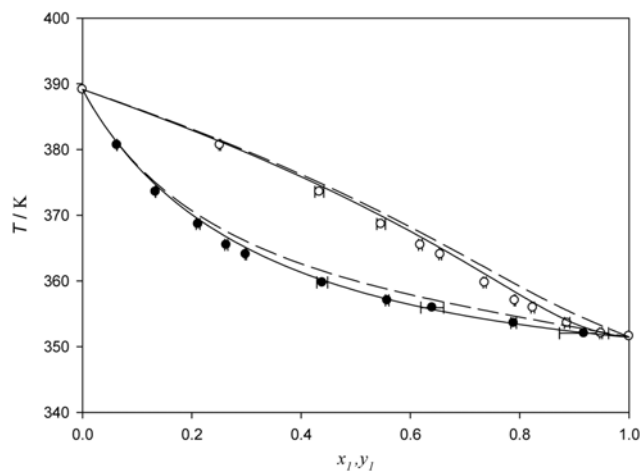


Fig. 4. Comparison of measured data with correlated values using UNIQUAC and NLF-HB EoS for ethanol (1)+MIBK (2): ●, experimental data of liquid phase at 101.3 kPa, this work; ○, experimental data of vapor phase at 101.3 kPa, this work; ---, correlated with UNIQUAC model; —, correlated with NLF-HB EoS (with the optimum value of proton acceptor).

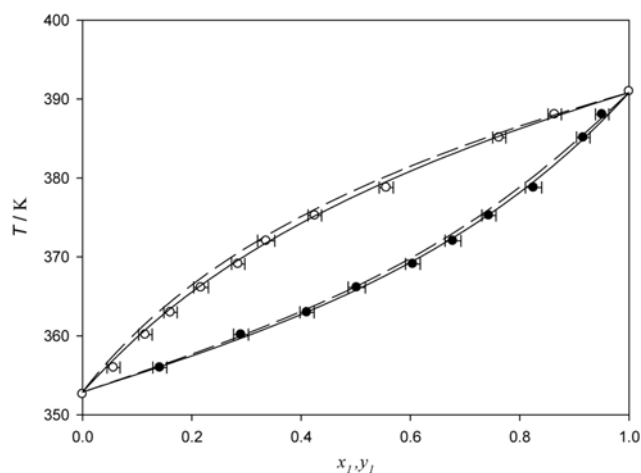


Fig. 5. Comparison of measured data with correlated values using UNIQUAC and NLF-HB EoS for 1-butanol (1)+MEK (2): ●, experimental data of liquid phase at 101.3 kPa, this work; ○, experimental data of vapor phase at 101.3 kPa, this work; ---, correlated with UNIQUAC model; —, correlated with NLF-HB EoS (with the optimum value of proton acceptor).

of bulky alkyl groups. 0 means no hydrogen bonding for ketones and 1 means the same surface fraction of oxygen atom in a ketone acts as proton acceptor as in an alcohol.

The size parameter r_i and interaction energy parameter ε_{ij} were calculated with the following equations:

$$\varepsilon_{ij}/k = \varepsilon_a + \varepsilon_b(T - T_0) + \varepsilon_c[\ln(T_0/T) + (T - T_0)] \quad (13)$$

$$r_i = r_a + r_b(T - T_0) + r_c[\ln(T_0/T) + (T - T_0)] \quad (14)$$

where, T_0 is the reference temperature (298.15 K). The coefficients for size and energy parameters are calculated by using the same procedure described in Kang et al. [2]. The values of param-

eters used in this study are summarized in Table 3.

