Liquid-liquid equilibria for water+2,3-butanediol+1-pentanol ternary system at different temperatures of 298.2, 308.2, and 318.2 K

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Abstract–Liquid-liquid equilibrium (LLE) data was measured for the water+2,3-butanediol+1-pentanol ternary system at 298.2, 308.2, and 318.2 K under atmospheric pressure. Binodal solubility curves and complete ternary phase diagrams were experimentally obtained in mass fraction at these three different temperatures. The consistency of the tie-line results was verified by using Othmer-Tobias and Hand plots. Distribution coefficients and separation factors of 2,3-butanediol were evaluated for each tie-line, and the effect of temperature was also investigated. It was found that the distribution coefficients and separation factors of 2,3-butanediol increased with temperature. The experimental LLE data were correlated by the UNIQUAC and NRTL models, and the binary interaction parameters calculated from these models have been reported. Both models successfully predict the experimental tie-line data within average root-mean-square deviations (RMSD) being less than 1.38% and 1.49% from the UNIQUAC and NRTL models, respectively.

Keywords: 2,3-Buthanediol, 1-Pentanol, Liquid-liquid Equilibrium, NRTL, UNIQUAC

INTRODUCTION

Depletion of crude oil has resulted in a growing interest in bio-based platform chemicals. 2,3-Butanediol is one such key chemical that can be obtained by fermentation [1]. It is considered as an important industrial chemical because of its application in the manufacture of explosives, cosmetics, plasticizers, perfumes, anti-freeze solutions, pharmaceuticals, and foods [2-5]. 2,3-Butanediol is also used as an intermediate in the synthesis of methyl ethyl ketone (MEK), acetoin, butadiene, and diacetyl [6-8].

Microbial production of 2,3-butanediol was first reported by Harden and Walpole in 1906 [9]. There have been many significant advances over the last 100 years in the manufacturing process utilizing this route [6,10-12]. However, a major limitation towards the industrial production of 2,3-butanediol is the cost of separation, which constitutes about 50% of the total production cost [4]. The fermentation broth usually includes many components such as residual sugars, salts, water, proteins, and other by-products (e.g., acetic acid, lactate, and succinic acid), which hinder the isolation of 2,3-butanediol. Furthermore, 2,3-butanediol is present in very low concentrations (below 10 wt%) [6], has a high boiling temperature (about 450 K), and exhibits hydrophilicity. Thus, the high cost of separation of 2,3-butanediol from aqueous solution is an obstacle to its commercial production.

To date, several downstream processing technologies such as countercurrent stream stripping [4], distillation [13], membrane technology, reverse osmosis, reactive extraction [14], pervaporation

[15], salting-out [16-19], and solvent extraction [20] have been employed to efficiently separate 2,3-butanediol from aqueous solution. Among these, liquid-liquid extraction has emerged as a promising technology because of low energy requirements and ease in operation and scale-up [21-23]. To optimize the extraction process, LLE data is essential. A number of studies have reported LLE data for water+2,3-butanediol+solvent ternary systems, aimed at finding the appropriate solvent for the 2,3-butanediol extraction process [24-30]. Snehal et al. [31] reported that C_4-C_6 alcohols are promising solvents for extracting 2,3-butanediol from the fermentation broth. Based on this result, we selected 1-pentanol in this study as a solvent for 2,3-butanediol extraction.

We studied the liquid-liquid phase equilibria of water+2,3-butanediol+1-pentanol mixture at 298.2-318.2 K (in 10 K interval) and 1 atm. As far as we know, LLE data for this system is not yet available in the literature. For the tie-line data, the consistency was verified by the Othmer-Tobias plot and Hand plot. The separation factors and distribution coefficients were also evaluated from the tie-line results for each ternary mixture. The universal quasi-chemical activity coefficient (UNIQUAC) and non-random two-liquid (NRTL) models were used to correlate the experimental tie-line data. Binary interaction parameters calculated from these models have also been reported.

EXPERIMENTAL

1. Chemicals

2,3-Butanediol and 1-pentanol were purchased from Sejinci Co. (Korea). We used HPLC grade water supplied by Daejeng Co. (Korea). To ascertain the purity of these pure components, we analyzed these materials by gas chromatography (GC). The resulting purity of 2,3-butanediol was greater than 99.5 and that of 1-pentanol

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was higher than 99.8 in mass %. Therefore, we used all substances as they were supplied.

