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Vapor-Liquid Equilibria Measurements and Modeling of the Isobutane+Butane+Ethanol System

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Abstract

The vapor-liquid equilibria of the isobutane+butane+ethanol system were measured at 313-403 K and the experimental pxy data were compared with the calculation results of the modified Redlich-Kwong (RK) equation of state (EOS) and predictive Soave-Redlich-Kwong (PSRK) EOS. Binary interaction parameters of the modified RK EOS for the butane+ethanol and isobutane+ethanol systems were determined from their binary vapor-liquid equilibrium data, while those for the butane+isobutane were set to zero. The average deviation between the modified RK EOS and experimental data was 0.05.

Introduction

To achieve efficient bioethanol production, it is important to develop energy-saving dehydration processes. Thus, there are many reports about energy-saving dehydration technology from a fermentative ethanol solution [1-5]. Horizoe et al. [6-8] developed an ethanol dehydration system that involved extractive distillation with a light hydrocarbon solvent. In Figure 1 our proposed system for bioethanol dehydration through extractive distillation is showed. It consists of a distillation column, an extractive distillation column, a solvent separation column, and a water-butane separation tank. During distillation, the bioethanol solution (5-10 wt%) is condensed to around 90-96 wt%. The condensed ethanol solution is then dehydrated using the extractive distillation column with butane as the solvent. Next, the dehydrated ethanol/butane mixture is flowed from the bottom of the column to a solvent separation column, where 99.9 wt% of the ethanol is recovered. Subsequently, butane is separated with water and recycled. The heat of vapor recompression is used as the heat source for the column reboiler for distillation and extractive distillation. To evaluate the energy consumption of this process, vapor-liquid equilibrium data and their accurate model are needed (Figure 1).

Vapor-liquid equilibrium data for the butane+ethanol system have been previously obtained by Deak et al. [9], Soo et al. [10], Kretschmer et al. [11], Holderbaum et al. [12], and Dahlhoff et al. [13]. Vapor-liquid equilibrium data for the isobutane+ethanol system have been obtained by Ouni et al. [14].

In an earlier publication, our group reported on the vapor-liquid equilibria of the butane+ethanol and isobutane+ethanol systems using process gas chromatography at 313-403 K, and determined the modified Redlich-Kwong (RK) equation of state (EOS) parameters to correlate the experimental data [15]. However, no data exists for the vapor-liquid equilibria of the mixed butane+ethanol system. To allow the use of mixed butane solvents, which are less expensive than isobutane and butane solvents, the vapor-liquid equilibria of the isobutane+butane+ethanol system were measured at 313-403 K. The measured data were compared with the calculation results of the modified RK EOS, of which parameters were determined in a previous work [16], and the predictive Soave-Redlich-Kwong (PSRK) EOS data.

Measurements

Materials

In Table 1, there is lists of purities and suppliers of the materials used in this study.

Apparatus and measuring procedure

The measurement apparatus and precise measurement procedures have been described in previous reports [15]. The vapor-liquid equilibrium cell has a viewing window and vapor and liquid phase are circulated with a magnetic pump respectively. The equilibrium system was immersed in an air-bath controlled to a ≤ 0.1°C using a PID. The temperature inside the equilibrium cell was measured using a platinum resistance probe (ChinoPt100 Class A, accuracy: 0.1 K). The pressure was measured using a digital gauge having 0-3 MPa range (PAA-33XEi, Keller AG, accuracy: 0.1% of the full scale).

The given amount of ethanol was provided for the equilibrium cell using a liquid pump and the liquid phase of mixed butane (Siphonic cylinder) was pressurized to the cell using a diaphragm pump. When equilibrium was achieved, the vapor and liquid phases were analyzed using the process gas chromatograph (Shimadzu GC-8A, TCD, Column Temp. 170°C, Porapak T). Each concentration data set was measured at least 3 times and the reproducibility was accurate to less than 0.001 mole fraction.

