Phase Diagrams for the Aqueous Solutions of Carboxylic Acid with Dipropyl Ether: Experimental and Correlated Data

Özmen, Dilek*+; Bekri, Sezin

Istanbul University-Cerrahpaşa, Engineering Faculty, Department of Chemical Engineering, 34320, Istanbul, TURKEY

ABSTRACT: *In this research, liquid-liquid equilibrium (LLE) data were experimentally obtained for the ternary systems of (water + carboxylic acid + dipropyl ether) at T = 298.2 K and P = 101.3 kPa. The carboxylic acids used in this study were isobutyric acid, valeric acid, and isovaleric acid. All these systems are according to Treybal classification, Type-2 systems because the two binary subsystems are partially miscible. The lowest distribution coefficients and separation factors were calculated for isobutyric acid (40 and 329, respectively). The authenticity of the experimental equilibrium data was identified from Hand and Othmer-Tobias correlations. The experimental tie-line data were correlated by using the nonrandom two-liquid (NRTL) and universal quasi-chemical (UNIQUAC) activity coefficient models. RMSD values are between 0.0112 and 0.0155 for NRTL model and are between 0.0083 and 0.0153 for UNIQUAC model.*

KEYWORDS: *Liquid-liquid equilibrium; Carboxylic acid; Dipropyl ether; NRTL; UNIQUAC.*

INTRODUCTION

Carboxylic acids are significant organic compounds which were produced by chemical reactions or fermentation methods [1, 2]. Volatile esters of valeric and isovaleric acid tend to have pleasant odors and are used in perfumes and cosmetics [3]. Esters of isobutyric acid are used as solvents for various applications where desirable odors and flavor characteristics are important. The potassium salt of isobutyric acid is effective as a solubility promoter in the caustic extraction of mercaptans from sour petroleum stocks. Recovery of carboxylic acids from aqueous solutions is vital [4]. Liquid-Liquid Equilibrium (LLE) data are in the interest of extraction applications and are important for improving a thermodynamic predictive and consistent method. Phase equilibrium data are fundamentally important for the separation processes. Liquid-liquid extraction of carboxylic acids from aqueous solutions with manifold solvents has been worked by several researchers [2, 5-13].

Şenol [14] concluded that xylene, chlorobenzene, benzyl ether gives the largest distribution ratios and separation factors, as compared to 1-phenyl ethanol, cyclohexanol and 1-decanol for isovaleric acid recovery from aqueous solutions. *Özmen* and *Şenoymak* [15] evaluated mixed solvent (dipropyl ether / diisopropyl ether) for the separation of acetic acid from aqueous solutions. *Sólimo et al.* [16] and *Zurita et al.* [17] concluded that the addition of salt provides a noteworthy increase in the distribution coefficients and selectivities,

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Table 1: Chemicals used in this work.

Chemicals	IUPAC nomenclature	Chemical formula	Source	CAS-no	Mass fraction purity*
Isobutyric acid	2-methylpropanoic acid	$(CH_3)_2CHCOOH$	Merck	79-31-2	0.99
Valeric acid	pentanoic acid	$CH_3(CH_2)_3COOH$	Merck	109-52-4	0.98
Isovaleric acid	3-methylbutanoic acid	$(CH_3)_2CHCH_2COOH$	Merck	503-74-2	0.99
Dipropyl ether	1-propoxypropane	$(CH_3CH_2CH_2)O$	Merck	111-43-3	0.99

*Purities were provided by the manufacturers; the chemicals were used without any additional treatment.

while the region of heterogeneity increases as compared to the no-salt condition.

This study is a part of a research program on the recovery and modelling of carboxylic acids from dilute aqueous solutions using organic solvents [2, 18]. In this work, liquid–Liquid Equilibrium (LLE) data for the ternary mixtures of water + carboxylic acid (isobutyric acid, valeric acid or isovaleric acid) + dipropyl ether were determined at $T = 298.2$ K and $P = 101.3$ kPa. There are no data in the literature on these ternary systems.

For the assessment of the extraction capacity of dipropyl ether, the distribution coefficients and the separation factors are calculated from our experimental results. The experimental tie-line data compatibility was carried out using the nonrandom two-liquid (NRTL) and universal quasi-chemical (UNIQUAC) activity coefficient models [19-20]. The binary interaction parameters were calculated from experimental equilibrium values for both model. Then, the calculated tie-line values were compared with the experimental ones. Good agreement between the experimental and calculated data was obtained. Furthermore, the UNIQUAC model gives lower root-mean-square deviation (RMSD) values than the NRTL model.

EXPERIMENTAL SECTION
Chemicals
All chemicals except water used in this work were supplied by Merck. The purity of the chemical reagents was analyzed by Gas Chromatography (GC) and no peak of impurity was detected out. Chemicals used in this study were presented in Table 1. Distilled water prepared in our laboratory was used throughout all experiments (New Human Power I Water Purification System).