2. Experimental Apparatus and Procedure

To study the liquid-liquid equilibria (LLE) for water+2,3-butanediol+1-pentanol ternary system, binodal solubility curve data and tie-line data were determined at 298.2-318.2 K under 1 atm. To obtain both data, an 80 mL water-jacketed glass equilibrium cell, which was connected to a constant temperature water circulator (RW3025G, Jeiotech Co., Korea) controlled within ±0.1 K was used. The mixture temperatures in the cell were measured by an RTD temperature probe located in the cell within the uncertainty of ±0.1 K. To prepare an accurate mass fraction of sample mixtures, a precision balance (Precias model 1212 M) with an accuracy of ±0.0001 g was used. All the samples were analyzed by a GC (Young-Lin Instrument Co. model YL6100, Korea) equipped with a TCD and a Porapak Q column (Alltech Co.). The temperatures of injector and detector were fixed at 513.2 K. The initial oven temperature was 373.2 K, followed by a 1 K/min increase up to 383.2 K, and finally increased up to 493.2 K with 20 K/min and held for 3 min. We used helium (99.999%) as a carrier gas, whose flow rate was 30 mL/min. Ethanol was used as an internal standard in order to analyze the contents of the liquid samples because it is a good solvent for all the three components. To ensure accuracy, we analyzed each sample at least three times in a row.

For measuring the binodal solubility curve data, the cloud point method was used. Most of the solubility curve data (central region of the ternary plot) were obtained by titrating the turbid binary mixtures of (water+1-pentanol) with 2,3-butanediol until the solution became clear. For the water-rich side, the (water+2,3-butanediol) binary mixtures titrated with 1-pentanol and for the solvent-rich side, (1-pentanol+2,3-butanediol) binary mixtures were titrated with water until the solution became hazy. To obtain more accurate solubility data, we repeated all experiments at least three times.

For measuring the tie-line data, ternary mixture samples of water, 2,3-butanediol, and solvent (1-pentanol) that lie within the two phase region of the ternary plot were prepared. About 50 g of sample was introduced into an 80 mL water-jacketed glass cell with a magnetic stir bar. The ternary mixture was agitated vigorously for 2 h at 550 rpm and then left for 12 h to completely separate the water-rich phase and the organic solvent-rich phase. When phase equilibrium was reached, approximately 1 mL of each phase samples was captured using a syringe through the top and side sampling ports, respectively. Gas chromatography was used to analyze the liquid samples captured from each phase. Each sample was analyzed at least three times to assure accuracy.

Combined uncertainties of mass fractions $(u(x_i))$ are reported in Table 2. According to the NIST and GUM [32,33], the combined uncertainties (u) were calculated by the following equations:

$$u = \sqrt{[(u_i^2)+(u_j^2)]} \tag{1}$$

Table 1. Experimental solubility curve data (mass fraction) of [water (1)+2,3-butanediol (2)+1-pentanol (3)] at different temperature

