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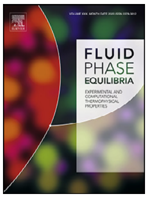

Isobaric vapor-liquid equilibria for two binary systems (2-methyl-1-pentanol + 2,3-butanediol and 3-methyl-1-butanol + 2,3-butanediol) at (40, 60, 80, and 101) kPa

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ABSTRACT

Isobaric vapor-liquid equilibrium data were measured for the two binary systems of 2-methyl-1-pentanol + 2,3-butanediol and 3-methyl-1-butanol + 2,3-butanediol using a modified Othmer still VLE apparatus at 40, 60, 80 and 101 kPa. The standard uncertainty of the pressure and temperature was 0.13 kPa and 0.1 K, respectively. To assess the thermodynamic consistency of the experimental data, Herington area test method and Van Ness-Byer-Gibbs test method have been used. The experimental data were also correlated with the two activity coefficient models, NRTL and UNIQUAC, and the binary parameters for the models have been calculated. For the quantitative analysis of the experimental data, we used the root-mean-square deviation (RMSD) and the average absolute deviation of the temperature (AAD-T) and the vapor-phase composition (AAD-y). Overall AAD-y were 4×10^{-4} (NRTL) and 5×10^{-4} (UNIQUAC) for 2-methyl-1-pentanol + 2,3-butanediol system, and 5×10^{-4} (NRTL) and 6×10^{-4} (UNIQUAC) for 3-methyl-1-butanol + 2,3-butanediol system, respectively. This test results support the validity of the models used for the two binary systems studied in this work.

1. Introduction

As the capacity of recoverable crude oil reserves shrinks globally and the need for non-petroleum based chemical feedstock increases to reduce carbon footprints, worldwide research efforts become intense to develop new sustainable technologies for the production of hydrocarbon chemicals. One of the developmental efforts that attract recent attention is the production of high value-added hydrocarbon compounds through bioconversion. 2,3-butanediol (2,3-BDO) is one of the such target substances. 2,3-BDO is a well-known raw material that has wide industrial applications in various fields including foods, chemicals, pharmaceuticals, and aviation fuels [1,2]. Although 2,3-BDO has various applications, a large scale manufacturing of 2,3-BDO production is difficult because the concentration of 2,3-BDO as a product in the fermentation broth is low and the costs for separation and purification are high, making the process economy unfavorable. Therefore, various separation methods for 2,3-BDO have been studied. They are, for example, simulated reverse osmosis [3], pervaporation [4], reactive extraction [5], salting-out extraction [6,7], sugaring-out extraction [8,9], and classical extraction [10,11] and distillation methods [12]. Among these, some technologies such as simulated moving bed, sugaring-out, and pervaporation have been shown to be promising, however; none of these have been developed for large scale separation and purification processes to date. From an economic perspective, the conventional solvent extraction and distillation processes are still considered to be competitive because industrial applications of 2,3-BDO production can be most effectively implemented by these well-established separation technologies [13].

In the past several years, our research group has been studying the solvent extraction processes, especially aimed at finding suitable solvents to extract 2,3-BDO from a dilute aqueous solution [14–16]. In our previous study [16], 2-methyl-1-pentanol and 3-methyl-1-butanol were investigated as potential solvents for extracting 2,3-BDO from an aqueous solution. Once a solvent is chosen and applied to an extraction process, it must be removed from 2,3-BDO by a separation process such as distillation. To design an effective distillation process, it is crucial to have available accurate vapor-liquid equilibrium (VLE) data for a 2,3-BDO and the solvent mixture.

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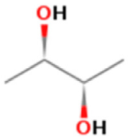
Table 1
Suppliers and mass fraction of materials.

Component	Source	CAS No.	Mass Fraction Purity	Analysis	T_b(101kPa)/K	
					Exp.	Lit.
2-methyl-1-penanol	Sigma-Aldrich (U.S.A)	105-30-6	> 0.980	GC[a]	421.5	421.2
3-methyl-1-butanol	Sejinci Co. (Korea)	123-51-3	> 0.990	GC[a]	403.8	403.7
levo[b]-2,3-butanediol	Sejinci Co. (Korea)	24347-58-8	> 0.980	GC[a]	453.7	454.2

[a] Gas chromatograph.



[b] Structure of levo-2,-3-butanediol used in this study levo-2,3-Butanediol, [R-(R*,R*)]- levo-2,3-butanediol, [R-R*,R*)]-

For this purpose, isobaric VLE data for the two representative binary systems, 2-methyl-1-pentanol + 2,3-BDO and 3-methyl-1-butanol + 2,3-BDO, have been measured in the present study at constant pressure of 40, 60, 80 and 101 kPa. We have also assessed the experimental data using two activity coefficient models, NRTL and UNIQUAC, using Aspen Plus® software and the relevant binary parameters obtained are presented.

2. Materials and methods

2.1. Materials

2-methyl-1-pentanol (> 98 wt.%, Sigma Aldrich), 3-methyl-1-butanol (> 99 wt.%, Sejinci Co. (Korea)) and 2,3-butanediol (> 98 wt.%, Sejinci Co. (Korea)) were used for this work as supplied without additional purification. Gas chromatograph (GC) (Young-Lin YL6100 GC, Korea) was used to measure the purity of each solvent. Table 1 shows the basic data of the chemicals used in our experimental work.

2.2. Experimental apparatus and procedure

The experimental apparatus is a 'modified Othmer still' illustrated in Fig. 1. It consists of three main parts: the boiling flask, the condenser, and the pressure generator. A sample solution was first loaded into a 500 mL three neck boiling flask. To maintain the temperature of the sample solution, the flask was placed in a heating mantle and the flask was wrapped with a heating tape. The temperature was measured using OMEGA DP41-TC-MDSS monogram temperature indicator attached with K-type thermocouple. The accuracy of the temperature measurement was 0.1 K. Then, a vacuum pump was used to adjust the pressure to a desired level and a U-shaped differential manometer was used to measure the pressure with an accuracy of within 0.13 kPa. A buffer tank and needle valve were also used for the fine adjustment of the pressure. The condenser temperature was maintained constant by circulating the cooling fluid with RW3025 refrigerated circulator (Lab Co.). Finally, the sampling ports were provided to take both liquid and vapor phase samples that were analyzed using a gas chromatograph equipped with a thermal conductivity detector (TCD) and a Porapak Q column. For the gas chromatographic analysis, GC-quality high-purity helium (99.9999 %) was used as a carrier gas at a constant flow rate of 20 mL/min. For 2-methyl-1-pentanol + 2,3-butanediol system, the oven temperature was initially set at 373.15 K and raised by 20 K/min to reach 413.15 K and held for 2 min. Then, the temperature was raised to 503.15 K and held for another 2 min. For 3-methyl-1-butanol + 2,3-butanediol system, the oven temperature was started at 373.15 K and raised by 10 K/min to reach 383.15 K and held for 2 min. Then, the temperature was raised to 508.15 K. The injector and detector temperature were fixed at 523.15 K for both systems. The injection volume of each sample was 1.0 μl. Every sample was analyzed at least three times and the averaged composition was obtained.