Method and Analysis
The experimental method and apparatus were explained in the previous studies [11-13]. For the experimental binodal (solubility) curves and the mutual solubilities of the (water-dipropyl ether) and (water-carboxylic acid) binaries were determined by the cloud point method using a thermostated shaker (NUVE ST 30) [10-13]. For the tie-line, the mixtures were prepared and put onto the thermostated shaker for 90 minutes. Preliminary tests showed that these 90 min durations were enough to achieve equilibrium. After shaking, all mixtures were centrifuged for 5 min. with a speed of 3000 rpm to separate water rich phase and solvent rich phase. At the end of the centrifuge time, all phases were transferred with special syringes to separate sample tubes. The liquid samples were analyzed by a Gas Chromatograph (HP6890 model), equipped with thermal conductivity detector (TCD) and flame ionization detector (FID) as parallel mode. Ultra1 Methyl Siloxane column (50m x 320μm x 0.17μm) was utilized to distinguish dipropyl ether, isobutyric acid, valeric acid and isovaleric acid of samples at tailorized oven programs. The FID and TCD detector temperatures were kept at $T = 493.2$ K while injection port temperature was held at $T = 473.2$ K. Injections were performed on the split 70/1 mode. Helium was used as a carrier at a rate of 1.2 $cm^3.min^{-1}$. Oven program was programmed starting from 333.2 K. This temperature was hold for 2 min. The temperature was increased at a rate of 303.2 K/min and held for 2 min. And finally, the temperature was ramped for 288.2 K/min and held at this temperature for 10 min. Thermal conductivity detector (TCD) was used to determine the composition of water. The precision of the compositions of the tie-lines was within 5×10^{-4} mole fraction. Experiments were performed in triplicate and repeated at least three times with similar results were obtained.

RESULTS AND DISCUSSION
LLE Experimental Data
The experimental tie-line data of (water + isobutyric acid + dipropyl ether), (water + valeric acid + dipropyl ether), and (water + isovaleric acid + dipropyl ether)

Table 2: Experimental tie-line data for water (1) + carboxylic acid (2) + dipropyl ether (3) ternary systems at
T = 298.2 K and P = 101.3 kPa^a.

x_{11}	x_{21}	x_{31}	x_{13}	x_{23}	x_{33}
water (1) + isobutyric acid (2) + dipropyl ether (3)					
0.9998[b]	0.0000	0.0002	0.0220 [b]	0.0000	0.9780
0.9394 [b]	0.0606	0.0000	0.8487 [b]	0.1513	0.0000
0.9935	0.0056	0.0009	0.0115	0.2168	0.7717
0.9891	0.0100	0.0009	0.0159	0.3962	0.5879
0.9856	0.0134	0.0010	0.0212	0.5107	0.4681
0.9818	0.0172	0.0010	0.0540	0.5952	0.3508
0.9782	0.0207	0.0011	0.0952	0.6623	0.2425
water (1) + valeric acid (2) + dipropyl ether (3)					
0.9998 [b]	0.0000	0.0002	0.0220 [b]	0.0000	0.9780
0.9918 [b]	0.0082	0.0000	0.4752 [b]	0.5248	0.0000
0.9982	0.0011	0.0007	0.0480	0.1783	0.7737
0.9970	0.0023	0.0007	0.0480	0.3118	0.6402
0.9959	0.0033	0.0008	0.0485	0.4069	0.5446
0.9953	0.0040	0.0007	0.0490	0.5032	0.4478
0.9947	0.0046	0.0007	0.0695	0.5743	0.3562
water (1) + isovaleric acid (2) + dipropyl ether (3)					
0.9998 [b]	0.0000	0.0002	0.0220 [b]	0.0000	0.9780
0.9890 [b]	0.0010	0.0000	0.4180 [b]	0.5820	0.0000
0.9974	0.0017	0.0009	0.0112	0.1920	0.7968
0.9959	0.0033	0.0008	0.0234	0.3604	0.6162
0.9948	0.0044	0.0008	0.0288	0.4848	0.4864
0.9942	0.0050	0.0008	0.0495	0.5841	0.3664
0.9930	0.0062	0.0008	0.0547	0.6808	0.2645

^{a} *Standard uncertainties u are u(x) = 0.0005, u(T) = 0.2 K and u(P) = 0.7 kPa.*
^{b} *Mutual solubility value*

at T =298.2 K were reported in Table 2, in which x_{i1} and x_{i3} refer to mole fractions of the *i*th component in the aqueous and solvent phase, respectively. All these systems are according to Treybal classification, Type-2 systems because the two binary subsystems are partially miscible (Figs. 1-3).

