

Liquid-liquid Equilibrium Data of Aqueous Mixtures of Butyric Acid with 2-Methylcyclohexanol at Different Temperatures and 102.1 kPa

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In the current study, ternary phase equilibria of (water + n-butyric acid + 2-methylcyclohexanol) were considered. Experimental tie-line data were measured at $T = 298.2, 308.5, \text{ and } 318.2$ K and 102.1 kPa. Type I LLE behavior was observed for the studied mixtures. Karl-Fischer and acid-base titrations were applied to analyze separated phases. The Hand and Othmer-Tobias equations were used to test the validity of obtained tie-line data. The regression coefficients of both equations were bigger than 0.99. Calculated separation factors (14.6 to 32.6) and distribution coefficients (1.5 to 4.8) proved that the studied solvent is very efficient for extraction of n-butyric acid from water. Thermodynamic modeling was performed by NRTL equation and root mean square deviations (3.54 to 4.11%) were calculated to investigate the quality of modeling.

Keywords: Liquid-liquid equilibria, n-Butyric acid, Hand, Othmer-Tobias, NRTL model

INTRODUCTION

The successful purification of fatty acids from water is of economic connotation in the pharmaceutical industry and fermentation processes. Several solvents in different classes have been examined and applied to progress the recovery of fatty acids from aqueous mixtures [1-15].

Liquid-liquid equilibrium (LLE) investigations have been executed for the mixtures including n-butyric acid (nBA) in a lot of organic solvents to develop the database for the separation and purification of the acid from water mixtures. Researchers have been interested in alcohols, esters, ketones, and hydrocarbons [16-43]. Between the studied solvents, alcohols have been excellent extractants for the recovery of nBA from water [16, 18, 20, 25, 36-38, 40]. Right-chain alcohols have received much attention in the extraction of fatty acids, but cyclic alcohols have been less taken into account. One cyclic alcohol with low vapor pressure is 2-methylcyclohexanol which has been used to

separate some fatty acids from the aqueous medium [44-46]. In this work, 2-methylcyclohexanol, the mixture of *cis* and *trans* (2MCH), was selected as an extractant to recover nBA from its aqueous solution. Tie-line data of the (water + nBA + 2MCH) ternary system were measured at different temperatures. The alcohol (2MCH) was investigated as a potentially proper solvent due to its possible ability for the removal of the acid because of suitable functional group, high boiling point (165-166 °C), and other positive parameters.

To choose a suitable solvent for the separation process using liquid-liquid extraction, 13 parameters must be inspected: separation factor (1), distribution coefficient (2), insolubility of solvent in raffinate (3), recoverability (4), density (5), interfacial tension (6), chemical reactivity (7), viscosity (8), vapor pressure (9), freezing point (10) non-toxicity (11), non-flammability (12) and low cost (13) [47]. By using 2MCH, 9 parameters (3-11) are satisfactorily good. Parameters 1 and 2 must be determined experimentally and according to this study, these two parameters are also proper. 2MCH is not a low-cost solvent

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but, it is recoverable because of chemical stability and the problem of cost could be neglected. As a result, 2MCH could be considered a very good solvent.

In the present research, experimental tie-line data were obtained at three different temperatures and in a wide range of biphasic region. The Hand [48] and Othmer-Tobias [49] empirical equations attested that the experimental data are reliable. The measured tie-line data of the ternary mixtures of the studied system were also regressed by the NRTL thermodynamic model of Renon and Prausnitz [50], and the values of the binary interaction parameters were optimized. Distribution coefficients and separation factors of the investigated system were afterward calculated by measured data to explore the efficiency of 2MCH for recovery of nBA.

Obtained experimental data and binary interaction parameters in this study have not been published until now and the valuable reported data could improve the literature database for the butyric acid purification process.

EXPERIMENTAL

2-Methylcyclohexanol and n-butyric acid were purchased from Merck. Bidistilled water was prepared in the lab. All materials were applied without any more purification. Information of used materials along with the refractive indices are inserted in Table 1.

The temperature of the solutions was controlled using a Testo (Model: 108-2) digital thermometer with an accuracy of ± 0.1 K and all weightings were performed by an electronic balance (KIA220) with an accuracy of ± 0.1 mg. Tie-line data of the ternary system (water + nBA + 2MCH) were obtained at 298.2, 308.2, and 318.2 K and atmospheric pressure (average of recorded pressures during the days of

experiments was 102.1 kPa).

Mixtures with known masses of water, nBA, and 2MCH were prepared in a water-jacketed glass cell with a volume of 50 ml. Each mixture was stirred for 2 h and after 2 h of relaxing, samples were taken from upper and lower (organic and aqueous) phases for analysis. The acid mass fraction in the organic phase was measured at different times and after 2 h of mixing and relaxing, no changes were observed in nBA mass fraction. This set of experiments was done before the main experiments to determine the proper equilibrium time. Each sample was titrated by Karl-Fischer (KF) and NaOH 0.1 M solutions. Acid-base titrations obtained mass fractions of nBA in aqueous (w_2^{aq}), and organic (w_2^{org}) phases while KF titrations obtained mass fractions of water in water (w_1^{aq}) and solvent (w_1^{org}) layers. The mass fractions of 2MCH in lower (w_3^{aq}) and upper (w_3^{org}) layers were obtained by mass balance equation ($w_1 + w_2 + w_3 = 1$). All experiments were done three times and averages were recorded. The standard uncertainty of all measurements was lower than ± 0.008 .