Modeling

The modified RK EOS proposed by Twu et al. [17,18] was selected for modeling the experimental pxy data, which can represent polar/non-polar systems. Tables 2 and 3 show the critical properties of each component, and the binary parameters for the modified RK EOS, which were determined in previous reports [15] respectively. The butane+isobutane parameters were set to zero. Connolly et al. reported the ideality of the butane+isobutane system by measuring the phase boundary pressure; the results showed that the deviation between the ideal and measured pressures is 0.2% [19]. The PSRK EOS was also used for comparing with the experimental data, which is a group

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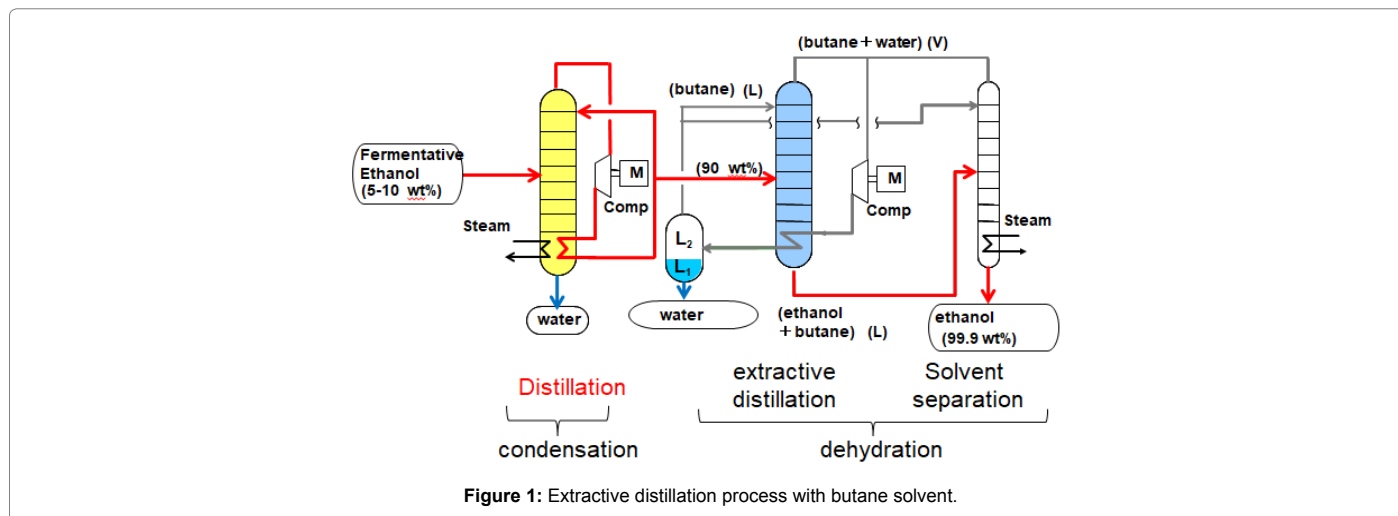
Figure 1: Extractive distillation process with butane solvent.

Material	Purity (wt%)	Supplier
Mixed butane (Isobutane/butane=30.3/69.7 (mole base))	98.5	Toyoko Kagaku Co., Ltd (Japan)
Ethanol	99.5	Wako Pure Chemical Industries, Ltd. (Japan)

Table 1: Properties and suppliers of the materials.

Component	Tc/K	Pc/MPa	ω
Butane	425.12	3.796	0.20016
Isobutane	408.14	3.648	0.18077
Ethanol	513.92	6.148	0.64525

Table 2: Pure component parameters of the modified RK EOS.

contribution EOS based on the Soave-Redlich-Kwong EOS with the UNIFAC method [16] for mixing rule (Tables 2 and 3).

The modified RK EOS is described by the following equations.