Reliability of Experimental Tie-Line Data

The Hand and Othmer-Tobias correlations [21-22] were applied to measure consistency of the experimental

tie-line data. These correlations were shown in Eqs. (1) and (2), respectively:

$$\ln\left(\frac{x_{23}}{x_{33}}\right) = A' + B'\left(\frac{x_{21}}{x_{11}}\right) \tag{1}$$

$$\ln\left(\frac{1-x_{33}}{x_{33}}\right) = A + B\ln\left(\frac{1-x_{11}}{x_{11}}\right) \tag{2}$$

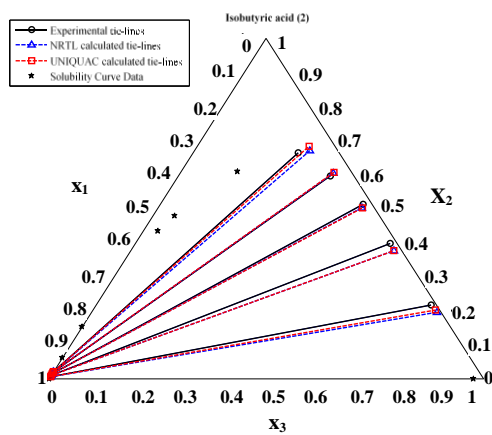where A', B' and A, B are the constants of the Hand and Othmer-Tobias correlation equations, respectively.

Fig. 1: Phase diagram for LLE data of the water (1) + isobutyric acid (2) + dipropyl ether (3) ternary mixture at T = 298.2 K and P = 101.3 kPa.

Fig. 2: Phase diagram for LLE data of the water (1) + valeric acid (2) + dipropyl ether (3) ternary mixture at T = 298.2 K and P = 101.3 kPa..

Fig. 1: Phase diagram for LLE data of the water (1) + isobutyric acid (2) + dipropyl ether (3) ternary mixture at T = 298.2 K and P = 101.3 kPa.
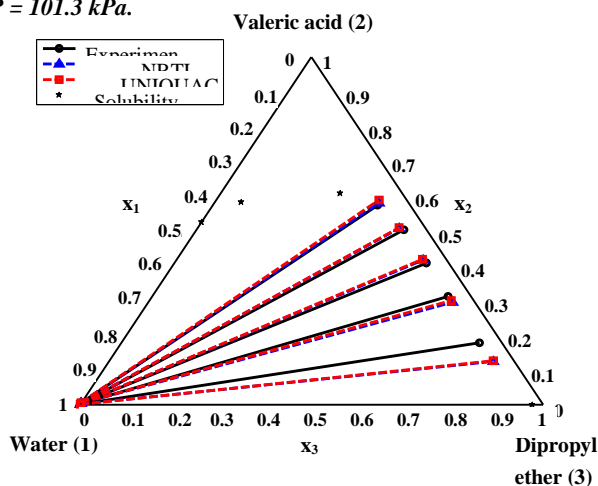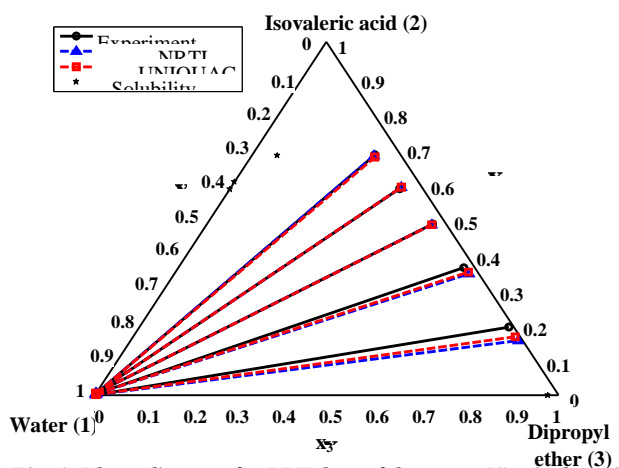
The value of the correlation factor (R^2) being close to unity, indicates the degree of consistency of the related data. The equation constants were listed in Table 3 and the Hand and Othmer-Tobias plots shown in Figs. 4 and 5 for the studied ternary systems.

Distribution Coefficients and Separation Factors

The effectiveness of extraction was confirmed with distribution coefficients (D_i) and the separation factors (S):

$$S = \frac{\text{distribution coefficient of carboxylic acid (D}_2)}{\text{distribution coefficient of water (D}_1)} = \quad (3)$$

$$\frac{x_{23}/x_{21}}{x_{13}/x_{11}}$$

If S is found to be greater than 1, it means that the extraction of acids by dipropyl ether is feasible. The distribution coefficients and separation factors for each carboxylic acid were given in Table 4. Also, the extracting performances of dipropyl ether for isobutyric acid, valeric acid and isovaleric acid are shown in Figs. 6 and 7.

When compared with our previous work (propionic acid and dipropyl ether) [23], the better results are obtained in terms of separation factor (S) for propionic acid. While in our previous work, the separation factor was calculated as 220 for propionic acid, in this study, the separation factor values are calculated as 10050, 3371 and 3345 for isovaleric, valeric and isobutyric acids, respectively. However, in the literature, there are some studies with better results for isovaleric and valeric acids [24, 25].