RESULTS AND DISCUSSION

Tie-line Data Treatments

Measured Tie-line data for the studied ternary system (water + nBA + 2MCH) are inserted in Table 2. Distribution coefficients of water ($D_1 = \frac{w_1^{org}}{w_1^{aq}}$) and nBA ($D_2 = \frac{w_2^{org}}{w_2^{aq}}$) and separation factors ($S = \frac{D_2}{D_1}$) calculated from experimental tie-lines are also given in the table.

As can be seen from the data of the table, mass fractions of water in the organic phase are between 8.2% at 298.2 K to 15.7% at 318.2 K. Little amounts of water in the organic of

Table 1. Source, Purity, and Refractive Indices of the Used Materials

Component	Acronym	CAS	Purity (mass percent)	Source/Purity analysis method	Refractive index (n_D^{20})
2-Methylcyclohexanol (mixture of <i>cis</i> and <i>trans</i> isomers)	2MCH	583-59-5	> 99.0	Merck/GC	1.333
n-Butyric acid	nBA	107-92-6	> 98.0	Merck/GC	1.399
Water	-	7732-18-5	> 99.5	-	1.461

Table 2. Measured Tie-line Data of the Ternary System (Water + n-Butyric acid + 2-Methylcyclohexanol) at 298.2, 308.2 and 308.2 K and Atmospheric Pressure

w_1^{aq}	w_2^{aq}	w_3^{aq}	w_1^{org}	w_2^{org}	w_3^{org}	D_1	D_2	S
$T = 298.2$ K								
0.953	0.031	0.016	0.082	0.087	0.831	0.086	2.81	32.6
0.934	0.049	0.017	0.096	0.196	0.708	0.103	4.00	38.9
0.917	0.066	0.017	0.112	0.302	0.586	0.122	4.58	37.5
0.899	0.083	0.018	0.125	0.385	0.490	0.139	4.64	33.4
0.874	0.107	0.019	0.136	0.501	0.363	0.156	4.68	30.1
0.851	0.128	0.021	0.145	0.612	0.243	0.170	4.78	28.1
$T = 308.2$ K								
0.936	0.042	0.022	0.087	0.083	0.830	0.093	1.98	21.3
0.918	0.058	0.024	0.099	0.189	0.712	0.108	3.26	30.2
0.896	0.079	0.025	0.119	0.296	0.585	0.133	3.75	28.2
0.879	0.094	0.027	0.131	0.381	0.488	0.149	4.05	27.2
0.850	0.120	0.030	0.143	0.497	0.360	0.168	4.14	24.6
0.826	0.142	0.032	0.149	0.607	0.244	0.180	4.27	23.7
$T = 318.2$ K								
0.920	0.051	0.029	0.094	0.076	0.830	0.102	1.49	14.6
0.899	0.069	0.032	0.104	0.181	0.715	0.116	2.62	22.7
0.876	0.090	0.034	0.128	0.289	0.583	0.146	3.21	22.0
0.863	0.102	0.035	0.135	0.374	0.491	0.156	3.67	23.4
0.829	0.133	0.038	0.152	0.490	0.358	0.183	3.68	20.1
0.805	0.154	0.041	0.157	0.598	0.245	0.195	3.88	19.9

Estimated standard uncertainties: Measured mass fractions, temperature and pressure: $u(w) = 0.008$, $u(T) = 0.1$ K and $u(P) = 0.5$ kPa.

phase causes better purification of nBA. One important parameter to justify the efficiency of liquid-liquid extraction is the amount of water transferring to the solvent phase. This amount affects to separation factor and the greater value of separation factor shows the better purification process. Mass fractions of acid in the organic phase are also larger than that of the aqueous phase and this causes saving in solvent consumption. Obtained data are also drawn in Fig. 1. The figure shows that the biphasic region is wide enough for an applied separation and the slope of tie-lines is suitable for efficient extraction. In addition, the temperature effect is obvious in the figure. The heterogeneous area gets smaller at higher temperatures and the slopes of tie-lines change but the effect is very tiny.

Distribution coefficients and separation factors reported

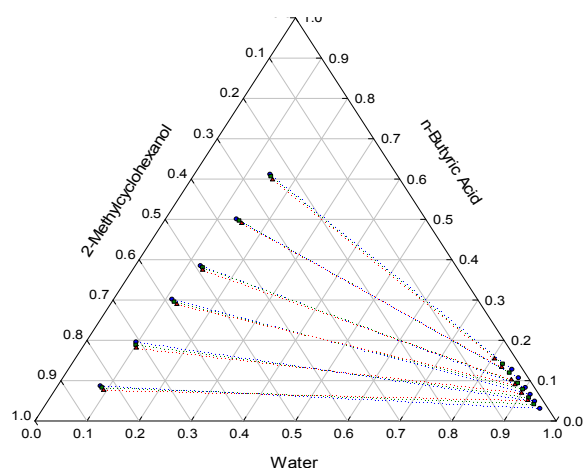


Fig. 1. Phase diagram of measured tie-line data of ternary system (water + n-butylc acid + 2-methylcyclohexanol) at (●) 298.2 K, (■) 308.2 K, and (▲) 318.2 K.

