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Correlation of Experimental Liquid−Liquid Equilibrium Data for Ternary Systems Using NRTL and GMDH-Type Neural Network

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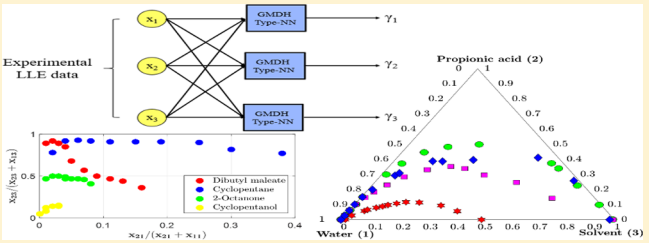
Supporting Information

ABSTRACT: In this work, liquid−liquid equilibrium (LLE) data for the ternary systems (water + propionic acid + solvent) were experimentally obtained at atmospheric pressure and 298.2 K. The ternary systems show type-1 behavior of LLE. Cyclopentane, cyclopentanol, 2-octanone, and dibutyl maleate were chosen as solvent and it has been noted that there are no data in the literature on these ternary systems. The consistency of the experimental tie-line data was checked using the Hand and Othmer-Tobias correlation equations. A comparison of the extracting capabilities of the solvent was made with respect to the distribution coefficients and separation factors. The correlation of the experimental tie-line data was confirmed by the NRTL thermodynamic model. A Group Method of Data Handling (GMDH)-type neural network (NN) was also used to correlate the experimental tie-lines. It is shown that the results of the both models cohere with the experimental values.



1. INTRODUCTION

Carboxylic acids are the major group of organic compounds that are produced by fermentation methods or chemical reactions. Recovering the carboxylic acids from dilute solutions obtained in the processes, especially in fermentation processes, are very important for industrially.[1−4] One of the most commonly used carboxylic acid is propionic acid, which is a short-chain fatty acid. In general, propionic acid exists in both industrial wastewater and fermentation broth. Propionic acid is largely used for esterification in producing thermoplastics, for mold prevention in baking, and in synthesizing multifarious perfume bases or flavors. Furthermore, propionic acid is a primary ingredient used as food additive and preservative for preventing food degradation.[5−7] Thus, the recovery of propionic acid from the dilute solutions obtained from chemical and fermentation operations or wastewater is economically and environmentally important.

Because of the lower energy requirement and costs, liquid−liquid extraction is considered as rather an effective and suitable method for carboxcylic acid recovery. For an efficient recycling of these compounds, many different solvents have been used so far by different researchers.[8−12] Ternary liquid−liquid equilibrium (LLE) data of carboxylic acids for aqueous solutions with organic solvents are of great importance in terms of both academic research and industrial applications. LLE data constitute a critical point in the design and improvement of various separation operations or chemical processes. Particularly, for the design of the industrial solvent extraction devices and for the success of the solvent extraction processes, there is a need for reliable LLE data of the mixture to be separated. For this reason, we can see many investigations in the literature about measurement and correlation to obtain dependable LLE data.[13−20]

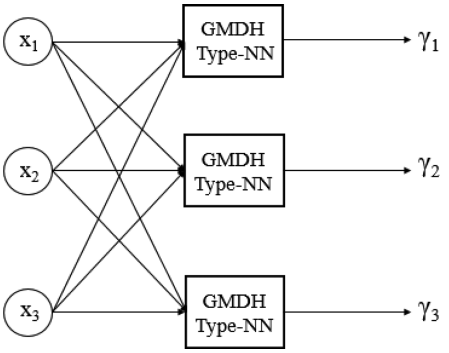


Figure 1. Block diagram of proposed GMDH-type NN.