Data Correlation Models

The NRTL and UNIQUAC models [19-20] were applied to correlate the experimental tie-line data. Firstly, for these thermodynamic models, the following objective function was minimized and optimum binary interaction parameters were obtained.

$$OF_1 = \sum_{j=1}^{N} \sum_{i=1}^{3} \frac{\left(x_{ij}^{I}\gamma_{ij}^{I} - x_{ij}^{II}\gamma_{ij}^{II}\right)^2}{\left(x_{ij}^{I}\gamma_{ij}^{I} + x_{ij}^{II}\gamma_{ij}^{II}\right)^2} \quad (4)$$

Where x^I_{ij} and x^{II}_{ij} refer to the experimental mole fractions of component i of water-rich and solvent-rich phase, respectively, along tie-line j. γ^I_{ij} and γ^{II}_{ij} are the corresponding activity coefficients. N indicates the number of tie-lines. Then, the optimum binary interaction

Table 3: Constants of Hand and Othmer-Tobias equation for the water + carboxylic acid + dipropyl ether ternary systems
*(R^2: regression coefficient).*

Ternary System	Hand correlation			Othmer-Tobias correlation		
	A'	B'	R^2	A	B	R^2
Water + isobutyric acid + dipropyl ether	7.3740	1.6801	0.9921	8.1466	1.8754	0.9896
Water + valeric acid + dipropyl ether	7.2635	1.2956	0.9654	8.7435	1.5918	0.9607
Water + isovaleric acid + dipropyl ether	9.8984	1.7955	0.9678	12.7960	2.3958	0.9826

Table 4: Experimental distribution coefficients (Di) of the (water and carboxylic acid) and seperation factors (S).

D_1	D_2	S
water (1) + isobutyric acid (2) + dipropyl ether (3)		
0.0116	39	3345
0.0161	40	2465
0.0215	38	1772
0.0550	35	629
0.0973	32	329
water (1) + valeric acid (2) + dipropyl ether (3)		
0.0481	162	3371
0.0481	136	2816
0.0487	123	2532
0.0492	126	2555
0.0699	125	1787
water (1) + isovaleric acid (2) + dipropyl ether (3)		
0.0112	113	10058
0.0235	109	4648
0.0290	110	3806
0.0498	117	2346
0.0551	110	1993
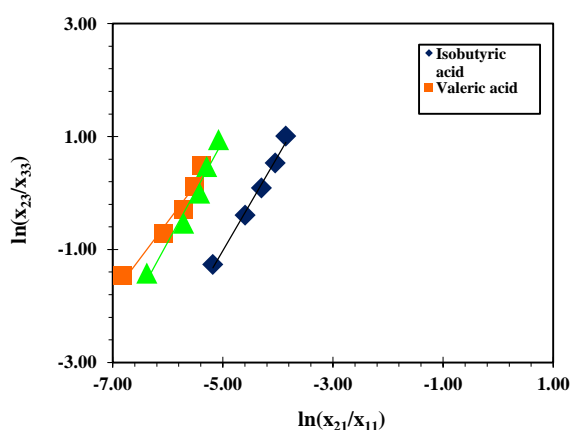
Fig. 4: Hand plot for LLE data of the water + carboxylic acid + dipropyl ether ternary systems at T= 298.2 K and P = 101.3 kPa.
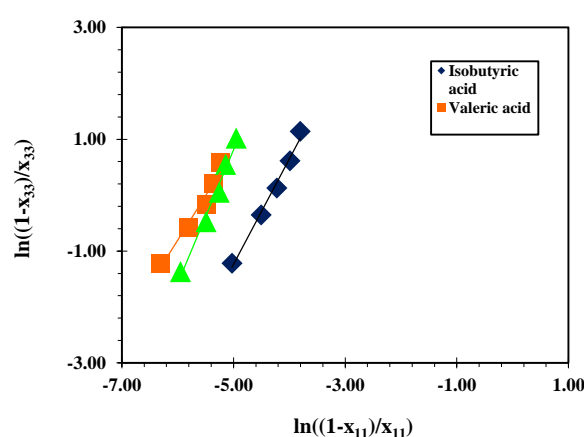
Fig. 5: Othmer-Tobias plot for LLE data of the water + carboxylic acid + dipropyl ether ternary systems at T= 298.2 K and P = 101.3 kPa.
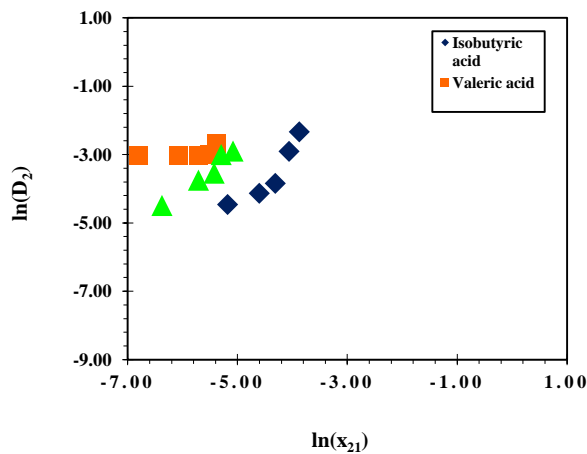
Fig. 6: Distribution coefficients of carboxylic acids (D₂) as a function of the mole fraction of carboxylic acids in water-rich phase (x₂₁).

parameters obtained above are used as the initial guesses of the *OF₂*.

$$OF_2 = \sum_k \sum_j \sum_i \left(x_{ijk}^{expl} - x_{ijk}^{calc} \right)^2 \tag{5}$$

Where x_{ijk}^{expl} and x_{ijk}^{calc} are the experimental and calculated compositions of component *i* in phase *j* along a tie-line *k*, respectively. The experimental and model calculated tie-line data from NRTL and UNIQUAC models are listed in Tables 5 and 6. The optimized NRTL and UNIQUAC binary interaction parameters of the researched ternary systems are reported in Table 7. The volume (r_i) and area (q_i) structural parameters for the UNIQUAC model are given in Table 8.