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)} \tag{1}$$

$$a(T) = a(T)a(T_c) \tag{2}$$

$$a(T_c) = 0.42748023354\, R^2\, T_c^2 / P_c \tag{3}$$

$$b = 0.086640349965 RT_c/P_c \tag{4}$$

$$\alpha = \alpha^{(0)} + \omega(\alpha^{(1)} - \alpha^{(0)}) \tag{5}$$

$$\alpha^{(0)} = T_r^{-0.201158} e^{0.141599(1-T_r^{2.29528})} \tag{6}$$

$$\alpha^{(1)} = T_r^{-0.660145} e^{0.500315(1-T_r^{2.63165})} \tag{7}$$

The mixing rule is described by the following equations:

$$a_m = \Sigma_i \Sigma_j x_i x_j a_{ij} \tag{8}$$

$$b_m = \Sigma_i x_i b_i \tag{9}$$

$$a_{ij} = (a_i a_j)^{1/2}\left[(1-K_{ij}) + \left(\frac{H_{ij}G_{ij}x_j^2}{x_i + G_{ij}x_j}\right)\right] \tag{10}$$

$$H_{ij} = k_{ij} - k_{ij} \tag{11}$$

$$G_{ij} = \exp(-\beta_{ij}H_{ij}) \tag{12}$$

$$K_{ij} = ka_{ij} + kb_{ij}/T \tag{13}$$

Pseudo-binary phase equilibrium (mixed butane+ethanol) calculations were carried out using the T-x flush calculation method.

Results and Discussion

Given figure compares the experimental data for the isobutane+butane binary system obtained by Connolly [19] with those calculated using the modified RK EOS. The calculation results showed good agreement with the experimental data; thus, the interaction parameters for isobutane+butane can be considered zero (Table 4; Figures 2 and 3).

The pxy data for the isobutane+butane+ethanol system are shown in Table 4 and plotted in Figure 3 with the calculation results of the modified RK EOS and PSRK EOS. The data in Figure 3 correspond to the mixed butane+ethanol pseudo-binary system. Thus, the modified RK EOS can represent the mixed butane+ethanol system. For the PSRK model, the composition of the liquid phase is slightly different, and these results are similar to those obtained in our previous reports for the butane+ethanol or isobutane+ethanol binary systems [15] (Table 5).

Table 5 shows the average deviation of the calculated and experimental data. The modified RK EOS shows better agreement with the experimental data in terms of pressure and ethanol vapor phase concentration, although agreement in the vapor phase concentrations of butane and isobutane is worse than that of PSRK. Gardeler et al. [20] reported the phase equilibrium data of alkane+alcohol systems and experimental data were compared with PSRK EOS. They concluded the reliability was not as good in the near critical point. In our experimental condition, the critical temperature of isobutane (408 K) and butane (425 K) are close to experimental condition (403 K), so the PSRK model may show systematic differences (Figure 4).

Figure 4 compares the phase equilibria data of the butane+ethanol, isobutane+ethanol, and mixed butane+ethanol systems. The data for the mixed butane+ethanol system were between those of the

System		Modified RK EOS parameters					
i	*j*	ka_{ij}	kb_{ij}	ka_{ji}	kb_{ji}	b_{ij}	b_{ji}
Butane	Ethanol	−0.1349	−8.490	0.9532	−228.2	6.491	−3.478
Isobutane	Ethanol	0.3818	−120.7	0.5512	−117.7	−81.30	−9.224
Isobutane	Butane	0	0	0	0	0	0

Table 3: Parameters of the modified RK EOS for the butane+ethanol and isobutane+ethanol systems.