in Table 1 are plotted in Figs. 2a and 2b versus the mass fraction of nBA in the organic phase. As can be seen from Fig. 2a, distribution coefficients are very large and the values show that 2MCH has a large capacity for removal of nBA from water, but increasing of temperature decreases the ability of the solvent for extraction of nBA. Separation factors are important parameters in separation processes and the values must be larger than 1 to have a successful separation. Separation factors (Fig. 2b) at 298.2 K are larger than the values of other temperatures. This results that temperature increase is not a positive function for extraction of nBA from water using 2MCH. Every 10 °C increase in temperature lessens the efficiency of the solvent 16% in distribution coefficients and 22% in separation factors on average. Increasing nBA in initial feed compositions raises the distribution coefficients but the separation factors go through a maximum of 0.20 to 0.18 of w_{23} in the studied temperature range.

The Hand [48] and the Othmer-Tobias [49] equations are comprehensively used by researchers to investigate the quality of measured tie-lines. The equations are as follow:

$$\text{Hand Eq. } \ln\left(\frac{w_{21}}{w_{11}}\right) = A + B \ln\left(\frac{w_{23}}{w_{33}}\right)$$

$$\text{Othmer-Tobias Eq. } \ln\left[\frac{1-w_{33}}{w_{33}}\right] = A' + B' \ln\left[\frac{1-w_{11}}{w_{11}}\right]$$

The parameters A , B , A' and B' are numerical constants and type of system, degree of immiscibility and equilibrium compositions affect the parameters. The plots of Hand and Othmer-Tobias equations are shown in Figs. 3a and 3b. Linear regressions data of the plots are summarized in Table 3. R square values are very close to 1 and this proves the quality of measured tie-lines.

For comparison of obtained experimental tie-lines in this study with literature data, Table 4 was prepared. In the table, experimental distribution coefficients of C1-C5 right-chain carboxylic acids and separation factors were compared. Data of formic, acetic, propionic, and pentanoic acids ternary systems were taken from reference #45. As can be seen from the table, butyric acid distribution coefficients and separation factors are close to propionic acid data and consistent with other ternary systems. The

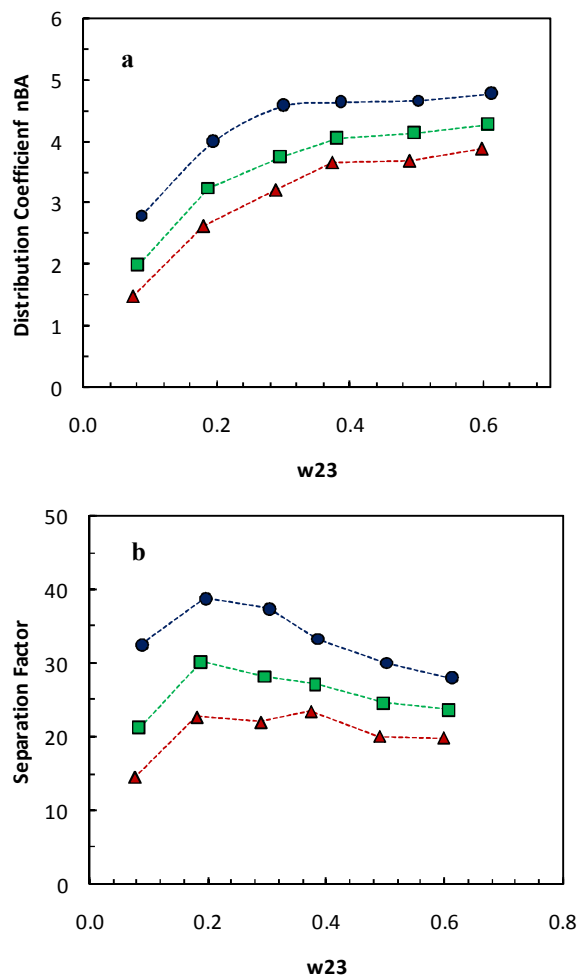


Fig. 2. Plots of (a) distribution coefficients and (b) separation factors for the ternary system (water + nBA + 2MCH) at (●) 298.2 K, (■) 308.2 K and (▲) 318.2 K.

ability of the solvent increases with increasing the number of carbons.