The root-mean-square deviation (RMSD) is used for the quality of the correlation model:

$$RMSD = \sqrt{\frac{\sum_{k=1}^{N} \sum_{j=1}^{2} \sum_{i=1}^{3} \left(x_{ijk} - \hat{x}_{ijk} \right)^2}{6N}} \tag{6}$$

The RMSD results were given in Tables 5 and 6, nearby the calculated tie-line data. The experimental and predicted tie-line data were plotted together in Figs. 1-3. From the figures, it can be seen that the immiscibility gap of the valeric acid is smaller than the others. Solubility curve data are given in the Table 9.
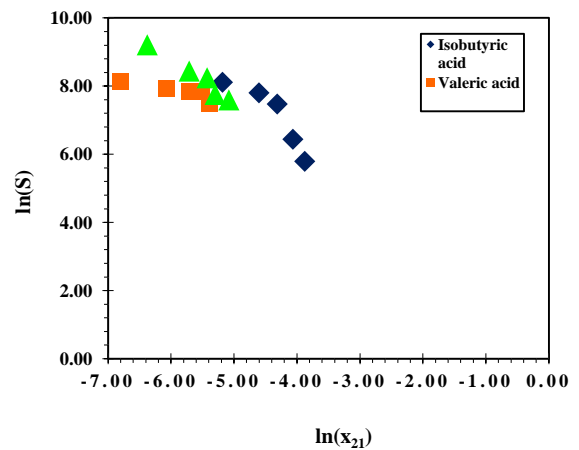

Fig. 7: Separation factors (S) as a function of the mole fraction of carboxylic acids in water-rich phase (x₂₁)

CONCLUSIONS

Liquid–liquid equilibrium data for the three ternary mixtures (water + carboxylic acid + dipropyl ether) were determined at 298.2 K and 101.3 kPa. All investigated ternaries demonstrate Type-2 system [26]. The slope of the tie lines show that all acids are more soluble in solvent-rich phases than in water-rich phases. The distribution coefficients (D_i), separation factors (S) and slopes of tie-lines proved that dipropyl ether was a favorable solvent for the extraction of each acid from dilute aqueous solutions.

The consistency of experimentally measured tie-line data was correlated by Hand and Othmer–Tobias equations, giving a correlation factor (R^2) approximate to 1. Although both models give good agreement with the experimental data, UNIQUAC model gives better RMSD values than the NRTL model. RMSD values are between 0.0112 and 0.0155 for NRTL model; and are between 0.0083 and 0.0153 for UNIQUAC model.

Nomenclature

A_{ij}	NRTL binary interaction parameter, $A_{ij}=\Delta g_{ij}/R$
A, B	The Othmer-Tobias equation constants
A', B'	The Hand equation constants
B_{ij}	UNIQUAC binary interaction parameter, $B_{ij}=\Delta u_{ij}/R$

***Table 5: Experimental and NRTL model calculated tie-line data for water (1) + carboxylic acid (2) + dipropyl ether (3)
ternary systems at T = 298.2 K and P = 101.3 kPa with RMSD values[a].***

Water-rich phase						Solvent-rich phase					
x_{11}		x_{21}		x_{31}		x_{13}		x_{23}		x_{33}	
Exp.	Model	Exp.	Model	Exp.	Model	Exp.	Model	Exp.	Model	Exp.	Model
water (1) + isobutyric acid (2) + dipropyl ether (3) RMSD=1.12x10^{-2}											
0.9935	0.9935	0.0056	0.0053	0.0009	0.0012	0.0115	0.0089	0.2168	0.1951	0.7717	0.7960
0.9891	0.9891	0.0100	0.0099	0.0009	0.0010	0.0159	0.0181	0.3962	0.3747	0.5879	0.6072
0.9856	0.9856	0.0134	0.0135	0.0010	0.0009	0.0212	0.0288	0.5107	0.5006	0.4681	0.4706
0.9818	0.9818	0.0172	0.0173	0.0010	0.0009	0.0540	0.0443	0.5952	0.6026	0.3508	0.3531
0.9782	0.9782	0.0207	0.0209	0.0011	0.0009	0.0952	0.0643	0.6623	0.6698	0.2425	0.2659
water (1) + valeric acid (2) + dipropyl ether (3) RMSD=1.55x10^{-2}											
0.9982	0.9982	0.0011	0.0009	0.0007	0.0009	0.0480	0.0445	0.1783	0.1245	0.7737	0.8310
0.9970	0.9970	0.0023	0.0022	0.0007	0.0008	0.0480	0.0469	0.3118	0.2955	0.6402	0.6576
0.9959	0.9959	0.0033	0.0034	0.0008	0.0007	0.0485	0.0507	0.4069	0.4153	0.5446	0.5340
0.9953	0.9953	0.0040	0.0041	0.0007	0.0006	0.0490	0.0562	0.5032	0.5070	0.4478	0.4368
0.9947	0.9947	0.0046	0.0047	0.0007	0.0006	0.0695	0.0631	0.5743	0.5800	0.3562	0.3569
water (1) + isovaleric acid (2) + dipropyl ether (3) RMSD=1.12x10^{-2}											
0.9974	0.9974	0.0017	0.0015	0.0009	0.0011	0.0112	0.0099	0.1920	0.1539	0.7968	0.8362
0.9959	0.9959	0.0033	0.0032	0.0008	0.0009	0.0234	0.0199	0.3604	0.3443	0.6162	0.6358
0.9948	0.9948	0.0044	0.0044	0.0008	0.0008	0.0288	0.0316	0.4848	0.4818	0.4864	0.4866
0.9942	0.9942	0.0050	0.0050	0.0008	0.0008	0.0495	0.0450	0.5841	0.5881	0.3664	0.3669
0.9930	0.9930	0.0062	0.0062	0.0008	0.0008	0.0547	0.0588	0.6808	0.6785	0.2645	0.2627