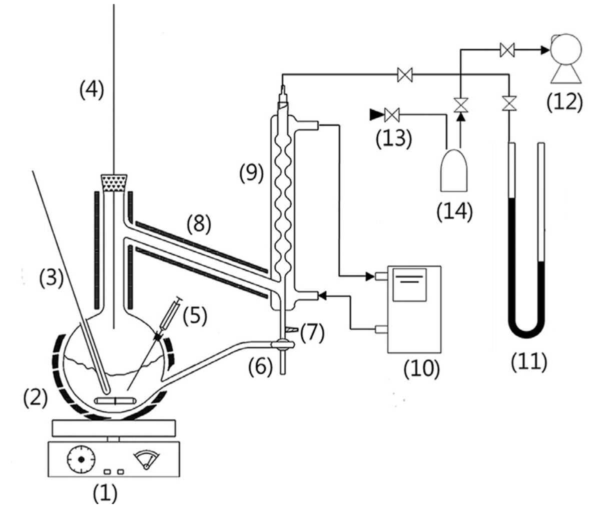


Fig. 1. Schematic diagram of the experimental vapor-liquid equilibrium apparatus: (1) Magnetic stirrer, (2) heating mantle, (3) thermocouple for liquid phase, (4) thermocouple for vapor phase, (5) sampling port for liquid phase, (6) sampling port for condensed vapor phase, (7) sampling port for vapor phase (for vacuum condition), (8) heating tape, (9) condenser, (10) coolant circulator, (11) manometer, (12) vacuum pump, (13) needle valve, (14) buffer flask.

To calculate the standard uncertainty (u_i), the following equations were used [17].

$$x_i = \frac{1}{n}\sum_{k=1}^{n} X_{i,\ k} \tag{1}$$

$$u_i = \left[\frac{1}{n(n-1)}\sum_{k=1}^{n}\left(X_{i,\ k} - x_i\right)^2\right]^{1/2} \tag{2}$$

where n is the number of experiments and $X_{i,\ k}$ is the value obtained under the same conditions of measurement.

To validate our new VLE experimental apparatus, we measured VLE data of water-methanol system at atmospheric pressure, and compared them with the well-known literature data of Dechema's data collection [18] in Fig. 2. As shown in this figure, our experimental data correspond well with the literature data.

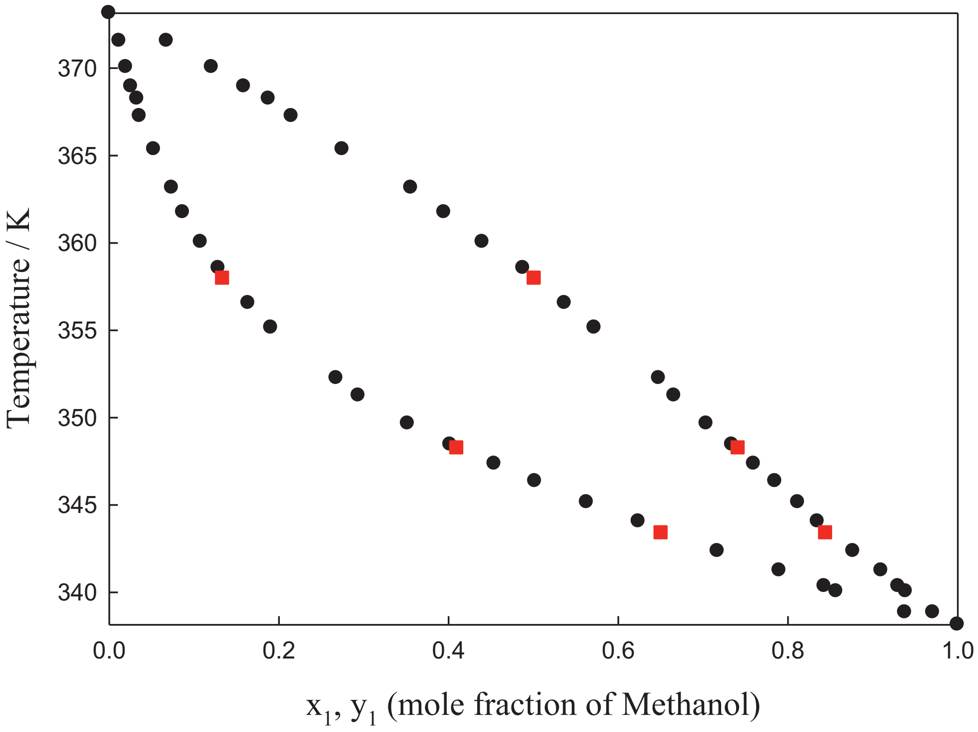


Fig. 2. T-x-y diagram of the water (1) + methanol (2) system at atmospheric pressure for comparison of our experimental data with literature data: 🟥, this study; ●, Dechema data [18].

3. Results and discussion

3.1. Experimental data

The experimental isobaric VLE data for the two binary systems at four pressure conditions (40, 60, 80 and 101 kPa) are shown in Tables 2 and 3 for (2-methyl-1-pentanol + 2,3-butanediol, 3-methyl-1-butanol + 2,3-butanediol) and (2-methyl-1-pentanol + 2,3-butanediol, 3-methyl-1-butanol + 2,3-butanediol), respectively. As mentioned in the previous section, the standard uncertainty was obtained by following the procedure in the NIST manual [17]. Since the pressure of all the systems were less than 1 atm, the vapor phase of the systems were assumed to follow the ideal gas law. Then, the activity coefficients γ_I can be calculated as

$$\gamma_i = \frac{y_i p}{x_i p_i^s} \tag{3}$$

where x_I, y_I, p, and p_i^s denote the equilibrium mole fractions of the liquid and vapor phases, the pressure of the system, and the saturated vapor pressure of pure component *I*, respectively. The vapor pressure of each component was calculated using Antoine equation with Aspen Plus® [19]. The calculated values of the activity coefficients are also listed in Tables 2 and 3. Figs. 3 and 4 show the Txy diagrams for the two binary systems. These figures also compare the experimental data with the calculated values from NRTL and UNIQUAC models. It is seen in Figs. 3 and 4 that all cases show positive deviations from Raoult's law and no azeotropic behaviors are observed. Comparing with 2-methyl-1-pentanol + 2,3-butanediol system, 3-methyl-1-butanol + 2,3-butanediol system shows larger differences between vapor and liquid compositions, which implies that 3-methyl-1-butanol + 2,3-butanediol can be relatively easier to separate by distillation than 2-methyl-1-pentanol + 2,3-butanediol system.

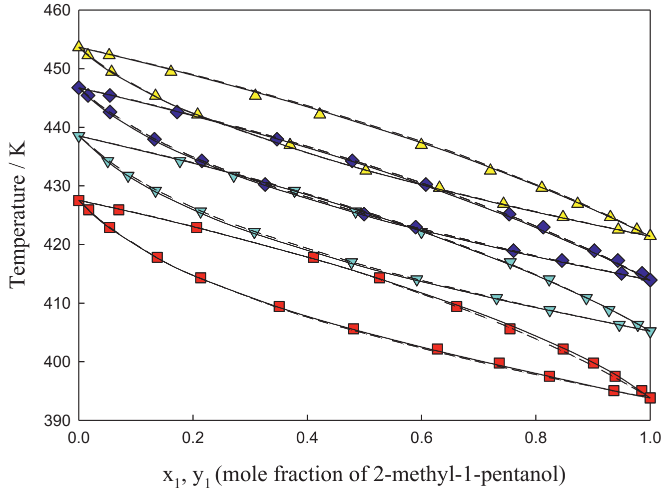


Fig. 3. Experimental and calculated T-x-y diagram for the 2-methyl-1-pentanol (1) + 2,3-butanediol (2) system using NRTL and UNIQUAC: △, 101 kPa; ◆, 80 kPa; ▽, 60 kPa; 🟥, 40 kPa; –, calculated data by NRTL; –-, calculated data by UNIQUAC.