Thermodynamic Modeling

In this study, thermodynamic modeling of tie-line data was performed using NRTL equation:

$$\text{NRTL Eq. } \ln(\gamma_i) = \frac{\sum_{j=1}^3 x_j \tau_{ji} G_{ji}}{\sum_{k=1}^3 x_k G_{ki}} + \sum_{j=1}^3 \frac{x_j G_{ij}}{\sum_{k=1}^3 x_k G_{kj}} \left[\tau_{ji} - \frac{\sum_{m=1}^3 x_m \tau_{mj} G_{mj}}{\sum_{k=1}^3 x_k G_{kj}} \right]$$

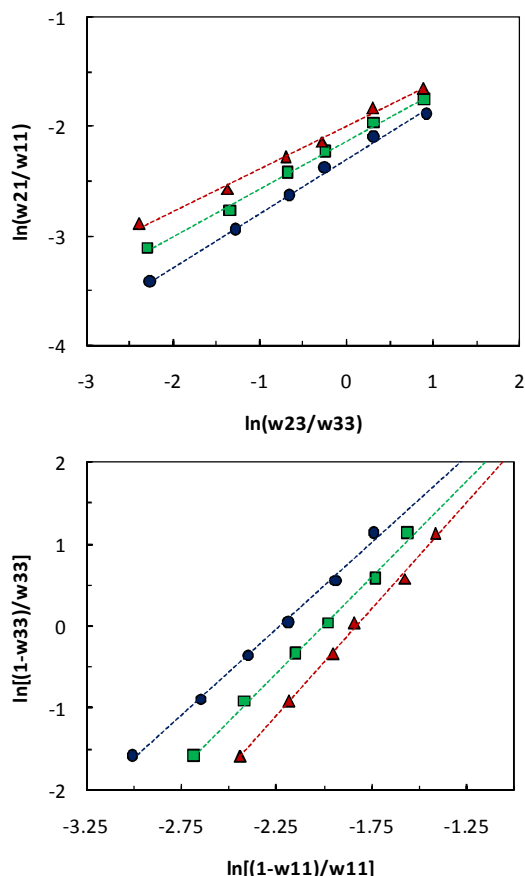


Fig. 3. The plots of (a) Hand and (b) Othmer-Tobias equations: (●) 298.2 K, (■) 308.2 K and (▲) 318.2 K.

where γ_i , x_i are the activity coefficient and mole fraction of component i and τ_{ij} is the interaction energy between molecules i and j . $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$ is a function of τ_{ij} and the parameter α_{ij} is a non-randomness value between 0 and 1 and usually is set to 0.3. In this research, the values 0.1, 0.2, 0.3, and 0.47 were tested for alpha value and best results were obtained when 0.3 had been selected as an alpha value. The binary NRTL parameters τ_{ij} and α_{ij} are adjustable and must be optimized for each ternary system. The primary rule is that $(\gamma_i x_i)^I = (\gamma_i x_i)^{II}$ which states that $\gamma_i x_i$ of two phases in equilibrium must be equal to each other.

Matlab software was employed to optimize parameters. After running the software, the range of parameters optimization was set between -1 to 1, -2 to 2, -3 to 3, -4 to 4, -5 to 5, and -6 to 6 and RMSD values were calculated to justify the best results. The optimized binary parameters for the ternary system (water + nBA + 2MCH) are inserted in Table 5. As can be seen from the table, binary parameters change with temperature increasing. The parameters τ_{12} , τ_{13} , and τ_{31} decrease with increasing the temperature and the rest have reverse behavior.

To investigate the effect of temperature on binary interaction parameters, the values were plotted against temperature in Fig. 4. The figure can clearly show that the temperature has a slight effect on binary interaction

Table 3. Results of Linear Regressions of the Hand and Othmer-Tibias Equations

Temperature	Hand parameters			Othmer-Tobias parameters		
	A	B	R ²	A'	B'	R ²
298.2 K	-2.300	0.494	0.995	4.708	2.106	0.995
308.2 K	-2.135	0.432	0.995	4.717	2.345	0.997
318.2 K	-1.997	0.387	0.994	4.773	2.603	0.997

Table 4. Distribution Coefficients and Separation Factors of the Ternary Systems (Water + Formic, Acetic, Propionic, Butyric, or Pentanoic Acid + 2-Methylcyclohexanol) at 298.2 K for nBa and 293.2 K for the Rest of Ternary Systems

D ₂	S	D ₂	S	D ₂	S	D ₂	S	D ₂	S
Formic	Acid	Acetic	Acid	Propionic	Acid	Butyric	Acid	Pentanoic	Acid
0.66	7.6	1.06	12.8	2.88	35.8	2.81	32.6	13.39	185.9
0.69	6.2	1.27	10.9	3.29	34.2	4.00	38.9	15.56	181.2
0.73	5.4	1.44	9.8	3.53	32.8	4.58	37.5	17.20	170.5
0.79	4.5	1.59	7.0	3.95	31.2	4.64	33.4	18.70	154.4
0.84	2.9	1.64	5.6	4.12	24.9	4.68	30.1	20.30	146.4

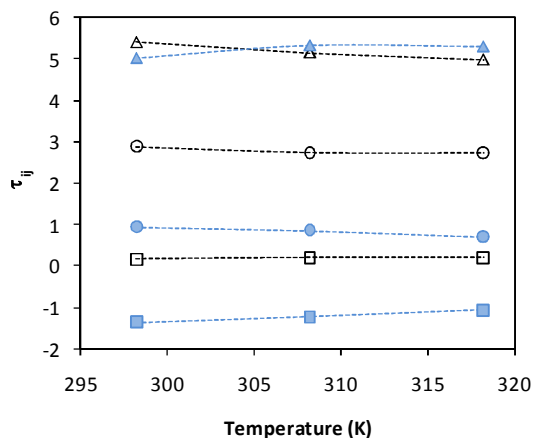


Fig. 4. The plot of binary interaction parameters *versus* temperature (K): (○) τ_{12} , (●) τ_{21} , (□) τ_{13} , (■) τ_{31} , (△) τ_{23} and (▲) τ_{32} .

parameters and this behavior can prove the consistency of obtained binary parameters because each optimization process was done separately and binary data are close to each other in different temperatures.