T/K	w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3
298.2	0.1100	0.0000	0.8900	0.2996	0.2271	0.4733	0.8381	0.1354	0.0265
	0.1156	0.0380	0.8464	0.3294	0.2446	0.4260	0.9554	0.0188	0.0258
	0.1210	0.0628	0.8162	0.3923	0.2717	0.3360	0.9737	0.0000	0.0263
	0.1447	0.0150	0.7503	0.4190	0.2820	0.2990			
	0.1715	0.1397	0.6888	0.4843	0.2820	0.2337			
	0.1923	0.1696	0.6381	0.6060	0.2802	0.1138			
	0.2155	0.1941	0.5904	0.6827	0.2555	0.0618			
	0.2530	0.2127	0.5343	0.7397	0.2229	0.0374			
308.2	0.1137	0.0000	0.8863	0.3170	0.2593	0.4237	0.5921	0.2844	0.1235
	0.1220	0.0624	0.8156	0.3351	0.2729	0.3920	0.6590	0.2724	0.0686
	0.1472	0.1080	0.7448	0.3560	0.2839	0.3601	0.7181	0.2487	0.0332
	0.1804	0.1443	0.6753	0.3869	0.2898	0.3233	0.7774	0.1966	0.0260
	0.2089	0.1804	0.6107	0.4223	0.2914	0.2863	0.8262	0.1518	0.0220
	0.2357	0.2061	0.5582	0.4540	0.2939	0.2521	0.9012	0.0762	0.0226
	0.2623	0.2265	0.5112	0.4871	0.2922	0.2207	0.9765	0.0000	0.0235
	0.2922	0.2444	0.4634	0.5225	0.2895	0.1879			
318.2	0.1132	0.0000	0.8868	0.3435	0.2533	0.4032	0.6051	0.2700	0.1249
	0.1236	0.0421	0.8343	0.3860	0.2617	0.3523	0.6638	0.2622	0.0740
	0.1325	0.0812	0.7863	0.4232	0.2663	0.3105	0.7172	0.2411	0.0417
	0.1499	0.1165	0.7336	0.4560	0.2681	0.2759	0.7585	0.2102	0.0313
	0.1731	0.1487	0.6782	0.4861	0.2709	0.2430	0.8018	0.1749	0.0233
	0.2059	0.1736	0.6205	0.5160	0.2697	0.2143	0.8367	0.1431	0.0202
	0.2367	0.1980	0.5653	0.5370	0.2697	0.1933	0.8710	0.1079	0.0211
	0.2637	0.2199	0.5164	0.5583	0.2689	0.1728	0.9084	0.0696	0.0220
	0.2966	0.2349	0.4685	0.5778	0.2687	0.1535	0.9763	0.0000	0.0237

where u_i is A-type uncertainty (statistical standard deviation analysis) and u_j is B-type uncertainty. Both are called standard uncertainties.

u_i is calculated by the following equations:

$$x_i = \frac{1}{n}\Sigma_{k=1}^n X_{i,k} \tag{2}$$

$$u_i = \left[\frac{1}{n(n-1)}\Sigma_{k=1}^n (X_{i,k}-x_i)^2\right]^{1/2} \tag{3}$$

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

u_j is calculated by the following equations:

$$a = \frac{(a_+ + a_-)}{2} \tag{4}$$

$$u_j = \frac{a}{\sqrt{3}} \tag{5}$$

where, a_+ is upper limits and a_- is lower limits.

Table 2. Tie-line data (in mass fraction) for water (1)+2,3-butanediol (2)+1-pentanol (3) system at T=298.2, 308.2, and 318.2 K[a] and pressure p=0.1 MPa

Water-rich phase				Solvent-rich phase			
w_1	$u(w_1)$	w_2	$u(w_2)$	w_1	$u(w_1)$	w_2	$u(w_2)$
298.2 K							
0.7352	0.0021	0.2191	0.0024	0.2168	0.0006	0.1662	0.0010
0.7516	0.0029	0.2085	0.0025	0.2040	0.0005	0.1533	0.0006
0.7777	0.0003	0.1876	0.0027	0.1730	0.0003	0.1264	0.0015
0.8204	0.0032	0.1574	0.0032	0.1490	0.0000	0.1065	0.0001
0.8412	0.0018	0.1355	0.0023	0.1369	0.0016	0.0892	0.0006
0.8489	0.0015	0.1278	0.0007	0.1360	0.0013	0.0838	0.0012
0.8774	0.0006	0.0987	0.0018	0.1251	0.0022	0.0579	0.0000
0.8964	0.0010	0.0822	0.0013	0.1197	0.0003	0.0453	0.0002
308.2 K							
0.6710	0.0014	0.2718	0.0016	0.3212	0.0002	0.2604	0.0013
0.7114	0.0008	0.2507	0.0001	0.2593	0.0032	0.2280	0.0028
0.7522	0.0020	0.2182	0.0012	0.2124	0.0012	0.1901	0.0007
0.7971	0.0011	0.1775	0.0006	0.1770	0.0003	0.1441	0.0029
0.8235	0.0012	0.1532	0.0009	0.1598	0.0001	0.1220	0.0025
0.8291	0.0005	0.1485	0.0002	0.1597	0.0013	0.1127	0.0010
0.8522	0.0006	0.1260	0.0003	0.1400	0.0014	0.0927	0.0009
318.2 K							
0.7231	0.0011	0.2346	0.0002	0.2762	0.0003	0.2373	0.0017
0.7577	0.0014	0.2102	0.0013	0.2287	0.0002	0.2018	0.0002
0.7641	0.0006	0.2041	0.0007	0.2278	0.0000	0.1963	0.0008
0.7625	0.0015	0.2066	0.0005	0.2224	0.0012	0.1966	0.0014
0.7840	0.0014	0.1885	0.0013	0.2056	0.0007	0.1757	0.0007
0.8231	0.0007	0.1525	0.0006	0.1768	0.0002	0.1385	0.0012
0.8410	0.0021	0.1357	0.0025	0.1566	0.0005	0.1177	0.0001
0.8593	0.0003	0.1181	0.0002	0.1535	0.0006	0.0989	0.0008
0.8730	0.0005	0.1062	0.0007	0.1414	0.0006	0.0875	0.0007