3.2. Data correlation

Our experimental VLE data were also correlated with NRTL [20] and UNIQUAC [21] models as follows.

3.2.1. NRTL

The activity coefficient of component *I* (γ_i) in the NRTL model is given by the following equation

$$\ln \gamma_i = \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left[\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k x_k G_{kj}} \right] \tag{4}$$

where, the subscripts *I*, *j*, and *k* denote the chemical species, x_i is the mole fraction of species *I* and τ_{ij}, τ_{ji}, τ_{kj}, G_{ij}, G_{ji} and G_{kj} are

Table 2
Experimental vapor-liquid equilibrium data for 2-methyl-1-pentanol + 2,3-butanediol at 101, 80, 60 and 40 kPa.

T/K	x_1	y_1	γ_1	γ_2
P = 101 kPa				
453.7	0.0000	0.0000		1.0000
452.3	0.0161	0.0534	1.2317	1.0738
449.4	0.0577	0.1615	1.1316	1.0934
445.4	0.1344	0.3092	1.0478	1.1222
442.2	0.2081	0.4220	1.0174	1.1453
437.0	0.3697	0.5995	0.9551	1.1959
432.6	0.5024	0.7204	0.9702	1.2380
429.7	0.6312	0.8105	0.9534	1.2583
426.9	0.7434	0.8730	0.9549	1.3442
424.7	0.8475	0.9305	0.9597	1.3440
422.5	0.9443	0.9768	0.9726	1.3350
421.5	1.0000	1.0000	1.0000	
P = 80 kPa				
446.8	0.0000	0.0000		1.0000
445.4	0.0164	0.0545	1.1988	1.0706
442.6	0.0547	0.1723	1.2367	1.0733
438.0	0.1325	0.3470	1.1843	1.0832
434.3	0.2156	0.4787	1.1274	1.0909
430.2	0.3263	0.6074	1.0772	1.1099
425.2	0.4994	0.7533	1.0272	1.1297
423.0	0.5896	0.8129	1.0099	1.1356
419.0	0.7609	0.9024	0.9936	1.1853
417.3	0.8456	0.9434	0.9904	1.1372
415.1	0.9499	0.9858	0.9936	0.9587
413.9	1.0000	1.0000	1.0000	
P = 60 kPa				
438.5	0.0000	0.0000		1.0000
434.2	0.0510	0.1771	1.3267	1.0714
431.8	0.0864	0.2714	1.2952	1.0746
429.2	0.1345	0.3776	1.2584	1.0656
425.7	0.2133	0.4846	1.1414	1.1055
422.2	0.3074	0.5997	1.1007	1.1131
417.0	0.4774	0.7552	1.0641	1.1027
414.1	0.5916	0.8233	1.0345	1.1419
410.9	0.7312	0.8883	1.0101	1.2466
408.8	0.8243	0.9280	1.0084	1.3387
406.3	0.9461	0.9783	1.0130	1.4575
405.2	1.0000	1.0000	1.0000	
P = 40 kPa				
427.5	0.0000	0.0000		1.0000
425.9	0.0174	0.0702	1.3425	1.0565
422.9	0.0540	0.2064	1.4045	1.0488
417.8	0.1375	0.4106	1.3030	1.0395
414.3	0.2135	0.5266	1.2139	1.0507
409.4	0.3509	0.6615	1.1019	1.1083
405.6	0.4812	0.7547	1.0505	1.1747
402.2	0.6279	0.8477	1.0237	1.1725
399.8	0.7360	0.9010	1.0144	1.1897
397.5	0.8240	0.9387	1.0289	1.2200
395.1	0.9365	0.9852	1.0405	0.9064
393.8	1.0000	1.0000	1.0000	

Standard uncertainties u of T, P, x and y are, u(T) = 0.1 K, u(P) = 0.13 kPa, u(x) = 0.0009, u(y) = 0.0009

Table 3
Experimental vapor-liquid equilibrium data for 3-methyl-1-butanol + 2,3-butanediol at 101, 80, 60 and 40 kPa.

T/K	x_1	y_1	γ_1	γ_2
P = 101 kPa				
453.7	0.0000	0.0000		1.0000
449.9	0.0250	0.1264	1.3241	1.0828
446.4	0.0531	0.2425	1.3071	1.0873
439.8	0.1277	0.4673	1.2451	1.0416
434.8	0.1873	0.5820	1.2112	1.0470
426.1	0.3001	0.7211	1.1995	1.1151
420.3	0.4082	0.8263	1.2014	1.0234
416.1	0.4857	0.8822	1.2271	0.9403
413.5	0.5367	0.8934	1.2208	1.0469
410.4	0.6135	0.9209	1.2163	1.0546
407.8	0.6828	0.9505	1.2284	0.8940
404.7	0.8388	0.9603	1.1207	1.6039
403.8	1.0000	1.0000	1.0000	
P = 80 kPa				
446.8	0.0000	0.0000		0.9984
444.1	0.0175	0.0990	1.3610	1.0677
439.6	0.0569	0.2729	1.2995	1.0489
434.7	0.1029	0.4195	1.2622	1.0471
429.4	0.1644	0.5555	1.2144	1.0433
421.2	0.2749	0.7174	1.1938	1.0398
414.9	0.3819	0.8152	1.1861	1.0193
411.6	0.4482	0.8706	1.1992	0.9119
407.4	0.5344	0.9028	1.1966	0.9630
404.6	0.5988	0.9263	1.2035	0.9516
401.1	0.6939	0.9368	1.1842	1.2394
398.4	0.8142	0.9605	1.1373	1.4325
397.4	1.0000	1.0000	1.0002	
P = 60 kPa				
438.5	0.0000	0.0000		1.0000
436.3	0.0188	0.1074	1.2694	1.0427
430.5	0.0715	0.3176	1.1603	1.0383
425.6	0.1252	0.4775	1.1478	1.0116
420.4	0.1882	0.6042	1.1285	1.0060
412.5	0.3034	0.7534	1.1169	0.9958
407.3	0.3958	0.8430	1.1352	0.9027
404.5	0.4434	0.8682	1.1464	0.9238
400.9	0.5199	0.9031	1.1507	0.9164
397.0	0.6090	0.9333	1.1646	0.9159
394.1	0.6921	0.9630	1.1739	0.7326
390.8	0.8316	0.9744	1.1164	1.0734
389.5	1.0000	1.0000	1.0000	
P = 40 kPa				
427.5	0.0000	0.0000		1.0000
424.1	0.0207	0.1365	1.3828	1.0534
418.5	0.0617	0.3133	1.2611	1.0834
413.4	0.1190	0.4867	1.1917	1.0541
409.4	0.1771	0.5991	1.1216	1.0354
403.3	0.2824	0.7433	1.0702	0.9783
399.3	0.3642	0.8197	1.0511	0.9191
395.9	0.4523	0.8856	1.0318	0.7844
392.3	0.5489	0.9262	1.0138	0.7201
389.9	0.6140	0.9508	1.0173	0.6248
387.6	0.6794	0.9594	1.0121	0.6891
383.1	0.8268	0.9728	1.0040	1.0525
379.1	1.0000	1.0000	1.0000	