[a] *Standard uncertainties u are u(x) = 0.0005, u(T) = 0.2 K and u(P) = 0.7 kPa.*

***Table 6: Experimental and UNIQUAC model calculated tie-line data for water (1) + carboxylic acid (2) + dipropyl ether (3)
ternary systems at T = 298.2 K and P = 101.3 kPa with RMSD values[a].***

Water-rich phase						Solvent-rich phase					
x_{11}		x_{21}		x_{31}		x_{13}		x_{23}		x_{33}	
Exp.	Model	Exp.	Model	Exp.	Model	Exp.	Model	Exp.	Model	Exp.	Model
water (1) + isobutyric acid (2) + dipropyl ether (3) RMSD=1.09x10⁻²											
0.9935	0.9935	0.0056	0.0054	0.0009	0.0011	0.0115	0.0094	0.2168	0.2002	0.7717	0.7904
0.9891	0.9891	0.0100	0.0099	0.0009	0.0010	0.0159	0.0177	0.3962	0.3762	0.5879	0.6061
0.9856	0.9856	0.0134	0.0135	0.0010	0.0009	0.0212	0.0275	0.5107	0.5010	0.4681	0.4715
0.9818	0.9818	0.0172	0.0173	0.0010	0.0009	0.0540	0.0416	0.5952	0.6050	0.3508	0.3534
0.9782	0.9782	0.0207	0.0208	0.0011	0.0010	0.0952	0.0608	0.6623	0.6815	0.2425	0.2577
water (1) + valeric acid (2) + dipropyl ether (3) RMSD=1.53x10⁻²											
0.9982	0.9982	0.0011	0.0009	0.0007	0.0009	0.0480	0.0442	0.1783	0.1263	0.7737	0.8295
0.9970	0.9970	0.0023	0.0022	0.0007	0.0008	0.0480	0.0477	0.3118	0.2996	0.6402	0.6527
0.9959	0.9959	0.0033	0.0034	0.0008	0.0007	0.0485	0.0511	0.4069	0.4183	0.5446	0.5306
0.9953	0.9953	0.0040	0.0041	0.0007	0.0006	0.0490	0.0552	0.5032	0.5103	0.4478	0.4345
0.9947	0.9947	0.0046	0.0047	0.0007	0.0006	0.0695	0.0602	0.5743	0.5882	0.3562	0.3516
water (1) + isovaleric acid (2) + dipropyl ether (3) RMSD=8.3x10⁻³											
0.9974	0.9974	0.0017	0.0016	0.0009	0.0010	0.0112	0.0104	0.1920	0.1642	0.7968	0.8254
0.9959	0.9959	0.0033	0.0032	0.0008	0.0009	0.0234	0.0201	0.3604	0.3489	0.6162	0.6310
0.9948	0.9948	0.0044	0.0044	0.0008	0.0008	0.0288	0.0312	0.4848	0.4827	0.4864	0.4861
0.9942	0.9942	0.0050	0.0051	0.0008	0.0007	0.0495	0.0447	0.5841	0.5880	0.3664	0.3673
0.9930	0.9930	0.0062	0.0062	0.0008	0.0008	0.0547	0.0584	0.6808	0.6738	0.2645	0.2678

[a] *Standard uncertainties u are u(x) = 0.0005, u(T) = 0.2 K and u(P) = 0.7 kPa.*

Table 7: NRTL and UNIQUAC Binary Interaction Parameters for the water (1) + carboxylic acid (2) + dipropyl ether (3)
Ternary Systems at T=298.2 K and P = 101.3 kPa*