Table 5. Optimized NRTL ($\alpha = 0.3$) Binary Parameters (τ_{ij}) for the System (Water + nBA + 2MCH) at 298.2, 308.2 and 318.2 K

Component <i>i</i>	Component <i>j</i>	298.2	308.2	318.2
		K	K	K
Water (1)	nBA (2)	2.89	2.73	2.72
nBA (2)	Water (1)	0.16	0.20	0.20
Water (1)	2MCH (3)	5.42	5.16	4.98
2MCH (3)	Water (1)	0.94	0.85	0.70
nBA (2)	2MCH (3)	-1.37	-1.23	-1.07
2MCH (3)	nBA (2)	5.02	5.34	5.31

The quality of modeling can be tested by calculation of root mean square deviation (RMSD):

$$\%RMSD = \sqrt{\frac{\sum (w_{ex} - w_{NRTL})^2}{N}} \times 100 \quad (2)$$

where N is the number of experimental data. Tie-line data obtained from NRTL modeling along with the RMSD values are inserted in Table 6. Small RMSD values prove

Table 6. Correlated Tie-line Data Obtained from NRTL Modeling ($\alpha = 0.3$) of Experimental Data of the System (Water + nBA + 2MCH) at 298.2, 308.2, and 318.2 K

<i>T</i> (K)	w_1^{aq}	w_2^{aq}	w_3^{aq}	w_1^{org}	w_2^{org}	w_3^{org}	%RMSD
298.2	0.953	0.031	0.016	0.081	0.087	0.832	3.54
	0.934	0.048	0.017	0.101	0.200	0.699	
	0.915	0.067	0.018	0.109	0.287	0.604	
	0.896	0.085	0.018	0.114	0.354	0.532	
	0.870	0.112	0.018	0.120	0.437	0.442	
	0.847	0.135	0.018	0.126	0.498	0.376	
308.2	0.936	0.041	0.024	0.085	0.083	0.832	4.11
	0.916	0.059	0.025	0.105	0.188	0.708	
	0.893	0.081	0.026	0.113	0.279	0.608	
	0.874	0.099	0.027	0.117	0.339	0.544	
	0.845	0.128	0.027	0.123	0.420	0.457	
	0.821	0.152	0.027	0.128	0.479	0.393	
318.2	0.919	0.050	0.031	0.090	0.075	0.835	3.87
	0.898	0.069	0.034	0.112	0.184	0.704	
	0.874	0.091	0.035	0.122	0.276	0.602	
	0.857	0.108	0.035	0.125	0.332	0.542	
	0.825	0.140	0.035	0.130	0.422	0.448	
	0.803	0.163	0.034	0.134	0.478	0.387	

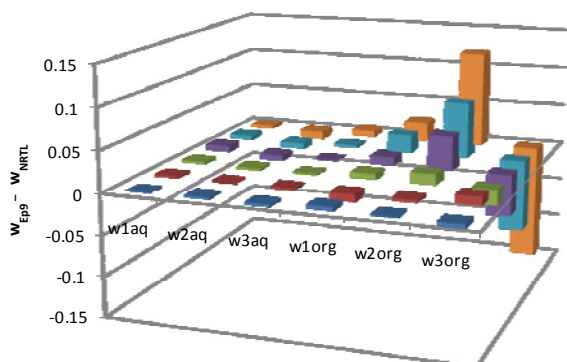


Fig. 5. The plot of differences between experimental and predicted data at 298.2 K.

the nearness of experimental and correlated data and the quality of modeling.

To show the differences between experimental and correlated tie-lines, a graph was prepared using data at 298.2 K. Figure 5 can demonstrate that the predictions in the aqueous phase and lower acid concentrations have better quality than that of the organic phase and higher concentrations of nBA.

CONCLUSIONS

Experimental LLE data for the (water + butyric acid + 2MCH) ternary system were measured at $T = 298.2, 308.2$ and 318.2 K. The R square values of Othmer-Tobias and Hand plots were larger than 0.99 and this showed that obtained data have a high degree of quality. Separation factors and distribution coefficients were calculated using tie-line data and the values were larger than 1.5 for D_2 and 20 for S and the values show that 2MCH is a very good solvent for the extraction of nBA from water. Temperature increasing decreased the ability of solvent for separation of acid from water. Both the distribution coefficients and separation factors were decreased in higher temperatures. NRTL modeling of tie-line data were finally performed and correlated data was obtained very close to experimental tie-lines (%RMSD < 4.11).