Standard uncertainties u of T, P, x and y are, u(T) = 0.1 K, u(P) = 0.13 kPa, u(x) = 0.0009, u(y) = 0.0009

the adjustable binary parameters. These parameters are calculated using the following equations;

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right) \text{ and } G_{ii} = 1 \tag{5}$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \tag{6}$$

$$\alpha_{ij} = \alpha_{ji} = c_{ij} \tag{7}$$

where a_{ij}, b_{ij}, c_{ij} are the NRTL binary parameters and T is the temperature in K. The non-randomness parameters (α_{ij} and α_{ji}) were set to 0.3.

3.2.2. UNIQUAC

The activity coefficient of component I (γ_i) in the UNIQUAC model is given by Eq. (8)

$$\ln\gamma_i = l_i - \frac{V_i}{x_i}\sum_j x_j l_j + \ln\frac{V_i}{x_i} + \frac{z}{2}q_i\ln\frac{F_i}{V_i} + q_i\left(1 - \sum_j \frac{F_j\tau_{ij}}{\sum_k F_k\tau_{kj}} - \ln\sum_j F_j\tau_{ji}\right) \tag{8}$$

where τ_{ij}, τ_{ji}, τ_{kj}, l_i and l_j are the adjustable parameters and z is the coordination number (set to 10). F_i, F_j and F_k are the Van der

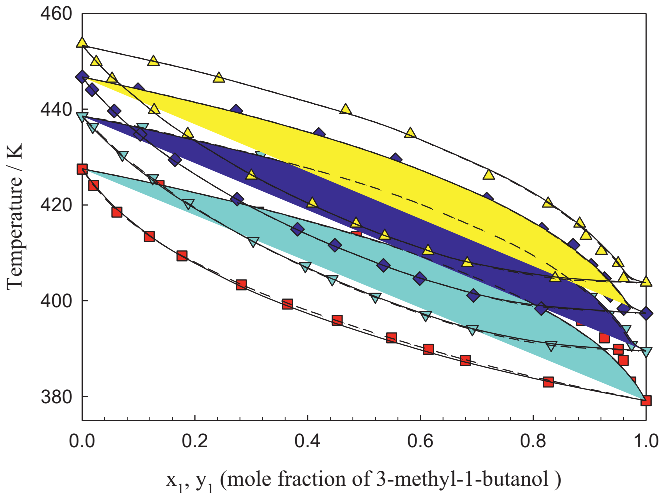


Fig. 4. Experimental and calculated T-x-y diagram for the 3-methyl-1-butatanol (1) + 2,3-butanediol (2) system using NRTL and UNIQUAC: △, 101 kPa; ◆, 80 kPa; ▽, 60 kPa; ■, 40 kPa; –, calculated data by NRTL; —-, calculated data by UNIQUAC.

Table 4
Van der Waals volume parameters r and surface parameters q for the UNIQUAC models calculated using the Bondi group contribution method [22].

Component	r	q
2-methyl-1-pentanol	4.80	4.13
3-methyl-1-butanol	4.13	3.59
levo-2,3-butanediol	3.76	3.32
Water	0.92	1.40

Table 5
Estimated binary interaction parameters of the NRTL and UNIQUAC models for 2-methyl-1-pentanol + 2,3-butanediol and 3-methyl-1-butanol + 2,3-butanediol systems.

	Parameters			
	a_{12}	a_{21}	b_{12}[a]	b_{21}[a]
NRTL	-6.2505	7.5617	2313.0600	-2452.0543
UNIQUAC	1.4480	-1.0736	-401.3727	82.4608
NRTL	-6.8863	6.9774	2709.5412	-2498.4552
UNIQUAC	1.7989	-1.4443	-652.6899	427.3101
NRTL	-8.1788	11.4694	3153.7641	-4253.9748
UNIQUAC	2.5121	-3.0555	-912.4989	1055.2020
NRTL	8.8301	-17.8730	-3966.3300	8005.9069
UNIQUAC	-1.4548	0.9294	691.0942	-522.2679
NRTL	-10.6993	16.9318	4327.5550	-6766.6342
UNIQUAC	-0.8813	1.2833	503.6707	-742.1475
NRTL	-10.3038	4.2923	5822.2789	-2349.7304
UNIQUAC	0.7420	-0.6163	-1202.1580	635.3391
NRTL	-12.1048	4.9961	6444.2340	-2607.5500
UNIQUAC	-0.2005	-0.6311	-804.3030	635.3391
NRTL	-8.9714	4.7574	5178.7881	-2518.1185
UNIQUAC	-0.7421	-0.6095	-628.9157	635.3391
NRTL	-3.2772	6.3884	2145.1054	-3023.7990
UNIQUAC	-0.8034	-0.6759	415.0523	165.0046
NRTL	4.2350	3.0477	-364.2850	-1788.3700
UNIQUAC	-6.0752	0.1227	1663.8840	312.5882

The non-randomness parameter (α) was set to 0.3 for all systems

[a] Unit of b_{12} and b_{21} is K^bBinary parameters were determined by using all the data for each system

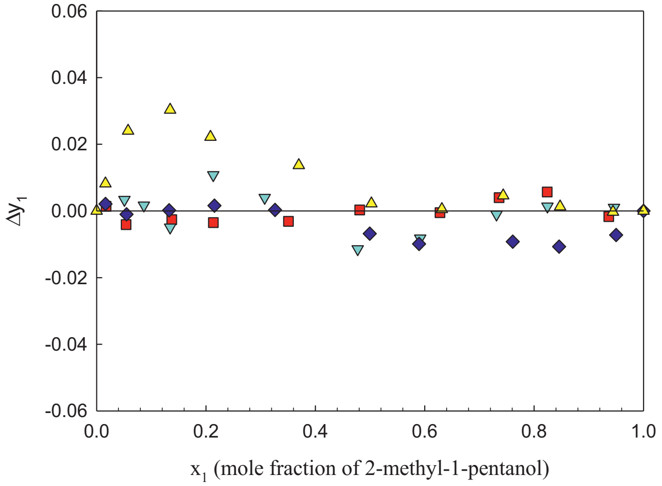


Fig. 5. Deviations of experimental vapor composition from calculated values using NRTL model for 2-methyl-1-pentanol (1) + 2,3-butanediol (2) system: △, 101 kPa; ◆, 80 kPa; ▽, 60 kPa; ■, 40 kPa.