The optimum binary parameter for UNIQUAC (Δu_{ij} , Δv_{ij}) and NLF-HB (λ_{ij}) was determined to minimize following objective function:

$$\begin{aligned} \text{OF} &= \sqrt{\Delta T^2 + \Delta y^2} \\ &= \frac{1}{N_{\text{data}}} \sqrt{\sum_i \left[\frac{T_i^{\text{exp}} - T_i^{\text{cd}}}{T_i^{\text{exp}}} \right]^2 \times 100 - \sum_i [y_i^{\text{exp}} - y_i^{\text{cd}}]^2 \times 100} \quad (15) \end{aligned}$$

RESULT AND DISCUSSION

The apparatus for the measurement of low-pressure VLE used in this study was tested by comparing the measured data with two

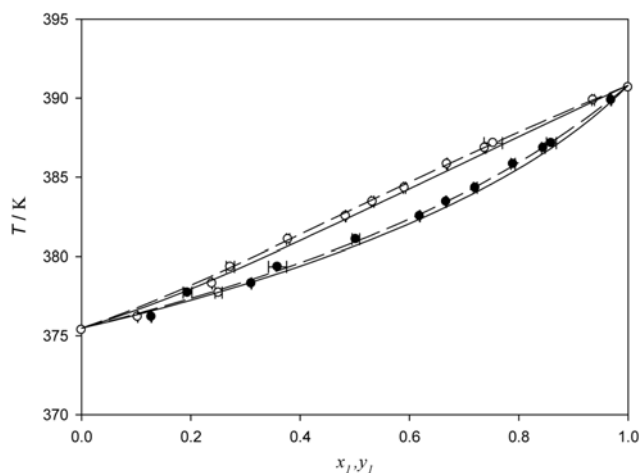


Fig. 6. Comparison of measured data with correlated values using UNIQUAC and NLF-HB EoS for 1-butanol (1)+MPK (2): ●, experimental data of liquid phase at 101.3 kPa, this work; ○, experimental data of vapor phase at 101.3 kPa, this work; ---, correlated with UNIQUAC model; —, correlated with NLF-HB EoS (with the optimum value of proton acceptor).

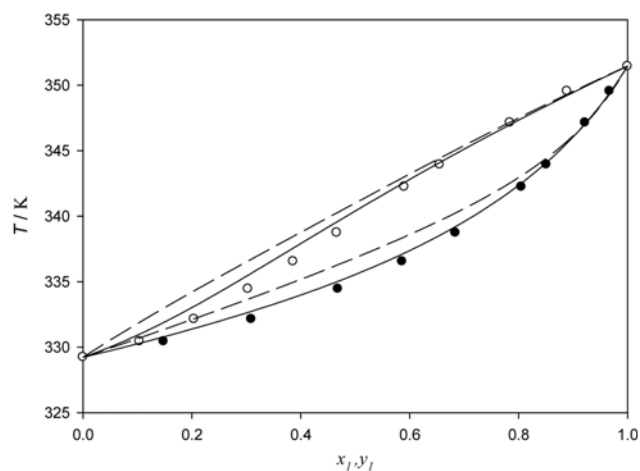


Fig. 7. Comparison of measured data with correlated values using UNIQUAC and NLF-HB EoS for ethanol (1)+acetone (2): ●, experimental data of liquid phase at 101.3 kPa [11]; ○, experimental data of vapor phase at 101.3 kPa [11]; ---, correlated with UNIQUAC model; —, correlated with NLF-HB EoS (with the optimum value of proton acceptor).

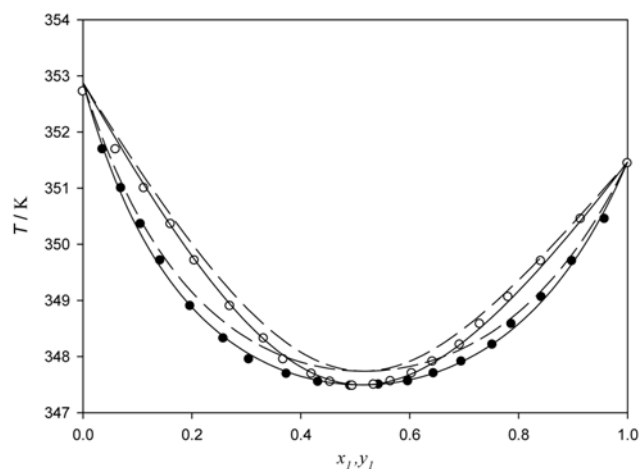


Fig. 8. Comparison of measured data with correlated values using UNIQUAC and NLF-HB EoS for ethanol (1)+MEK (2): ●, experimental data of liquid phase at 101.3 kPa [13]; ○, experimental data of vapor phase at 101.3 kPa [13]; ---, correlated with UNIQUAC model; —, correlated with NLF-HB EoS (with the optimum value of proton acceptor).