[a]The combined uncertainty for temperature, u(T)=0.1 K

CORRELATION

The experimental data for the studied systems were used to estimate binary parameters for the NRTL [34] and UNIQUAC [35] activity coefficient models by using the Aspen plus V8.4 software. The NRTL and UNIQUAC models are commonly used to correlate liquid-liquid equilibrium data.

The thermodynamics criteria and mass balance equation in the water-rich and solvent-rich phase at equilibrium were defined as follows:

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \tag{6}$$

$$\Sigma x_i^I = 1 \text{ and } \Sigma x_i^{II} = 1 \tag{7}$$

where γ is the activity coefficient, x_i is the mole fraction of component i, and I denote the solvent-rich and II denote the water-rich phase.

RESULTS AND DISCUSSION

The measured solubility data and tie-line data for this ternary system are given in Tables 1 and 2, respectively; w_i, in Table 2, represents the mass fraction of i component. Figs. 1-3 show the triangular phase diagrams at these temperatures.

The consistency of the tie-line results was confirmed by Othmer-Tobias [37] and Hand correlation methods [38]. The Othmer-

Table 3. Van der Waals volume parameters r and surface parameters q for the UNIQUAC models

Component	r	q
Water	0.92	1.40
2,3-Butanediol	3.76	3.32
1-Pentanol	4.13	3.59
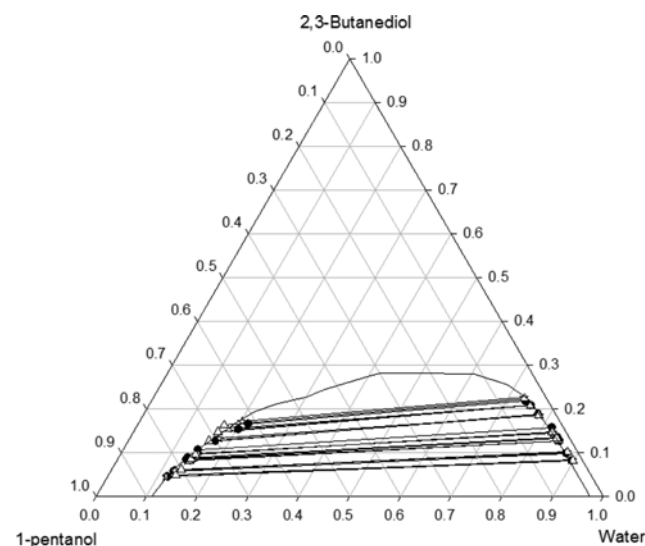
Fig. 1. LLE data (mass fraction) for water (1)+2,3-butanediol (2)+1-pentanol (3) ternary systems at T=298.2 K; (—) experimental solubility data, (●—●) experimental tie-line data, (☆—☆) calculated tie-line data by NRTL, (△—△) calculated tie-line data by UNIQUAC.
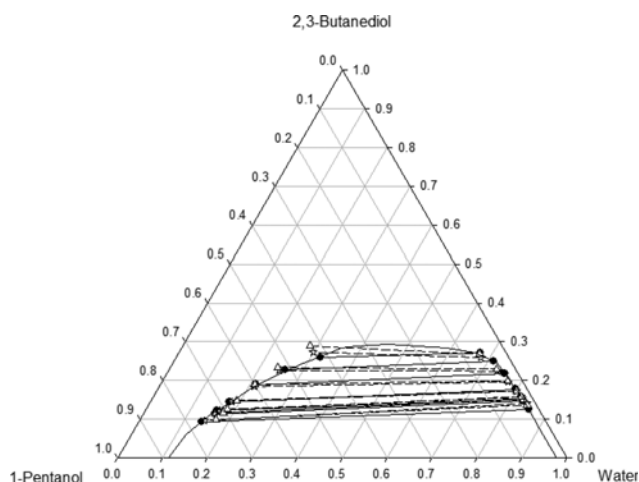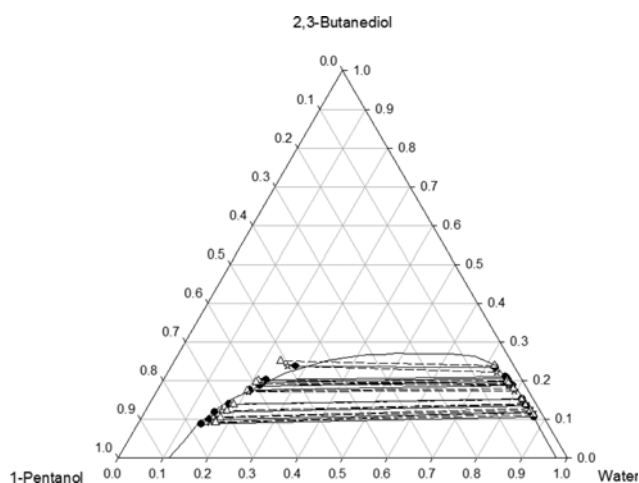
Fig. 2. LLE data (mass fraction) for water (1)+2,3-butanediol (2)+ 1-pentanol (3) ternary systems at T=308.2 K; (—) experimental solubility data, (●—●) experimental tie-line data, (☆—☆) calculated tie-line data by NRTL, (△—△) calculated tie-line data by UNIQUAC.