Waals surface areas and V_i is the volume fractions of component *i*. The UNIQUAC model parameters are calculated as follows:

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \tag{9}$$

$$\tau_{ij} = a_{ij} + b_{ij}/T + c_{ij}\ln T + d_{ij}T \tag{10}$$

$$V_i = \frac{x_i r_i}{\sum r_i x_i} \tag{11}$$

$$F_i = \frac{x_i q_i}{\sum x_i q_i} \tag{12}$$

where a_{ij}, b_{ij}, c_{ij} and d_{ij} are the binary interaction parameters. r_i is the volume parameter and q_i is the surface area parameter, which are listed in Table 4. The r_i and q_i are calculated using the Bondi group contribution method [22].

The data were regressed using the maximum likelihood as the objective function. The regressed parameters for each model were determined at each pressure as well as at the whole pressure range by using all the data at each system, and they are shown in Table 5. Table 6 shows the vapor-liquid equilibrium data correlated with NRTL and UNIQUAC methods for 2-methyl-1-pentanol + 2,3-butanediol at P = 101, 80, 60, 40 kPa. The vapor-liquid equilibrium data correlated with NRTL, UNIQUAC methods for 3-methyl-1-butanol + 2,3-butanediol at P = 101, 80, 60, 40 kPa are shown in Table 7. In both Tables 6 and 7, the differences between the calculated vapor mole fraction and experimental vapor mole fraction values are also shown.

The root-mean-square deviations (RMSD) and average absolute deviations (AAD) with respect to the vapor phase composition and the temperature have been calculated using the following equations;

$$\mathrm{RMSD}(y_i) = \sqrt{\sum_{I} \left(y_i^{exp} - y_i^{cal}\right)^2 / N} \tag{13}$$

$$\mathrm{RMSD(T)} = \sqrt{\sum_{I} \left(T_i^{exp} - T_i^{cal}\right)^2 / N}, \tag{14}$$

$$\mathrm{AAD - y} = \frac{1}{N}\sum_{i}^{N} \left|y_i^{exp} - y_i^{cal}\right| \tag{15}$$

$$\mathrm{AAD - T} = \frac{1}{N}\sum_{i}^{N} \left|T_i^{exp} - T_i^{cal}\right| \tag{16}$$

where N is the total number of experimental data points and the superscripts “exp” and “cal” denote the experimental and calculated data. Fig. 5 compares the experimental vapor composition with the calculated values using NRTL model for 2-methyl-

Table 6
Vapor-liquid equilibrium data correlated with NRTL, UNIQUAC for 2-methyl-1-pentanol + 2,3-butanediol at P = 101, 80, 60, 40 kPa.

Experimental Data		NRTL		UNIQUAC	
x_1	y_1	y_1	Δy_1	y_1	Δy_1
P = 101 kPa					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0161	0.0534	0.0616	0.0082	0.0618	0.0084
0.0577	0.1615	0.1855	0.0240	0.1854	0.0239
0.1344	0.3092	0.3395	0.0303	0.3384	0.0292
0.2081	0.4220	0.4442	0.0222	0.4432	0.0212
0.3697	0.5995	0.6132	0.0137	0.6139	0.0144
0.5024	0.7204	0.7226	0.0022	0.7238	0.0034
0.6312	0.8105	0.8110	0.0005	0.8120	0.0015
0.7434	0.8730	0.8776	0.0046	0.8781	0.0051
0.8475	0.9305	0.9318	0.0013	0.9319	0.0014
0.9443	0.9768	0.9765	-0.0003	0.9765	-0.0003
1.0000	1.0000	1.0000	0.0000	1.0000	0.0000
P = 80 kPa					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0164	0.0545	0.0566	0.0021	0.0564	0.0019
0.0547	0.1723	0.1713	-0.0010	0.1713	-0.0010
0.1325	0.3470	0.3472	0.0002	0.3478	0.0008
0.2156	0.4787	0.4803	0.0016	0.4808	0.0021
0.3263	0.6074	0.6077	0.0003	0.6074	0.0000
0.4994	0.7533	0.7465	-0.0068	0.7455	-0.0078
0.5896	0.8129	0.8030	-0.0099	0.8020	-0.0109
0.7609	0.9024	0.8932	-0.0092	0.8928	-0.0096
0.8456	0.9434	0.9327	-0.0107	0.9327	-0.0107
0.9499	0.9858	0.9786	-0.0072	0.9787	-0.0071
1.0000	1.0000	1.0000	0.0000	1.0000	0.0000
P = 60 kPa					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0510	0.1771	0.1805	0.0034	0.1799	0.0028
0.0864	0.2714	0.2731	0.0017	0.2730	0.0016
0.1345	0.3676	0.3727	-0.0049	0.3731	-0.0045
0.2133	0.4746	0.4954	0.0108	0.4960	0.0114
0.3074	0.5797	0.6037	0.0040	0.6038	0.0041
0.4774	0.7552	0.7438	-0.0114	0.7433	-0.0119
0.5916	0.8233	0.8151	-0.0082	0.8145	-0.0088
0.7312	0.8883	0.8873	-0.0010	0.8871	-0.0012
0.8243	0.9280	0.9294	0.0014	0.9294	0.0014
0.9461	0.9783	0.9793	0.0010	0.9794	0.0011
1.0000	1.0000	1.0000	0.0000	1.0000	0.0000
P = 40 kPa					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0174	0.0702	0.0716	0.0014	0.0769	0.0067
0.0540	0.2064	0.2023	-0.0041	0.2049	-0.0015
0.1375	0.4106	0.4080	-0.0026	0.3991	-0.0115
0.2135	0.5266	0.5231	-0.0035	0.5168	-0.0098
0.3509	0.6615	0.6584	-0.0031	0.6660	0.0045
0.4812	0.7547	0.7550	0.0003	0.7684	0.0137
0.6279	0.8477	0.8472	-0.0005	0.8568	0.0091
0.7360	0.9010	0.9050	0.0040	0.9088	0.0078
0.8240	0.9387	0.9444	0.0057	0.9444	0.0057
0.9365	0.9852	0.9835	-0.0017	0.9822	-0.0030
1.0000	1.0000	1.0000	0.0000	1.0000	0.0000

Standard uncertainties u of T, P, x and y are, u(T) = 0.1 K, u(P) = 0.13 kPa, u(x) = 0.0009, u(y) = 0.0009

1-pentanol (1) + 2,3-butanediol (2) system. Fig. 6 show the comparison of the vapor phase composition values obtained from the experiments and UNIQUAC model calculations for 2-methyl-1-pentanol (1) + 2,3-butanediol (2) system. Figs. 7 and 8 also present the experimental and calculated data for 3-methyl-1-butanol (1) + 2,3-butandiol (2) systems using NTRT and UNIQUAC methods, respectively. In these figures, we observe that, since both UNIQUAC and NRTL regressed data follow similar trends, the deviation plots are also quite similar.

For 2-methyl-1-pentanol + 2,3-butanediol system, the values of RMSD(y_I) lie between 0.0029 and 0.0138 and the values of RMSD(T) lie between 0.2 and 0.3 K. For 3-methyl-1-butanol + 2,3-butanediol system, the values of RMSD(y_I) and RMSD(T) are between 0.0042 and 0.0138 and between 0.1 and 0.5 K, respectively.