	NRTL model (α_{ij}=0.20)	UNIQUAC model
water (1) + isobutyric acid (2) + dipropyl ether (3)		
i,j[a]	$A^b_{ij}=\Delta g_{ij}/R$	$B^c_{ij}=\Delta u_{ij}/R$
1,2	1305.8328	67.9470
2,1	129.1792	620.6020
1,3	1421.1359	91.0592
3,1	1175.7735	1103.1225
2,3	3293.2390	5451.4289
3,2	-20.0449	-194.7991
water (1) + valeric acid (2) + dipropyl ether (3)		
i,j	A_{ij}	B_{ij}
1,2	1574.9471	96.1629
2,1	214.2901	638.2331
1,3	1685.8231	128.8545
3,1	461.6221	607.2971
2,3	2248.3767	970.4875
3,2	-225.8838	-215.5112
water (1) + isovaleric acid (2) + dipropyl ether (3)		
i,j	A_{ij}	B_{ij}
1,2	1384.6156	88.7979
2,1	233.2692	605.0217
1,3	1454.6978	93.0631
3,1	1043.6876	1059.9919
2,3	1279.1038	999.7494
3,2	-346.9380	-202.9134

*Standard uncertainty u are u (T) = 0.2 K and u(P) = 0.7 kPa.
[a] i-j pair of components: water (1), carboxylic acid (2), dipropyl ether (3). [b] $A_{ij}=(g_{ij}-g_{jj})/R$ [c] $B_{ij}=(u_{ij}-u_{jj})/R$

Table 8: The volume (r_i) and area (q_i) structural parameters for the UNIQUAC model.

Component	r	q
Water	0.9200	1.4000
Isobutyric acid	3.5504	3.1480
Valeric acid	4.2256	3.6920
Isovaleric acid	4.2248	3.6880
Dipropyl ether	4.7437	4.0960

***Table 9: Experimental Solubility Curve Data for the water (1) + carboxylic acid (2) + dipropyl ether (3)
ternary mixture at T = 298.2 K and P = 101.3 kPa[a].***

x_1	x_2	x_3
water (1) + isobutyric acid (2) + dipropyl ether (3)		
0.5327	0.4321	0.0353
0.4704	0.4783	0.0516
0.2620	0.6072	0.1308
water (1) + valeric acid (2) + dipropyl ether (3)		
0.3591	0.5829	0.0580
0.1338	0.6072	0.2590
water (1) + isovaleric acid (2) + dipropyl ether (3)		
0.2677	0.6767	0.0556

[a] *Standard uncertainties u are u(x) = 0.003, u(T) = 0.2 K and u(P) = 0.7 kPa.*

D_i	Distribution coefficient of component i
Δg_{ij}	NRTL binary parameter for the interaction energy between components i and j relative to the interaction energy of j with itself
g_{ij}	NRTL energy parameter, J/mol
N	Number of tie-lines
q	The relative van der Waals surface area parameter
R	The universal gas constant
R^2	Correlation factor for Othmer-Tobias and Hand equations
RMSD	Root mean square deviation
r	The relative van der Waals volume parameter
S	Separation factor
T	Temperature, K
Δu_{ij}	UNIQUAC binary parameter for the interaction energy between components i and j relative to the interaction energy of j with itself
u_{ij}	UNIQUAC energy parameter, J/mol
x_i	Mole fraction of component i
x_{ij}	Mole fraction of component i in phase j
x_{ijk}	The experimental mole fraction of component i in phase j along tie-line k

Greek letters

α_{ij}	The nonrandomness parameter
γ_{ij}	Activity coefficient of component i along a tie-line j
τ_{ij}	NRTL ($\tau_{ij}=A_{ij}/T$) and UNIQUAC ($\tau_{ij}=-B_{ij}/T$) interaction parameters

Subscripts

calc	Calculated values
expl	Experimental values
I	Aqueous phase
II	Solvent phase

REFERENCES

[1] Lidén G., Carboxylic Acid Production, *Fermentation*, **46**:1-3 (2017).

[2] Turkmenoğlu A., Özmen D., Bekri S., Phase Equilibrium Study and Data Correlations for the Ternary Mixture of (Water–Butyric Acid-[Hmim][Pf6]) At Different Temperatures, *Journal of Chemical Engineering of Japan*, **52**:1–7 (2019).

[3] Saeed A., Iqbal Z., Gulzar Z., Hai Z., Akram M., Liaqat L., Tara Z., Mansha M., Khalil H.I., Gc-Fid and Physicochemical Studies of Oil from The Leaves of Ficus Elastic Linn, *World Journal of Pharmaceutical Research*, **6**: 47-53 (2017).

[4] Isobutyric Acid (Last Access Date: July 25, 2019)

[5] Badakhshan A., Chowdhury A.I., Leung R., Effect of Temperature on Liquid-Liquid Equilibria for Three Systems Containing Acetic Acid-Water-Toluene, Propionic Acid-Water-Cyclohexane, Propionic Acid-Water-Toluene at Atmospheric Pressure, *J. Chem. Eng. Data*, **30**: 416-421 (1985).

[6] Timedjeghdine M., Hasseine A., Binous H., Bacha O., Attarakih M., Liquid–Liquid Equilibrium Data for Water + Formic Acid + Solvent (Butyl Acetate, Ethyl Acetate, and Isoamyl Alcohol) at T = 291.15 K, *Fluid Phase Equilib.*, **415**: 51-57 (2016).