REFERENCES

- [1] Ghanadzadeh Gilani, H.; Ghanadzadeh Gilani, A.; Borji Peydeh, F.; Seyed Saadat, S.; Ahmadifar, S., Experimental and theoretical study of phase equilibria in aqueous mixtures of lactic acid with benzyl Alcohol and *p*-xylene at various temperatures. *Phys. Chem. Res.* **2016**, *4*, 489-505, DOI: 10.22036/pcr.2016.15062.
- [2] Shekarsaraee, S.; Naimi, A.; Bussary, B., Measurement, correlation and prediction of LLE data for the ternary system water + lactic acid + diethyl ether at 293.2 K. *Phys. Chem. Res.* **2021**, *9*, 181-192, DOI: 10.22036/pcr.2020.250264.1840.
- [3] Zarei, H.; Omidi, M.; Behroozi, M., Study of excess properties of binary and ternary mixtures of trichloroethene, ethanoic acid, and N,N-dimethylformamide at different temperatures. *Phys. Chem. Res.* **2019**, *7*, 347-363, DOI: 10.22036/pcr.2019.166303.1583.
- [4] Bahrpaima, Kh.; Bijanzadeh, A. R.; Behzadi, M., Effect of magnetic field on the liquid-liquid equilibria of (water + acetic acid + organic solvent) ternary systems. *Phys. Chem. Res.* **2017**, *5*, 125-134, DOI: 10.22036/pcr.2017.38854.
- [5] Merzougui, A.; Hasseine, A.; Kabouche, A.; Korichi, M., LLE for the extraction of alcohol from aqueous solutions with diethyl ether and dichloromethane at 293.15 K, parameter estimation using a hybrid genetic based approach. *Fluid Phase Equilib.* **2011**, *309*, 161-167, DOI: 10.1016/j.fluid.2011.07.011.
- [6] Behroozi, M.; Vahedpour, M.; Shardi Manaheji, M., Separation of formic acid from aqueous solutions by liquid extraction technique at different temperatures. *Phys. Chem. Res.* **2019**, *7*, 201-215, DOI: 10.22036/pcr.2019.154646.1557.
- [7] Xu, D.; Li, H.; Gao, J.; Liu, Z.; Zhang, L.; Liu, D.; Ma, X., Measurement and thermodynamic modeling of ternary liquid-liquid equilibrium for extraction of thioglycolic acid from aqueous solution with different solvents. *J. Chem. Thermodyn.* **2017**, *113*, 229-235, DOI: 10.1016/j.jct.2017.06.015.
- [8] Behroozi, M.; Armozd, P.; Badieh, M. M. S., Determination of liquid-liquid equilibria data for (water + propanoic acid + 3-methylbutan-1-ol) ternary mixture at 293.15 K to 313.15 K. *J. Mol. Liq.* **2017**, *243*, 513-518, DOI: 10.1016/j.molliq.2017.08.021.
- [9] Shekarsaraee, S.; Taherpour Nahzomi, H.; Nasiri-Touli,