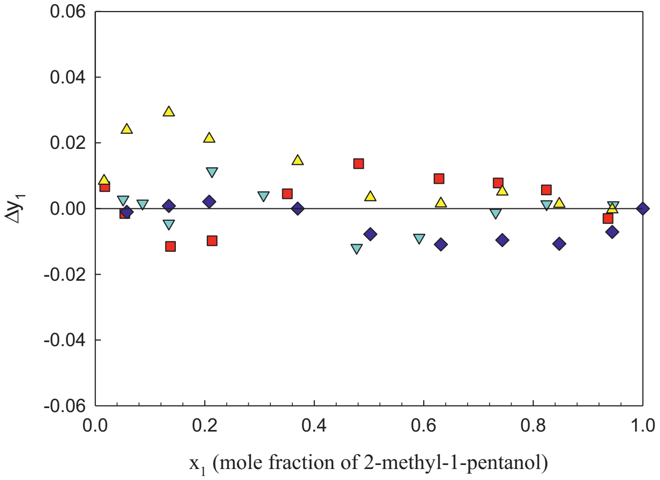


Fig. 6. Deviations of experimental vapor composition from calculated values using UNIQUAC model for 2-methyl-1-pentanol (1) + 2,3-butanediol (2) system: △, 101 kPa; ◆, 80 kPa; ▽, 60 kPa; ■, 40 kPa.

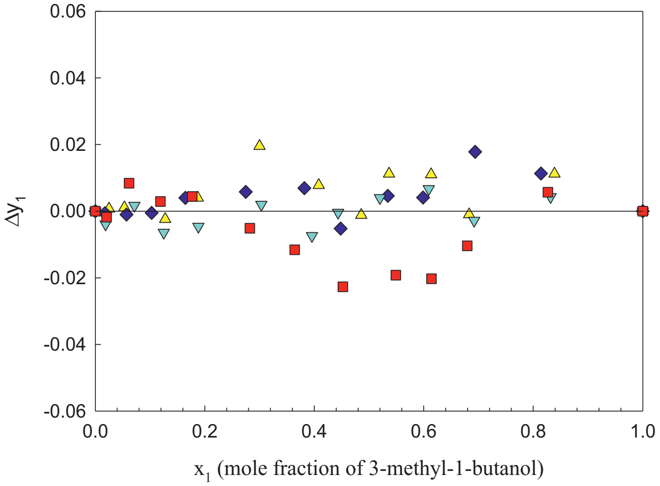


Fig. 7. Deviations of experimental vapor composition from calculated values using NRTL model for 3-methyl-1-butanol (1) + 2,3-butanediol (2) system: △, 101 kPa; ◆, 80 kPa; ▽, 60 kPa; ■, 40 kPa.

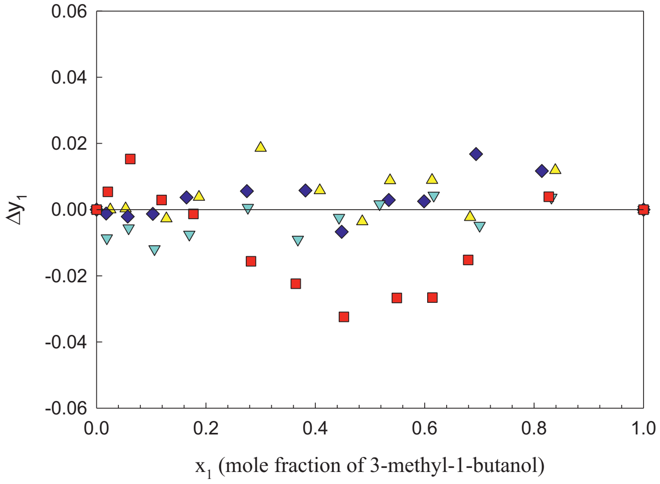


Fig. 8. Deviations of experimental vapor composition from calculated values using UNIQUAC model for 3-methyl-1-butanol (1) + 2,3-butanediol (2) system: △, 101 kPa; ◆, 80 kPa; ▽, 60 kPa; ■, 40 kPa.

Table 7
Vapor-liquid equilibrium data correlated with NRTL, UNIQUAC for 3-methyl-1-butanol + 2,3-butanediol at P = 101, 80, 60, 40 kPa.

Experimental Data		NRTL		UNIQUAC	
x_1	y_1	y_1	Δy_1	y_1	Δy_1
P = 101 kPa					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0250	0.1264	0.1271	0.0007	0.1264	0.0000
0.0531	0.2425	0.2436	0.0011	0.2428	0.0003
0.1277	0.4673	0.4649	-0.0024	0.4646	-0.0027
0.1873	0.5820	0.5860	0.0040	0.5858	0.0038
0.3001	0.7211	0.7406	0.0195	0.7397	0.0186
0.4082	0.8263	0.8341	0.0078	0.8321	0.0058
0.4857	0.8822	0.8810	-0.0012	0.8786	-0.0036
0.5367	0.8934	0.9046	0.0112	0.9022	0.0088
0.6135	0.9209	0.9319	0.0110	0.9298	0.0089
0.6828	0.9505	0.9495	-0.0010	0.9482	-0.0023
0.8388	0.9603	0.9715	0.0112	0.9722	0.0119
1.0000	1.0000	1.0000	0.0000	1.0000	0.0000
P = 80 kPa					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0175	0.099	0.0984	-0.0006	0.0978	-0.0012
0.0569	0.2729	0.2719	-0.0010	0.2708	-0.0021
0.1029	0.4195	0.4190	-0.0005	0.4182	-0.0013
0.1644	0.5555	0.5595	0.0040	0.5592	0.0037
0.2749	0.7174	0.7232	0.0058	0.7230	0.0056
0.3819	0.8152	0.8221	0.0069	0.8210	0.0058
0.4482	0.8706	0.8654	-0.0052	0.8639	-0.0067
0.5344	0.9028	0.9074	0.0046	0.9057	0.0029
0.5988	0.9263	0.9304	0.0041	0.9288	0.0025
0.6939	0.9368	0.9546	0.0178	0.9536	0.0168
0.8142	0.9605	0.9718	0.0113	0.9722	0.0117
1.0000	1.0000	1.0000	0.0000	1.0000	0.0000
P = 60 kPa					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0188	0.1074	0.1035	-0.0039	0.0988	-0.0086
0.0715	0.3176	0.3193	0.0017	0.3120	-0.0056
0.1252	0.4775	0.4711	-0.0064	0.4656	-0.0119
0.1882	0.6042	0.5996	-0.0046	0.5967	-0.0075
0.3034	0.7534	0.7554	0.0020	0.7540	0.0006
0.3958	0.8430	0.8356	-0.0074	0.8340	-0.0090
0.4434	0.8682	0.8678	-0.0004	0.8658	-0.0024
0.5199	0.9031	0.9071	0.0040	0.9048	0.0017
0.6090	0.9333	0.9400	0.0067	0.9376	0.0043
0.6921	0.9630	0.9602	-0.0028	0.9582	-0.0048
0.8316	0.9744	0.9787	0.0043	0.9781	0.0037
1.0000	1.0000	1.0000	0.0000	1.0000	0.0000
P = 40 kPa					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0207	0.1365	0.1347	-0.0018	0.1419	0.0054
0.0617	0.3133	0.3217	0.0084	0.3286	0.0153
0.1190	0.4867	0.4896	0.0029	0.4896	0.0029
0.1771	0.5991	0.6035	0.0044	0.5978	-0.0013
0.2824	0.7433	0.7382	-0.0051	0.7277	-0.0156
0.3642	0.8197	0.8081	-0.0116	0.7973	-0.0224
0.4523	0.8856	0.8629	-0.0227	0.8532	-0.0324
0.5489	0.9262	0.9070	-0.0192	0.8995	-0.0267
0.6140	0.9508	0.9305	-0.0203	0.9242	-0.0266
0.6794	0.9594	0.9490	-0.0104	0.9442	-0.0152
0.8268	0.9728	0.9785	0.0057	0.9767	0.0039
1.0000	1.0000	1.0000	0.0000	1.0000	0.0000