Table 4. Constants of the Othmer-Tobias equation and Hand equation for water (1)+2,3-butanediol (2)+1-pentanol (3) system (R^2: regression coefficient)

T/K	Othmer-Tobias correlation			Hand correlation		
	a	b	R^2	c	d	R^2
298.2	0.9801	−0.4990	0.9846	0.7521	−0.1948	0.9959
308.2	0.6896	−0.8890	0.9899	0.6248	−0.5599	0.9928
318.2	0.7792	−0.9411	0.9901	0.6912	−0.5799	0.9953

Fig. 3. LLE data (mass fraction) for water (1)+2,3-butanediol (2)+ 1-pentanol (3) ternary systems at T=318.2 K; (—) experimental solubility data, (●—●) experimental tie-line data, (☆—☆) calculated tie-line data by NRTL, (△—△) calculated tie-line data by UNIQUAC.
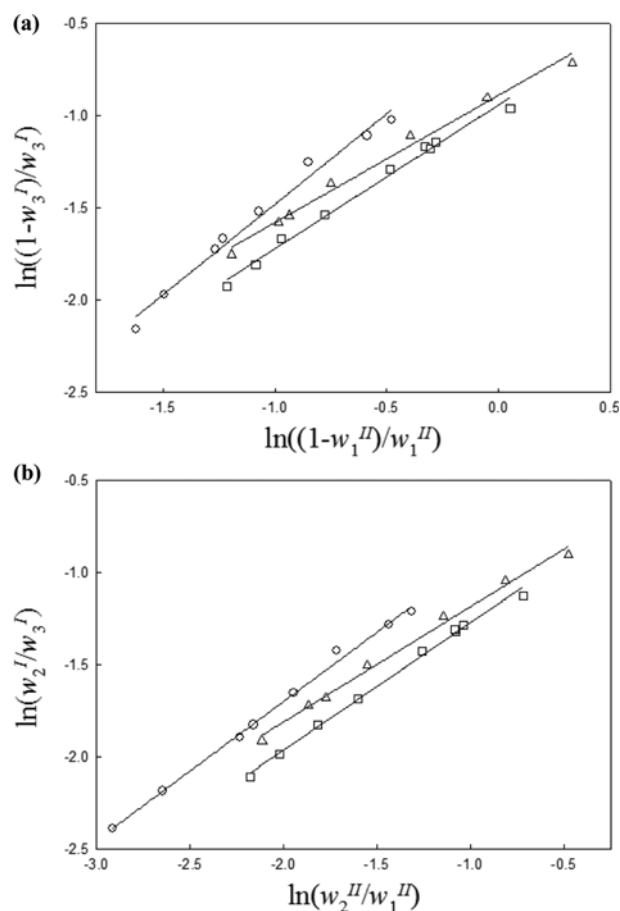
Fig. 4. (a) Othmer-Tobias plot and (b) Hand plot for water (1)+2,3-butanediol (2)+1-pentanol (3) ternary systems; (○) 298.2 K, (△) 308.2 K, (□) 318.2 K.