- E., Phase diagrams for the system water/butyric acid/propylene carbonate at $T = 293.2\text{-}313.2$ K and $p = 101.3$ kPa. *Russ. J. Phys. Chem. A* **2017**, *91*, 2078-2084, DOI: 10.1134/S0036024417110267.
- [10] Shekarsaraee, S.; Kazemi, K., Measurement and correlation of LLE data for the ternary system water + phosphoric acid + 1-pentanol at 278.2 K and 288.2 K. *Adv. J. Chem. A* **2020**, *3*, 432-441, DOI: 10.33945/SAMI/A JCA.2020.4.5.
- [11] Ghanadzadeh, H.; Ghanadzadeh, A.; Moein, M.; Shekarsaraee, S.; Jamshidi, Y., Binodal curves and tie line data of the water-propionic acid-iso-butyl acetate at $T = (298.2, 308.2, 318.2, \text{ and } 328.2)$ K. *Thermochim. Acta* **2012**, *540*, 116-122, DOI: 10.1016/j.tca.2012.04.020.
- [12] Behroozi, M.; Heidari, S.; Malekpour, A., Phase equilibrium study of the aqueous solution of propanoic acid with acetates at different temperatures. *J. Chem. Eng. Data* **2021**, *66*, 867-877, DOI: 10.1021/acs.jced.0c00151.
- [13] Laiadi, D.; Hasseine, A.; Merzougui, A., Liquid-liquid equilibria for ternary mixtures of (water + carboxylic acid + MIBK), experimental, simulation, and optimization. *Int. J. Chem. Mol. Eng.* **2013**, *7*, 384-388, DOI: 10.5281/zenodo.1073154.
- [14] Seyed Saadat, S. L.; Ghanadzadeh Gilani, A.; Ghanadzadeh Gilani, H.; Kashef, A.; Fallahi, S., Liquid phase equilibria of aqueous mixtures of carboxylic acids (C1-C4) with ethylbenzene: Thermodynamic and mathematical modeling. *J. Chem. Eng. Data* **2016**, *61*, 3391-3397, DOI: 10.1021/acs.jced.6b00112.
- [15] Mohadesi, M.; Rezaei, R., Separation of acetic acid from water using organic solvents: Liquid-liquid equilibrium thermodynamic investigation. *Phys. Chem. Res.* **2020**, *8*, 267-280, DOI: 10.22036/pcr.2020.205810.1693.
- [16] Gilani, A. G.; Amouzadeh, F.; Taki, T., A comparative study on liquid phase equilibria of aqueous mixtures of two structurally close carboxylic acids with sec-amyl alcohols at 298.2 K. *J. Mol. Liq.* **2021**, *324*, 114733, DOI: 10.1016/j.molliq.2020.114733.
- [17] Yalın, I.; Cehreli, S.; Andreatta, A. E.; Senol, A., Phase equilibria of ternary liquid-liquid systems (water + C1-C4 monocarboxylic acids+ dibutyl ether) at three different temperatures: Modeling with A-UNIFAC. *J. Solution Chem.* **2020**, *49*, 1009-1028, DOI: 10.1100/2012/471417.
- [18] Gilani, A. G.; Amouzadeh, F.; Ghalami-Choobar, B., A comparative study of liquid-liquid equilibria for aqueous mixtures of straight chain and branched chain carboxylic acids with methyl isobutyl carbinol. *J. Chem. Thermodyn.* **2020**, *143*, 106026, DOI: 10.1016/j.jct.2019.106026.
- [19] Türkmenoğlu, A.; Özmen, D.; Bekri, S., Phase equilibrium study and data correlations for the ternary mixture of (water-butyric acid-[Hmim][P6]) at different temperatures. *J. Chem. Eng. Jap.* **2019**, *52*, 377-383, DOI: 10.1252/jcej.18we120.
- [20] Yu, C.; Wu, S.; Zhao, Y.; Zeng, Z.; Xue, W., Liquid-liquid equilibrium data of water + butyric acid + {butanal or n-butanol} ternary systems at 293.15, 308.15, and 323.15 K. *J. Chem. Eng. Data* **2017**, *62*, 2244-2252, DOI:10.1021/acs.jced.6b00941.
- [21] Shekarsaraee, S.; Nahzomi, H. T.; Nasiri-Touli, E., Phase diagrams for the system water/butyric acid/propylene carbonate at $T = 293.2\text{-}313.2$ K and $p = 101.3$ kPa. *Rus. J. Phy. Chem. A* **2017**, *91*, 2078-2084, DOI: 10.1134/S0036024417110267.
- [22] Chen, Y.; Wang, Y.; Zhou, S.; Chen, H.; Liu, D.; Li, L., Liquid phase equilibrium of the ternary systems, water+ propionic or butyric acid + mesityl oxide, at (298.2 and 323.2) K. *J. Chem. Thermodyn.* **2017**, *111*, 72-79, DOI: 10.1016/j.jct.2017.03.018.
- [23] Liu, D.; Li, L.; Luo, L.; Chen, Y., Liquid phase equilibria of the water + propionic or butyric acid + methyl tert-butyl ketone ternary systems at (298.15 and 323.15) K. *J. Chem. Eng. Data* **2015**, *60*, 2612-2617, DOI: 10.1021/acs.jced.5b00214.
- [24] 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.* **2015**, *403*, 30-35, DOI: 10.1016/j.fluid.2015.06.003.
- [25] Lalikoglu, M.; Bilgin, M., Ternary phase diagrams for aqueous mixtures of butyric acid with several solvents: Experimental and correlated data. *Fluid Phase Equilib.* **2014**, *371*, 50-56, DOI: 10.1016/j.fluid.2014.03.008.