Standard uncertainties u of T, P, x and y are, u(T) = 0.1 K, u(P) = 0.13 kPa, u(x) = 0.0009, u(y) = 0.0009

For 2-methyl-1-pentanol + 2,3-butanediol system, the overall AAD-y are 4×10^{-4} (NRTL) and 5×10^{-4} (UNIQUAC) and the overall AAD-T are 0.2 (NRTL) and 0.15 (UNIQUAC). Also, it is observed that the overall AAD-y values are 5×10^{-4} (NRTL) and 6×10^{-4} (UNIQUAC) and the overall AAD-T values are 0.25 (NRTL) and 0.15 (UNIQUAC) for 3-methyl-1-butanol + 2,3-butanediol system. These small values of deviations indicate that both activity coefficient models are satisfactory for correlating the data investigated in our study. The RMSD and AAD values for the VLE systems investigated are listed in Tables 8 and 9, respectively.

3.3. Thermodynamic consistency test

To evaluate the reliability of the VLE data obtained in our experimental work, the data were processed using the two well-known thermodynamic consistency tests [23-25]

3.3.1. Herington area test

According to the Herington area test [23], the experimental data must satisfy the condition of $|D - J| < 10$ to pass the test where D and J are defined as

$$D = 100\frac{\left|\int_0^1 \ln\frac{\gamma_1}{\gamma_2}dx\right|}{\int_0^1 \left|\ln\frac{\gamma_1}{\gamma_2}\right|dx} \tag{17}$$

$$J = 150\left|\frac{T_{max} - T_{min}}{T_{min}}\right| \tag{18}$$

In the above, T_{max} and T_{min} represent the highest and lowest temperatures for the system, respectively. The minimum value of $|D - J|$ of our experimental data was 2.3034 and the maximum was 9.6169. Thus, from this consistency test, we can confirm that the experimental data from this work satisfy the thermodynamic consistency.

3.3.2. Van Ness-Byer-Gibbs test

Van Ness-Byer-Gibbs test [24,25] for the NRTL activity coefficient model is also performed to evaluate the thermodynamic consistency of the VLE data obtained in this study. In this paper, we followed the procedure given by NIST thermodynamic consistency test. Van Ness-Byer-Gibbs test for isobaric VLE data is carried out using the following two equations:

$$\Delta P = \frac{1}{N}\sum_{i=1}^{N}\Delta P_i = \frac{1}{N}\sum_{i=1}^{N}100\left|\frac{P_i^{exp} - P_i^{cal}}{P_i^{exp}}\right| \tag{19}$$

$$\Delta y = \frac{1}{N}\sum_{i=1}^{N}\Delta y_i = \frac{1}{N}\sum_{i=1}^{N}100\left|y_i^{exp} - y_i^{cal}\right| \tag{20}$$

where N is the number of data points, P_i^{exp} and y_i^{exp} are the experimentally measured pressure and vapor phase mole fraction. P_i^{cal}, y_i^{cal} represent the calculated values obtained from the NRTL activity coefficient models. To pass the thermodynamic consistency test, both ΔP and Δy should be less than 1.0. As shown in Table 10, every VLE system studied in this work passes the test.

4. Conclusions

In this work, the experimental isobaric vapor-liquid equilibrium data for two binary systems, (2-methyl-1-pentanol + 2,3-butanediol and 3-methyl-1-pentanol + 2,3-butanediol), have been obtained at 40, 60, 80 and 101 kPa. The data showed positive deviations from Raoult's law and no azeotropic behavior was observed in both systems. From the experimental result, it is found that 3-methyl-1-butanol + 2,3-butanediol system showed larger differences between vapor and liquid phase compositions than the 2-methyl-1-pentanol + 2,3-butanediol system, suggesting the former is more favorable for separation by distillation method. To evaluate the thermodynamic consistency of the VLE data obtained in our experimental work, Herington area test and Van Ness-Byer-Gibbs test were applied to both data. Two activity coefficient models, NRTL and UNIQUAC were used to correlate the experimental data. The result of thermodynamic consistency tests and the very small deviation values of RMSD, AAD-T and AAD-y show excellent agreement with the experimental data, supporting the high fidelity of our vapor-liquid equilibrium data.

Table 8
Root mean square deviations of T and y for 2-methyl-1-pentanol + 2,3-butanediol and 3-methyl-1-butanol + 2,3-butanediol systems.

	2-methyl-1-pentanol + 2,3-butanediol				3-methyl-1-butanol + 2,3-butanediol			
	NRTL		UNIQUAC		NRTL		UNIQUAC	
Pressure (kPa)	RMSD(T)	RMSD(y_1)	RMSD(T)	RMSD(y_1)	RMSD(T)	RMSD(y_1)	RMSD(T)	RMSD(y_1)
101	0.2	0.0138	0.1	0.0135	0.3	0.0080	0.2	0.0074
80	0.3	0.0058	0.2	0.0061	0.3	0.0068	0.2	0.0066
60	0.2	0.0056	0.2	0.0058	0.2	0.0042	0.1	0.0059
40	0.2	0.0029	0.1	0.0075	0.5	0.0114	0.1	0.0170
whole range	0.2	0.0079	0.2	0.0093	0.9	0.0099	0.8	0.0089

Table 9
Average absolute deviations of T and y for 2-methyl-1-pentanol + 2,3-butanediol and 3-methyl-1-butanol + 2,3-butanediol systems.

	2-methyl-1-pentanol + 2,3-butanediol				3-methyl-1-butanol + 2,3-butanediol			
	NRTL		UNIQUAC		NRTL		UNIQUAC	
Pressure (kPa)	AAD-T	AAD-y_1	AAD-T	AAD-y_1	AAD-T	AAD-y_1	AAD-T	AAD-y_1
101	0.1	0.0008	0.1	0.0008	0.2	0.0004	0.2	0.0004
80	0.3	0.0003	0.2	0.0004	0.2	0.0004	0.2	0.0004
60	0.2	0.0003	0.2	0.0003	0.2	0.0003	0.1	0.0004
40	0.2	0.0002	0.1	0.0005	0.4	0.0007	0.1	0.0010
whole range	0.1	0.0058	0.2	0.0060	0.6	0.0067	0.6	0.0064

Table 10
Van Ness-Byer-Gibbs test results for 2-methyl-1-pentanol + 2,3-butanediol and 3-methyl-1-butanol + 2,3-butanediol systems.