T/K	p/MPa	x_1	x_2	x_3	y_1	y_2	y_3
313.2	0.203	0.027	0.074	0.9	0.295	0.627	0.078
313.2	0.309	0.057	0.15	0.793	0.315	0.635	0.05
313.2	0.39	0.115	0.292	0.592	0.328	0.635	0.037
313.3	0.408	0.149	0.378	0.473	0.33	0.636	0.034
333.2	0.296	0.021	0.062	0.917	0.26	0.596	0.145
333.2	0.493	0.054	0.144	0.802	0.289	0.612	0.099
333.3	0.635	0.111	0.284	0.606	0.307	0.631	0.062
333.3	0.669	0.143	0.365	0.492	0.311	0.634	0.056
353.2	0.43	0.019	0.056	0.925	0.251	0.614	0.134
353.2	0.737	0.051	0.136	0.813	0.285	0.626	0.089
353	0.967	0.104	0.272	0.624	0.288	0.622	0.09
353.2	1.035	0.139	0.358	0.504	0.302	0.64	0.059
373.2	0.621	0.016	0.05	0.934	0.183	0.473	0.345
373.1	1.047	0.046	0.126	0.827	0.244	0.56	0.196
373.2	1.401	0.098	0.258	0.644	0.265	0.597	0.137
373.2	1.513	0.13	0.342	0.528	0.271	0.606	0.124
403.2	1.085	0.015	0.045	0.94	0.135	0.354	0.512
403.2	1.671	0.042	0.115	0.843	0.197	0.47	0.333
403.2	2.264	0.09	0.239	0.671	0.227	0.533	0.24
403.3	2.466	0.119	0.314	0.567	0.234	0.551	0.215
ᵃ$u(x)=u(y)$=0.001, $u(T)$=0.1 K, $u(p)$=0.003 MPa							

Table 4: Vapor–liquid equilibrium data for the isobutane (1)+butane (2)+ethanol (3) systemᵃ.

	Modified RK EOS	PSRK
p/MPa	0.0281	0.0827
y_1	0.0528	0.0078
y_2	0.0724	0.0496
y_3	0.0196	0.0574
y_{total}	0.0483	0.0383

$$AAD = 1/n \sum \left\| C^{calc} - C^{exp} \right\|$$

Table 5: Absolute average deviation (AAD) between calculation and experimental data.

isobutane+ethanol and butane+ethanol systems. The butane+ethanol system has an azeotropic point, but the isobutane+ethanol system does not. For the mixed butane+ethanol system, the appearance of an azeotropic point depends on its ethanol free butane concentration. From the viewpoint of the bioethanol dehydration system, mixed butane has a lower azeotropic region than the pure butane solvent, so it leads to lower ethanol loss from the process. Thus, since mixed butane is also less expensive than butane or isobutene, it may be a suitable solvent for ethanol dehydration.

Conclusion

Vapor-liquid equilibria for the ternary system butane+isobutene+ethanol were obtained in the 313-403 K range. The modified RK EOS with our previously determined parameters corresponded well with experimental one, though in the PSRK EOS, liquid phase concentration showed a systematic deviation. These results may depend on the trend of PSRK model whose calculation results show the deviation in the near critical point.

Acknowledgements

List of Symbols

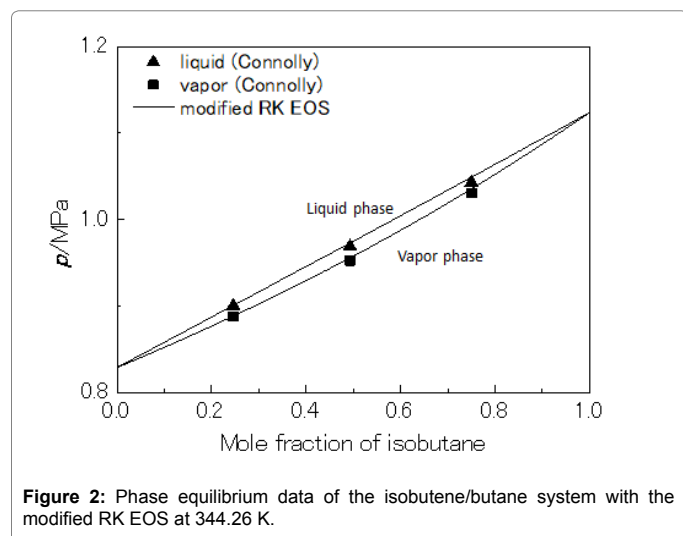| ka, kb	parameters of the modified RK EOS
K	equilibrium ratio (=y/x)
P	total pressure (MPa)
R	gas constant (m²kg/s²·Kmol)
T	temperature (K)
V	molar volume (m³/mol)
X	liquid-phase mole fraction
Y	vapor-phase mole fraction