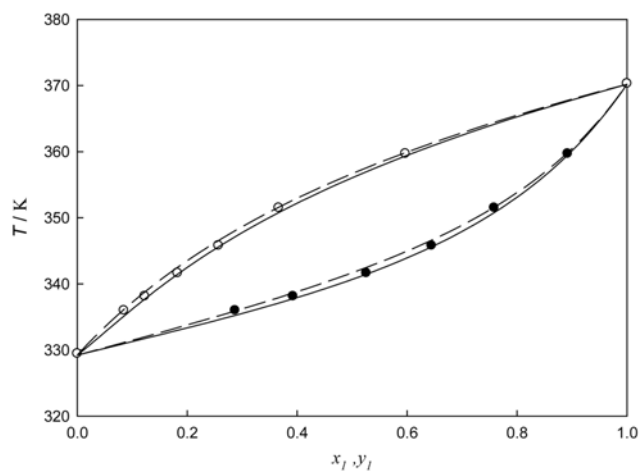


Fig. 9. Comparison of measured data with correlated values using UNIQUAC and NLF-HB EoS for 1-propanol (1)+acetone (2): ●, experimental data of liquid phase at 101.33 kPa [9]; ○, experimental data of vapor phase at 101.3 kPa [9]; ---, correlated with UNIQUAC model; —, correlated with NLF-HB EoS (with the optimum value of proton acceptor).

literature data [15,16] for ethanol (1)+1-butanol system at 101.3 kPa. The measured data are listed in Table 4. As shown in Fig. 3, the measured data were in good agreement with literature data within experimental uncertainties.

The measured experimental data for alcohol+ketone systems are listed in Tables 5-7. The experimental data were tested for thermodynamic consistency using the van Ness method [17]. The calculation results are compared in Figs. 4-12, and the numerical results are presented in Table 8. The UNIQUAC model has differences in temperature ranging from (0.037 to 0.383) % and mole fraction error ranging from (0.0016 to 0.0118). According to the van Ness Test,

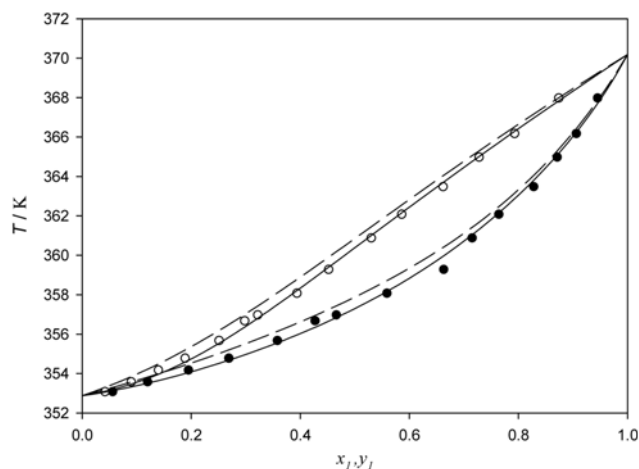


Fig. 10. Comparison of measured data with correlated values using UNIQUAC and NLF-HB EoS for 1-propanol (1)+MEK (2); ●, experimental data of liquid phase at 101.33 kPa [12]; ○, experimental data of vapor phase at 101.3 kPa [12]; ---, correlated with UNIQUAC model; —, correlated with NLF-HB EoS (with the optimum value of proton acceptor).