Tobias plot Eq. (8) and Hand plot Eq. (9) are presented as the following equations.

$$\ln\left[\frac{1-w_3^I}{w_3^I}\right] = a + b\ln\left[\frac{1-w_1^{II}}{w_1^{II}}\right] \tag{8}$$

$$\ln\left[\frac{w_2^I}{w_3^I}\right] = c + d\ln\left[\frac{w_2^{II}}{w_1^{II}}\right] \tag{9}$$

where, a, b, c and d are the Othmer-Tobias and Hand plot parameters. w_1 is a mass fraction of water, w_2 is that of 2,3-butanediol and w_3 is that of 1-pentanol, and superscripts I and II refer to the solvent- and water-rich phase, respectively. The calculation param-

eters and standard deviations (R^2) are given in Table 4 and linearity plots are shown in Fig. 4. R^2 is greater than 0.9899, which indicates that the experimental data is in good agreement with theory. Mostly, the Hand correlation method showed a better linear fit compared to Othmer-Tobias correlation in this study.

To evaluate the efficacy of 1-pentanol as a solvent in the extraction of 2,3-butanediol from water, distribution coefficient (D) and separation factor (S) were calculated from the experimental tie-line data. The distribution coefficient (D) and separation factor (S) are presented as follows,

$$D_2 = \frac{w_2^I}{w_2^{II}} \tag{10}$$

Table 5. Distribution coefficients (D_2) and separation factors (S) of 2,3-butanediol for water (1)+2,3-butanediol (2)+1-pentanol (3) system at different temperatures

| T/K	w_2^{II}	D_2	S
298.2	0.2191	0.76	2.58
	0.2085	0.74	2.71
	0.1876	0.67	3.03
	0.1574	0.68	3.73
	0.1355	0.66	4.05
	0.1278	0.66	4.09
	0.0987	0.59	4.11
	0.0822	0.55	4.13
308.2	0.2718	0.96	2.00
	0.2507	0.91	2.50
	0.2182	0.87	3.09
	0.1775	0.81	3.66
	0.1532	0.8	4.10
	0.1485	0.76	3.94
	0.1260	0.74	4.48
318.2	0.2346	1.01	2.65
	0.2102	0.96	3.18
	0.2041	0.96	3.23
	0.2066	0.95	3.26
	0.1885	0.93	3.55
	0.1525	0.91	4.23
	0.1357	0.87	4.66
	0.1181	0.84	4.69
	0.1062	0.82	5.09

^{II}Water-rich phase

$$S = \frac{w_2^I/w_2^{II}}{w_1^I/w_1^{II}} = \frac{D_2}{D_1} \quad (11)$$

where w_1^I and w_2^I are the mass fractions of water and 2,3-butanediol in the solvent-rich phase, respectively and w_1^{II} and w_2^{II} are the mass fractions of water and 2,3-butanediol in the water-rich phase, respectively. The separation factor (S) and distribution coefficient (D) are listed in Table 5.

As shown in Fig. 5, the distribution coefficients of 2,3-butanediol increased slightly with increase in temperature from 298.2 to 318.2 K. Thus, it can be concluded that there is a favorable effect of increasing temperature on the distribution coefficients, which also increase with the increasing 2,3-butanediol concentration. On the other hand, the separation factors increased with decreasing concentration of 2,3-butanediol.