Figure 2: Phase equilibrium data of the isobutene/butane system with the modified RK EOS at 344.26 K.
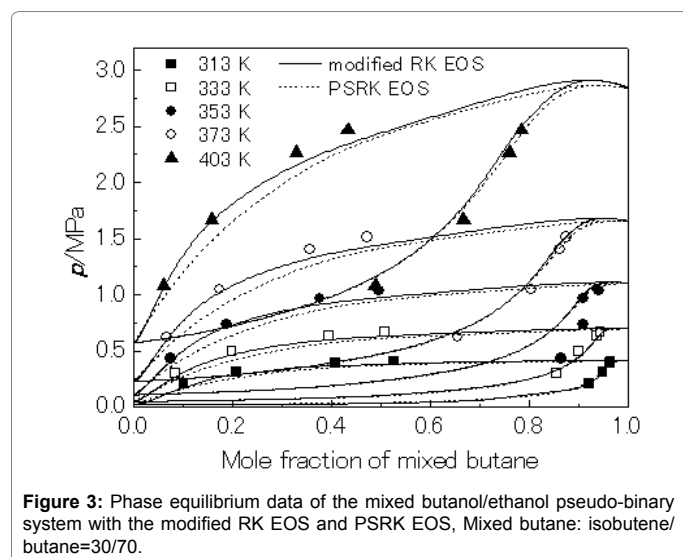

Figure 3: Phase equilibrium data of the mixed butanol/ethanol pseudo-binary system with the modified RK EOS and PSRK EOS, Mixed butane: isobutene/butane=30/70.
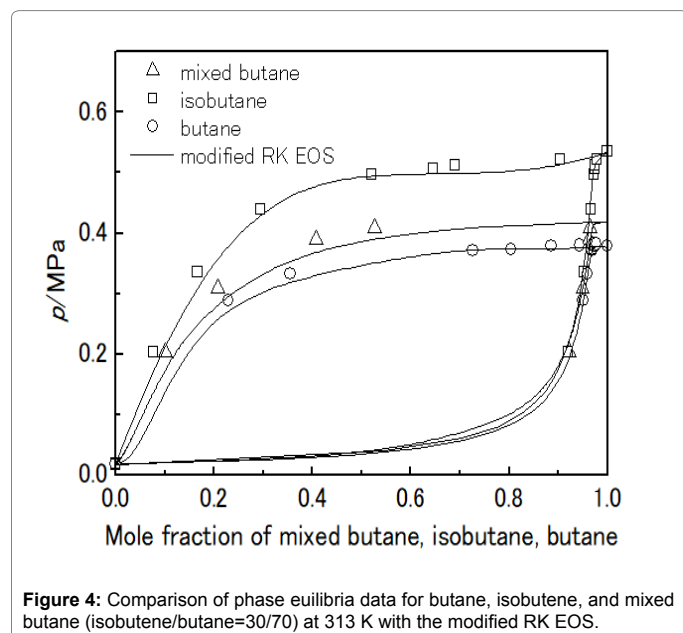

Figure 4: Comparison of phase euilibria data for butane, isobutene, and mixed butane (isobutene/butane=30/70) at 313 K with the modified RK EOS.

Greek letters

α	alpha function defined in eqn. [2]
β_{ij}	binary interaction parameter in eqn. [12]
ω	acentric factor

Subscripts

C	critical property
i, j	property of component i, j
ij	property of the i-j interaction
m	mixture property
r	reduced property

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