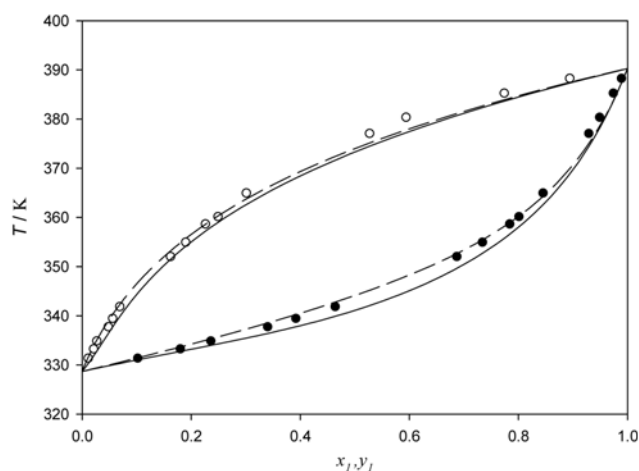


Fig. 11. Comparison of measured data with correlated values using UNIQUAC and NLF-HB EoS for 1-butanol (1)+acetone (2); ●, experimental data of liquid phase at 99.46 kPa [11]; ○, experimental data of vapor phase at 101.3 kPa [11]; ---, correlated with UNIQUAC model; —, correlated with NLF-HB EoS (with the optimum value of proton acceptor).

the appropriate range of vapor composition error should be less than 0.01. However, mixtures composed of alcohol and ketone cannot be reasonably represented by UNIQUAC equation, and vapor phase errors are slightly larger than the consistency test passing range.

Table 9 shows the NLF-HB calculation result depending on the number of proton acceptors for ketones. Optimum values normally lie between 0.33 and 0.68. As shown in Table 9, reasonable values are found considering the effect of steric hindrance of hydrogen-bonding formation. If larger alkyl groups are present near a ketone group (C=O group), smaller values of proton acceptor number were obtained to minimize VLE prediction error. The optimum calculation results using NLF-HB EoS are shown in Figs. 4-12 together with UNIQUAC calculation results. In most cases, NLF-HB EoS was found to give a better result than the UNIQUAC model. It should be also noted that near the optimum values of number of proton acceptors, the absolute values of binary interaction parameters are

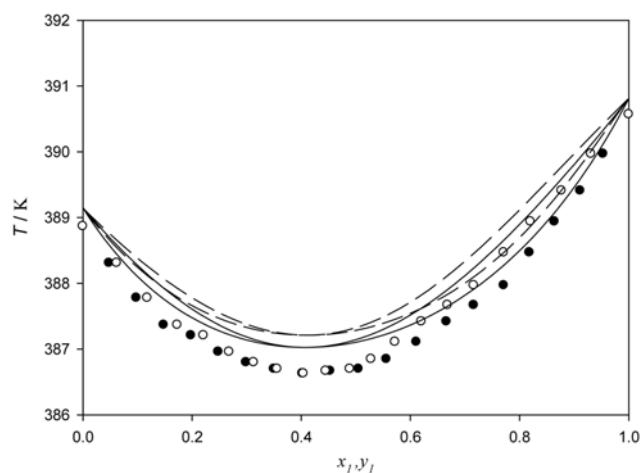


Fig. 12. Comparison of measured data with correlated values using UNIQUAC and NLF-HB EoS for 1-butanol (1)+MIBK (2); ●, experimental data of liquid phase at 101.3 kPa [10]; ○, experimental data of vapor phase at 101.3 kPa [10]; ---, correlated with UNIQUAC model; —, correlated with NLF-HB EoS (with the optimum value of proton acceptor).

Table 8. Calculation results using UNIQUAC model

System	100 δ (T)	100 δ (y)	Parameter	
			Δu_{ij}	Δu_{ji}
Ethanol+acetone [8]	0.252	0.736	27.00	210.82
Ethanol+MEK [14]	0.059	0.411	-355.45	998.72
Ethanol+MIBK	0.383	1.134	-55.45	371.07
1-Propanol+acetone [10]	0.101	0.097	-270.79	652.66
1-Propanol+MEK [13]	0.128	0.384	-303.76	752.26
1-Butanol+acetone [12]	0.223	0.408	-163.86	569.88
1-Butanol+MEK	0.147	1.181	-507.78	945.85
1-Butanol+MPK	0.037	0.736	39.04	190.58
1-Butanol+MIBK [11]	0.116	0.159	-511.60	1074.29

$$\delta(T) = \frac{1}{N_{data}} \sum_i \left| \frac{T_i^{exp} - T_i^{cal}}{T_i^{exp}} \right|, \quad \delta(y) = \frac{1}{N_{data}} \sum_i |y_i^{exp} - y_i^{cal}|$$