Among the various organic solvents that have been studied for extracting the 2,3-butanediol from the aqueous solution, 1-butanol is one of the most promising candidates. This is because 1-butanol has a high distribution coefficient, D_2=0.9954 at T=318.2 K, and the separation factor is larger than one [30]. Fig. 6 shows the comparison of distribution coefficients and separation factor between 1-pentanol and n-butanol. As shown, almost all the separation factor and distribution coefficient of 1-pentanol are greater than that of 1-butanol, which indicates that 1-pentanol could be a
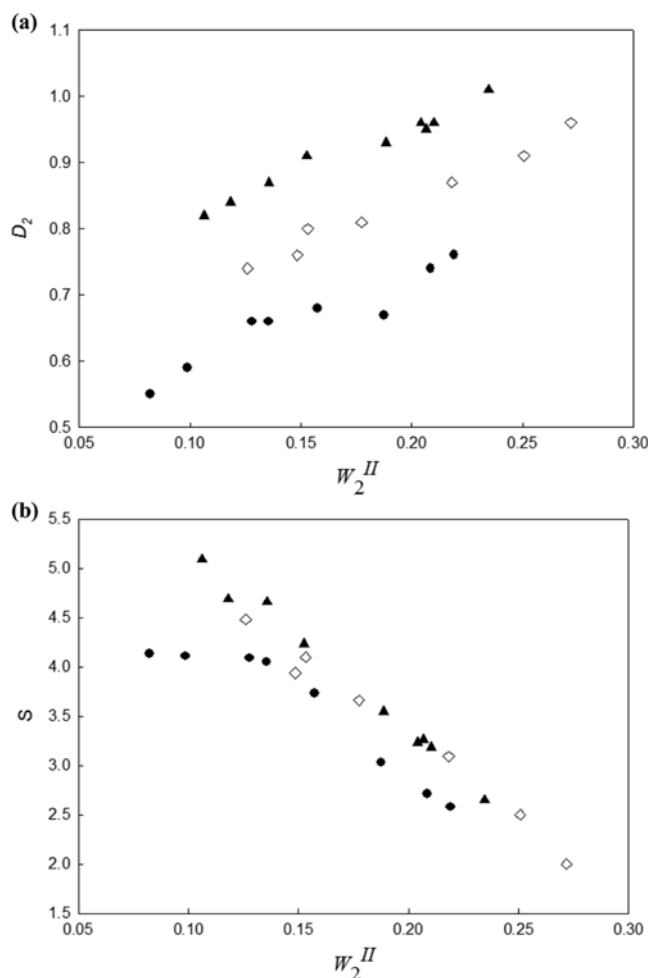
Fig. 5. (a) Distribution coefficients (D_2) and (b) separation factor (S) plotted against the mass fraction of 2,3-butanediol in water-rich phase (w_2^{II}) for water+2,3-butandiol+1-pentanol system at different temperature; (●) 298.2 K, (◇) 308.2 K, (▲) 318.2 K.
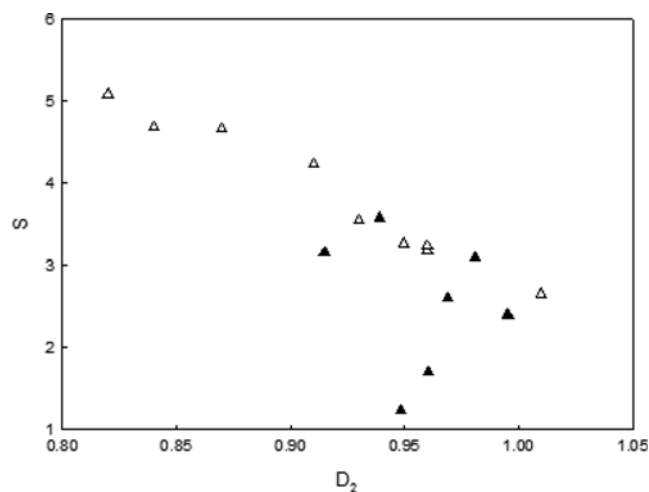
Fig. 6. Comparison of distribution coefficients of 2,3-butanediol (D_2) and separation factor (S) for water+2,3-butandiol+solvent system at 318.2 K; (△) 1-pentanol, (▲) 1-butanol.