- [26] Gilani, H. G.; Gilani, A. G.; Janbaz, M., (Liquid + liquid) equilibria of aqueous solutions of butyric acid with n-heptane and toluene at T = (298.2, 308.2, and 318.2) K. *J. Chem. Thermodyn.* **2013**, *57*, 152-159, DOI: 10.1016/j.jct.2012.08.029.
- [27] Gilani, A. G.; Gilani, H. G.; Saadat, S. S.; Janbaz, M., Ternary liquid-liquid equilibrium data for the (water + butyric acid + n-hexane or n-hexanol) systems at T = (298.2, 308.2, and 318.2) K. *J. Chem. Thermodyn.* **2013**, *60*, 63-70. DOI: 10.1016/j.jct.2013.01.015.
- [28] Ghanadzadeh, H.; Ghanadzadeh, A.; Asgharzadeh, S.; Moghadam, M., Measurement and correlation of phase equilibrium data of the mixtures consisting of butyric acid, water, cyclohexanone at different temperatures. *J. Chem. Thermodyn.* **2012**, *47*, 288-294. DOI: 10.1016/j.jct.2011.11.001.
- [29] Ghanadzadeh, H.; Ghanadzadeh, A.; Janbaz, M.; Shekarsaraee, S., Experimental determination and correlation of tie line data for the system (water + butyric acid + methylcyclohexane) at four temperatures. *Fluid Phase Equilib.* **2012**, *332*, 151-158. DOI: 10.1016/j.fluid.2012.07.003.
- [30] Çehreli, S.; Gündođdu, T., Phase equilibria of (water-carboxylic acid-diethyl maleate) ternary liquid systems at 298.15 K. *Fluid Phase Equilib.* **2011**, *303*, 168-173, DOI: 10.1016/j.fluid.2011.01.020.
- [31] Gök, A.; Kırbařlar, ř. İ.; Uslu, H.; Gilani, H. G., Liquid-liquid equilibria of (water + butyric acid + diethyl succinate or diethyl glutarate or diethyl adipate) ternary systems. *Fluid Phase Equilib.* **2011**, *303*, 71-75, DOI: 10.1016/j.fluid.2011.01.012.
- [32] Ghanadzadeh, H.; Ghanadzadeh, A.; Asgharzadeh, S.; Dastmoozeh, N., Phase diagrams for the aqueous solutions of butyric acid with cyclohexane at different temperatures: Experimental and correlated data. *Thermochim. Acta* **2011**, *523*, 154-160, DOI: 10.1016/j.tca.2011.05.017.
- [33] 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.* **2008**, *269*, 12-18, DOI: 10.1016/j.fluid.2008.04.014.
- [34] Kırbařlar, ř. İ.; řahin, S.; Bilgin, M., (Liquid + liquid) equilibria of (water + butyric acid + esters) ternary systems. *J. Chem. Thermodyn.* **2007**, *39*, 1279-1285, DOI: 10.1016/j.jct.2007.01.013.
- [35] Kırbařlar, ř. İ.; řahin, S.; Bilgin, M., (Liquid + liquid) equilibria of (water + butyric acid + dibasic esters) ternary systems. *J. Chem. Thermodyn.* **2007**, *39*, 284-290, DOI: 10.1016/j.jct.2006.07.002.
- [36] Bilgin, M.; Kırbařlar, ř. İ.; Özcan, Ö.; Dramur, U., Distribution of butyric acid between water and several solvents. *J. Chem. Eng. Data* **2006**, *51*, 1546-1550, DOI: 10.1021/je060025z.
- [37] Kırbařlar, ř. İ., (Liquid + liquid) equilibria of the (water + butyric acid + dodecanol) ternary system. *J. Chem. Thermodyn.* **2006**, *38*, 696-700, DOI: 10.1016/j.jct.2005.07.025.
- [38] Bilgin, M., Phase equilibria of liquid (water + butyric acid + oleyl alcohol) ternary system. *J. Chem. Thermodyn.* **2006**, *38*, 1634-1639, DOI: 10.1016/j.jct.2006.03.017.
- [39] Kırbařlar, ř. İ.; Bilgin, M.; Batr, D., (Liquid + liquid) equilibria of (water + butyric acid + cyclohexyl acetate) ternary system. *J. Chem. Thermodyn.* **2005**, *37*, 175-180, DOI: 10.1016/j.jct.2004.09.002.
- [40] Bilgin, M.; Kırbařlar, ř. İ.; Özcan, Ö.; Dramur, U., (Liquid + liquid) equilibria of (water + butyric acid + isoamyl alcohol) ternary system. *J. Chem. Thermodyn.* **2005**, *37*, 297-303, DOI: 10.1016/j.jct.2004.09.022.
- [41] Li, Z.; Qin, W.; Dai, Y., Liquid- liquid equilibria of acetic, propionic, butyric, and valeric acids with trioctylamine as extractant. *J. Chem. Eng. Data* **2002**, *47*, 843-848, DOI: 10.1021/je015526t.
- [42] Sabolova, E.; Schlosser, ř.; Martak, J., Liquid- liquid equilibria of butyric acid in water + solvent systems with trioctylamine as extractant. *J. Chem. Eng. Data* **2001**, *46*, 735-745, DOI: 10.1021/je000323a.
- [43] Letcher, T. M.; Redhi, G. G., Liquid-liquid equilibria for mixtures of acetonitrile + a carboxylic acid + heptane at 298.15 K. *J. Chem. Eng. Data* **1999**, *44*, 1183-1186, DOI: 10.1021/je990112+.
- [44] Arda, N.; Sayar, A. A., (Liquid + liquid) equilibria of (water + tetrahydrofuran + 1-methylcyclohexanol) and of (water + tetrahydrofuran + 2-methylbutyl ethanoate) at the temperature (293.16 ± 0.30) K and pressure (101.325 ± 0.070) kPa. *J. Chem. Thermodyn.* **1992**, *24*,

- 145-149, DOI: 10.1016/S0021-9614(05)80043-6.
- [45] Senol, A., Liquid-liquid equilibria for systems of (water + carboxylic acid + methylcyclohexanol) at 293.15 K: Modeling considerations. *J. Chem. Eng. Data* **2004**, *49*, 1815-1820, DOI: 10.1021/je0497606.
- [46] Senol, A., Phase equilibria for ternary liquid systems of (water + levulinic acid + cyclic solvent) at T = 298.2 K: Thermodynamic modeling. *J. Chem. Thermodyn.* **2005**, *37*, 1104-1110, DOI: 10.1016/j.jct.2005.01.014.
- [47] Treybal, R. E.; Mass Transfer Operations. New York, McGraw-Hill: 1980, pp. 488-490.
- [48] Hand, D. B., Dimeric distribution. *J. Phys. Chem.* **1930**, *34*, 1961-2000, DOI: 10.1021/j150315a009.
- [49] Othmer, D.; Tobias, P., Liquid-liquid extraction data-the line correlation. *Ind. Eng. Chem.* **1942**, *34*, 693-696, DOI: 10.1021/ie50390a600.
- [50] Renon, H.; Prausnitz, J. M., Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135-144, DOI: 10.1002/aic.690140124.