Table 9. Calculation results using NLF-HB EoS

System	N_a	100δ (T)	100δ (y)	λ_{ij}
Ethanol+acetone [8]	0	0.337	3.647	-0.05012
	0.58*	0.087	0.933	0.03637
	1	0.030	1.219	0.08426
Ethanol+MEK [14]	0	0.326	3.864	-0.05418
	0.50*	0.017	0.497	1.601E-03
	1	0.051	0.574	0.07644
Ethanol+MIBK	0	0.546	3.490	-0.05902
	0.32*	0.233	0.945	6.211E-03
	1	0.130	0.897	0.05926
1-Propanol+acetone [10]	0	0.437	2.173	-0.04223
	0.68*	0.104	0.098	0.01473
	1	0.245	0.458	0.08457
1-Propanol+MEK [13]	0	0.407	2.561	-0.03785
	0.42*	0.072	0.406	0.01098
	1	0.053	0.510	0.06637
1-Butanol+acetone [12]	0	0.723	2.052	-8.164E-03
	0.60*	0.409	0.760	0.06277
	1	0.626	1.109	0.1017
1-Butanol+MEK	0	0.338	1.777	-0.04340
	0.50*	0.103	1.101	-4.726E-05
	1	0.112	1.164	0.05316
1-Butanol+MPK	0	0.242	2.433	-0.04355
	0.45*	0.067	0.382	0.03652
	1	0.058	0.393	0.04270
1-Butanol+MIBK [11]	0	0.228	2.388	-0.03762
	0.40*	0.076	0.177	5.117E-03
	1	0.087	0.392	0.03926

N_a : Number of proton acceptor for NLF-HB EoS for ketones

* Denotes optimum value to minimize VLE errors

$$\delta(T) = \frac{1}{N_{data}} \sum_i \left| \frac{T_i^{exp} - T_i^{cal}}{T_i^{exp}} \right|, \quad \delta(y) = \frac{1}{N_{data}} \sum_i |y_i^{exp} - y_i^{cal}|$$

very small (less than 0.03) - this means that even without binary interaction parameters, the NLF-HB EoS can still calculate the phase equilibrium of such systems with reasonable accuracy. In such a situation, NLF-HB EoS only requires component type-specific hydrogen bonding energies and slight adjustment of proton acceptor numbers for the consideration of steric hindrance of hydrogen bonding. Such calculation is almost impossible using UNIQUAC with zero interaction parameters.

CONCLUSIONS

Isobaric vapor-liquid equilibrium data for binary ethanol+methyl isobutyl ketone, 1-butanol+methyl ethyl ketone, and 1-butanol+methyl propyl ketone systems were measured at the pressure of (101.3 ± 0.1) kPa. The measured experimental data and literature data for other alcohol+ketone mixtures were correlated using the UNIQUAC model and the NLF-HB EoS. Although UNIQUAC can correlate phase behavior reasonably well with two system-specific binary interaction parameters, NLF-HB EoS can calculate VLE of such

system with better accuracy with one system-specific binary interaction parameter plus hydrogen bonding parameters, which depends only on the nature of the chemical species.

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NOMENCLATURE

k	: boltzmann constant
l_i	: bulkiness factor
N	: number of molecules
N_{ij}	: number of i-j contacts
N_a	: number of proton acceptor for NLF-HB EoS
N_d	: number of proton donor for NLF-HB EoS
N_{data}	: number of experimental data
N_r	: total number of lattice sites
P	: pressure
q_i	: surface area parameter
q_M	: mole fraction average of q_i
R	: gas constant
r_i	: segment number
r_M	: mole fraction average of r_i
S	: entropy
T	: temperature
U	: internal energy
V	: volume
V_H	: unit lattice cell volume [cm^3]
x	: mole fraction of liquid phase
y	: mole fraction of vapor phase
z	: lattice coordination number (=10)

Greek Letters

Φ	: volume fraction
β	: = 1/kT
ε	: molecular interaction energy
μ	: chemical potential
ρ	: density
θ	: surface area fraction
γ	: activity coefficient

Superscripts

cal	: calculated values
exp	: experimental data
HB	: hydrogen bonding

Subscripts

M	: mixture value
i, j, k, l	: index for component, donor group or acceptor group

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