Table 6. Parameters of the NRTL models for water (1)+2,3-butane-diol (2)+1-pentanol (3) system and their RMSD values at T=298.2, 308.2, and 318.2 K and atmospheric pressure

T/K	τ_{ij}^a			RMSD
298.2	$\tau_{12}=1025.31$	$\tau_{13}=1586.4$	$\tau_{23}=1695.04$	0.0055
	$\tau_{21}=-869.76$	$\tau_{31}=193.533$	$\tau_{32}=-727.261$	
308.2	$\tau_{12}=-6348.32$	$\tau_{13}=1917.81$	$\tau_{23}=-287.263$	0.0101
	$\tau_{21}=35.5549$	$\tau_{31}=291.302$	$\tau_{32}=-4873.49$	
318.2	$\tau_{12}=-7738.58$	$\tau_{13}=1911.07$	$\tau_{23}=-283.614$	0.0094
	$\tau_{21}=173.933$	$\tau_{31}=216.879$	$\tau_{32}=-6200$	

$^a\tau_{ij}$ is a binary interaction parameter (dimensionless)

Table 7. Parameters of the UNIQUAC models for water (1)+2,3-butanediol (2)+1-pentanol (3) system and their RMSD values at T=298.2, 308.2, and 318.2 K and atmospheric pressure

T/K	τ_{ij}^a			RMSD
298.2	$\tau_{12}=-228.791$	$\tau_{13}=-359.054$	$\tau_{23}=-141.474$	0.0112
	$\tau_{21}=248.496$	$\tau_{31}=-4.94838$	$\tau_{32}=-132.671$	
308.2	$\tau_{12}=935.597$	$\tau_{13}=-465.79$	$\tau_{23}=-231.251$	0.0149
	$\tau_{21}=310.027$	$\tau_{31}=61.3889$	$\tau_{32}=1387.54$	
318.2	$\tau_{12}=404.274$	$\tau_{13}=-455.651$	$\tau_{23}=-287.266$	0.0138
	$\tau_{21}=249.436$	$\tau_{31}=60.3528$	$\tau_{32}=823.981$	

$^a\tau_{ij}$ is a binary interaction parameter (dimensionless)

more effective solvent than 1-butrhanol for extracting 2,3-butandiol. Root-mean-square deviation (RMSD) was calculated to confirm that both UNIQUAC and NRTL models successfully correlate the measured LLE data. Root-mean-square deviation is calculated by the following equation:

$$\text{RMSD} = \left[\frac{\Sigma_i^n \Sigma_j^n \Sigma_k^n (x_{ijk}^{exp} - x_{ijk}^{cal})^2}{6n} \right]^{1/2} \tag{12}$$

Table 6 and Table 7 summarize RMSD values and the calculated binary parameters determined by the UNIQUAC and NRTL models, respectively. We set the non-randomness parameter of the NRTL model (α_{ij}) to 0.3. Root-mean-square deviations of the UNIQUAC and NRTL model were less than 0.0149 and 0.0104, respectively. By comparing these values, it may be inferred that rather than UNIQUAC model, the NRTL model provides a better correlation for water+2,3-butanediol+1-pentanol ternary system. In general, if the RMSD values are shown to be less than 5%, the experimental data have a good correlation with the theoretical models used. Thus, it is concluded that the studied system could be successfully calculated by using the UNIQUAC and NRTL models. Both models and binary parameters suggested in this study could provide good help in optimizing or designing the 2,3-butanediol extraction process.

CONCLUSION

Liquid-liquid equilibria (LLE) were measured for the ternary system of 2,3-butanediol+water+1-pentanol at 298.2-318.2 K (in

10 K interval) and 1 atm. The separation factor (S) of 1-pentanol to 2,3-butanediol was found to be greater than that of 1-butanol and the distribution coefficients (D) were almost the same or slightly larger than those of 1-butanol in the temperature range studied in this work. This implies that 1-pentanol could be a promising organic solvent for extracting 2,3-butanediol from the fermentation broth. The regression coefficients (R^2) of the Othmer-Tobias plot and Hand plot were close to 1, which ascertained the consistency of the experimental LLE data. Furthermore, the UNIQUAC and NRTL models used to correlate the LLE data were found to fit well with the experimental results.

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