[7] Radwan G.M., Al Muhtaseb S.A., Phase Equilibria of the Ternary System Water + Propionic Acid + 2-Butanol, *Sep. Sci. and Technol*., **32**: 1463-1476 (1997).

[8] Luo L., Liu D., Li L., Chen Y., Phase Equilibria of (Water + Propionic Acid or Butyric Acid + 2-Methoxy-2-Methylpropane) Ternary Systems at 298.2 K And 323.2 K, *Fluid Phase Equilib*., **403**: 30-35 (2015).

[9] Lalikoglu M., Bilgin M., Ternary Phase Diagrams for Aqueous Mixtures of Butyric Acid with Several Solvents: Experimental and Correlated Data, *Fluid Phase Equilib*., **371**: 50-56 (2014).

[10] Ghanadzadeh Gilani A., Ghanadzadeh Gilani H., Amouzadeh F., Tie Line Data for the (Water + Butyric Acid + N-Butyl Alcohol or Amyl Alcohol) at T = (298.2, 308.2, And 318.2) K and (Water + Butyric Acid + Isoamyl Alcohol) At T = 298.2 K, *J. Chem. Thermodyn.*, **71**: 103-111 (2014).

[11] Özmen D., Çehreli S., Dramur U., (Liquid + Liquid) Equilibria of (Water + Propionic Acid + Dimethyl Phthalate) at Several Temperatures, *J. Chem. Thermodyn*., **37**: 837-842 (2005).

[12] Özmen D., Determination and Correlation of Liquid–Liquid Equilibria for the (Water + Carboxylic Acid + Dimethyl Maleate) Ternary Systems At T = 298.2 K, *Fluid Phase Equilib*., **269**: 12-18 (2008).

[13] Çehreli S., Özmen D., Tatlı B., (Liquid + Liquid) Equilibria of (Water + Propionic Acid + Diethyl Phthalate) at Several Temperatures, *J. Chem. Thermodyn*., **37**: 1144-1150 (2005).

[14] Şenol A., Optimization and Modeling of Extraction Equilibria of the Type 2 Ternary Systems Containing (Water + Isovaleric Acid + Solvent), *J. Chem. Thermodyn*., **91**: 211–224 (2015).

[15] Özmen D., Şenoymak M. İ., Liquid + Liquid Equilibria For The Quaternary Systems of (Water + Acetic Acid + Mixed Solvent) at 298.2 K and Atmospheric Pressure, *Fluid Phase Equilib.*, **298**: 293-297 (2010).

[16] Sólimo H.N., Bonatti C.M., Zurita J.L., Gramajo De Doz M.B, Liquid-Liquid Equilibria for the System Water + Propionic Acid + 1-Butanol at 303.2 K. Effect of Addition of Sodium Chloride, *Fluid Phase Equilib*., **137**: 163-172 (1997).

[17] Zurita J.L., Gramajo De Doz M.B., Bonatti C.M., Sólimo H.N., Effect of Addition of Calcium Chloride on the Liquid−Liquid Equilibria of the Water + Propionic Acid + 1-Butanol System at 303.15 K, *J. Chem. Eng. Data*., **43**: 1039-1042 (1998).

[18] Bekri S., Özmen D., Özmen A., Correlation of Experimental Liquid–Liquid Equilibrium Data for Ternary Systems Using Nrtl and Gmdh-Type Neural Network, *J. Chem. Eng. Data.*, **62**: 1797-1805 (2017).

[19] Renon H., Prausnitz J. M., Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures, *AIChE J*., **14**: 135-144 (1968).

[20] Poling B.E., Prausnitz J.M., O'Connell J.P., "The Properties of Gases and Liquids", Fifth Edition, Mcgraw-Hill Inc, (2001).

[21] Hand D.B., Dinaric Distribution, *J. Phys. Chem*., **34**: 1961-2000 (1929).

[22] Othmer T.F., Tobias P.E., Liquid-Liquid Extraction Data - The Line Correlation, *Ind. Eng. Chemistry*, **34**: 693-696 (1942).

[23] Özmen D., (Liquid + Liquid) Equilibria of (Water + Propionic Acid + Dipropyl Ether or Diisopropyl Ether) at T = 298.2 K, *J. Chem. Thermodyn*., **39**: 123-127 (2007).

[24] Şenol A., Baslıoğlu B., Bilgin M., Estimation of Liquid-Liquid Equilibrium of Type 2 Systems (Water + Valeric Acid + Monobasic Ester or Dibasic Ester or Alcohol) Using Serlas, Serlas-Modified, and Serlas-Integrated, *The Canadian J. of Chemical Engineering*, **96**: 815-828 (2018).

[25] Şenol A., Optimization and Modeling of Extraction Equilibria of the Type 2 Ternarysystems Containing (Water + Isovaleric Acid + Solvent) Optimization and Modeling of Extraction Equilibria of the Type 2 Ternarysystems Containing (Water + Isovaleric Acid + Solvent), *J. Chem. Thermodynamics*, **91**: 211–224 (2015).

[26] Treybal R.E., "Liquid Extraction", Mcgraw-Hill, New York, (1963).