	2-methyl-1-pentanol + 2,3-butanediol		3-methyl-1-butanol + 2,3-butanediol	
Pressure (kPa)	ΔP	Δy	ΔP	Δy
101	0.9509	0.4243	0.9511	0.6092
80	0.7871	0.2540	0.7159	0.4162
60	0.8912	0.4604	0.7914	0.3489
40	0.8440	0.3576	0.8183	0.4770
Avg.	0.8683	0.3741	0.8192	0.4628

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Joon-Hyuk Yim: Writing - original draft. **Hyun Ji Kim:** Writing - review & editing, Validation. **Jai June Oh:** Validation. **Jong Sung Lim:** Supervision. **Kyu Yong Choi:** Writing - review & editing.

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References

[1] X.-J. Ji, H. Huang, P.-K. Ouyang, Microbial 2, 3-butanediol production: a state-of-the-art review, Biotechnol. Adv. 29 (2011) 351–364 https://doi.org/10.1016/j.biotechadv.2011.01.007.

[2] A.-P. Zeng, W. Sabra, Microbial production of diols as platform chemicals: recent progresses, Curr. Opin. Biotechnol. 22 (2011) 749–757 https://doi.org/10.1016/j.copbio.2011.05.005.

[3] S. Sridhar, Zur Abtrennung von butandiol-2,3 aus fermenter-Brühen mit Hilfe der Umkehrosmose, Chem. Ing. Tech. 61 (1989) 252–253 https://doi.org/10.1002/cite.330610316.

[4] N. Qureshi, M.M. Meagher, R.W. Hutkins, Recovery of 2,3-butanediol by vacuum membrane distillation, Sep. Sci. Technol. 29 (1994) 1733–1748 https://doi.org/10.1080/01496399408002168.

[5] Y. Li, Y. Wu, J. Zhu, J. Liu, Separation of 2,3-butanediol from fermentation broth by reactive-extraction using acetaldehyde-cyclohexane system, Biotechnol. Bioprocess Eng. 17 (2012) 337–345 https://doi.org/10.1007/s12257-011-0675-5.

[6] S.D. Birajdar, S. Rajagopalan, J.S. Sawant, S. Padmanabhan, Continuous countercurrent liquid-liquid extraction method for the separation of 2,3-butanediol from fermentation broth using n-butanol and phosphate salt, Process Biochem. 50 (2015) 1449–1458 https://doi.org/10.1016/j.procbio.2015.05.016.

[7] Y.Y. Wu, K. Chen, J.W. Zhu, B. Wu, L. Ji, Y.L. Shen, Enhanced extraction of 2,3-butanediol by medley solvent of salt and n-butanol from aqueous solution, Can. J. Chem. Eng. 92 (2014) 511–514 https://doi.org/10.1002/cjce.21831.

[8] B. Wang, T. Ezejias, H. Feng, H. Blaschek, Sugaring-out. A novel phaseseparation and extraction system, Chem. Eng. Sci. 63 (2008) 2595–2600 https://doi.org/10.1016/j.ces.2008.02.004.

[9] B. Wang, H. Feng, T. Ezeji, H. Blaschek, Sugaring-out separation of acetonitrile-from its aqueous solution, Chem. Eng. Technol. 31 (2008) 1869–1874 https://doi.org/10.1002/ceat.200800003.

[10] M.M.L. Duarte, J. Lozar, G. Malmary, J. Molinier, Equilibrium diagrams at 19°c of water-malic acid-2-methyl-1-propanol, water-malic acid-1-pentanol, and water-malic acid-3-methyl-1-butanol ternary systems, J. Chem. Eng. Data. 34 (1989) 43–45 https://doi.org/10.1021/je00055a014.

[11] M.A. Eiteman, J.L. Gainer, In situ extraction versus the use of an external column in fermentation, Appl. Microbiol. Biotechnol. 30 (1989) 614–618 https://doi.org/10.1007/BF00255368.

[12] R.H. Blom, D.L. Reed, A. Efron, G.C. Mustakas, Recovery of 2,3-butylene glycol from fermentation liquors, Ind. Eng. Chem. 37 (1945) 865–870 https://doi.org/10.1021/ie50429a021.

[13] L.Y. Garcia-Chavez, B. Schuur, A.B. De Haan, Conceptual process design and economic analysis of a process based on liquid-liquid extraction for the recovery of glycols from aqueous streams, Ind. Eng. Chem. Res. 52 (2013) 4902–4910 https://doi.org/10.1021/ie303187x.

[14] A.Y. Jeong, J.A. Cho, Y. Kim, H.-K. Cho, K.Y. Choi, J.S. Lim, Liquid-liquid equilibria for water+2,3-butanediol+1-pentanol ternary system at different temperatures

of 298.2, 308.2, and 318.2 K, Korean J. Chem. Eng. 35 (2018) 1328–1334 https://doi.org/10.1007/s11814-018-0036-6.

[15] J.-H. Yim, K.W. Park, J.S. Lim, K.Y. Choi, Liquid–liquid equilibrium measurements for the ternary system of water/2,3-butanediol/4-methyl-2-pentanol at various temperatures, J. Chem. Eng. Data. 64 (2019) 3882–3888 https://doi.org/10.1021/acs.jced.9b00290.

[16] H.J. Kim, J.-H. Yim, J.S. Lim, Measurement and correlation of ternary system {water + 2,3-butanediol + 2-methyl-1-pentanol} and {water + 2,3-butanediol + 3-methyl-1-butanol} liquid-liquid equilibrium data, Fluid Phase Equilib. 15 (2020) 112639 https://doi.org/10.1016/j.fluid.2020.112639.

[17] B.N. Taylor, C.E. Kuyatt, NIST technical note 1297 1994 edition, guidelines for evaluating and expressing the uncertainty of nist measurement results, Natl. Inst. Stand. Technol. (1994) 1–20.

[18] J. Gmehling, U. Onken, in: Vapor-Liquid Equilibrium Data Collection, Dechema, 1, Frankfurt, Germany, 1977, p. 60.

[19] G.W. Thomson, The Antoine equation for vapor-pressure data, Chem. Rev. (1946) https://doi.org/10.1021/cr60119a001.

[20] H. Renon, J.M. Prausnitz, Local compositions in thermodynamic excess functions for liquid mixtures, AICHE J. 4 (1968) 135–144 https://doi.org/10.1002/aic.690140124.

[21] D.S. Abrams, J.M. Prausnitz, Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems, AICHE J. 21 (1975) 116–128 https://doi.org/10.1002/aic.690210115.

[22] A. Bondi, Physical Properties Of Molecular Crystals, Liquids & Glasses, Wiley, New York, 1968.

[23] E.F.G. Herington, Tests for the consistency of experimental isobaric vapour-liquid equilibrium data, J. Inst. Petrol. 37 (1951) 457–470.

[24] H.C. Van Ness, S.M. Byer, R.E. Gibbs, Vapor-liquid equilibrium: part I. an appraisal of data reduction methods, AICHE J. 19 (1973) 238–244 https://doi.org/10.1002/aic.690190206.

[25] P.L. Jackson, R.A. Wilsak, Thermodynamic consistency tests based on the Gibbs-Duhem equation applied to isothermal, binary vapor-liquid equilibrium data: data evaluation and model testing, Fluid Phase Equilibria 103 (1995) 155–197.