In the present work, LLE data of the (water + propionic acid + solvent) ternary systems were measured at atmospheric pressure and 298.2 K. Four different solvents were selected from four different functional groups (hydrocarbon, alcohol, ketone, ester) to recover the propionic acid from aqueous solutions. These solvents used in this research are cyclopentane (hydrocarbon), cyclopentanol (alcohol), 2-octanone (ketone), and dibutyl maleate (ester). There is also need to specify that there are no data in the literature on these ternary systems. The solubility

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Table 1. Purities, Densities (ρ), and Refractive Indexes (n_D) of the Chemicals at T = 293.15 K and P = 101.3 kPa[35,36a]

chemical	supplier	purity (wt %)[b]	ρ (g·cm^{-3}) (literature)	ρ (g·cm^{-3}) (experimental)	n_D (literature)	n_D (experimental)
propionic acid	Merck	≥99	0.9882	0.9880	1.3809	1.3809
cyclopentane	Merck	≥98	0.7457	0.7457	1.4065	1.4066
cyclopentanol	Merck	≥99	0.9488	0.9487	1.4530	1.4531
2-octanone	Merck	≥98	0.8200	0.8199	1.4151	1.4151
dibutyl maleate	Merck	≥97	0.9900	0.9901	1.4451[b]	1.4452
water		distilled	0.9970	0.9971	1.3330	1.3327

[a]Standard uncertainties u are $u(\rho)$ = 0.004 g·cm^{-3}, (n_D) = 0. 0005, $u(T)$ = 0.01 K, and $u(P)$ = 0.7 kPa [b]Defined by the supplier.

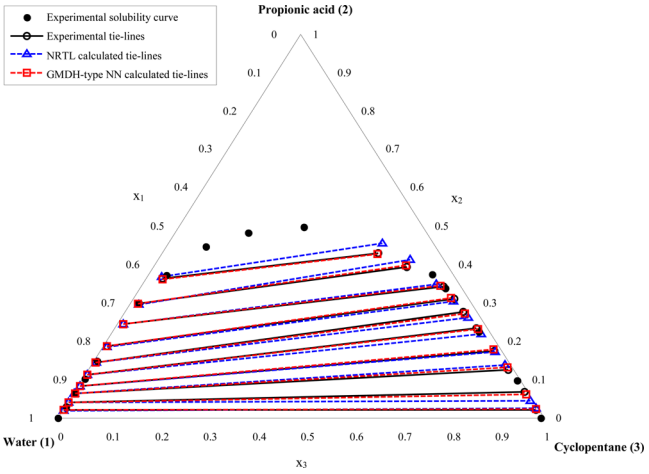

Figure 2. Liquid−liquid equilibrium phase diagram of water (1) + propionic acid (2) + cyclopentane (3) ternary system at T = 298.2 K and P = 101.3 kPa.

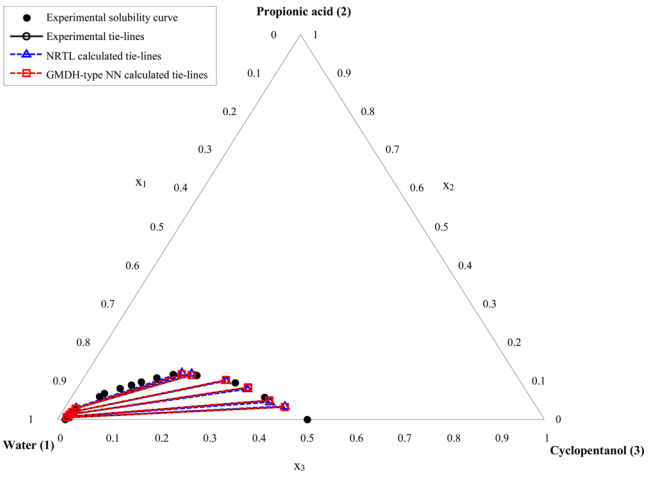

Figure 3. Liquid−liquid equilibrium phase diagram of water (1) + propionic acid (2) + cyclopentanol (3) ternary system at T = 298.2 K and P = 101.3 kPa.

curves and the tie-lines were plotted and shown in the ternary phase diagrams for each system. Separation factors (S) and distribution coefficients (D_i) were determined from the tie-line data values to establish the extraction ability of the solvents. The Othmer-Tobias[21] and Hand[22] equations were used to test the reliability of the experimental tie-line data. The nonrandom two-liquid (NRTL) model of Renon and Prausnitz[23] was used to regress the experimental tie-line data (eq 1)

$$\ln \gamma_i = \frac{\sum_{j=1}^{C} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{C} G_{ki} x_k} + \sum_{j=1}^{C} \left[\frac{x_j G_{ij}}{\sum_{k=1}^{C} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{k=1}^{C} x_k \tau_{kj} G_{kj}}{\sum_{k=1}^{C} G_{kj} x_k} \right) \right] \quad (1)$$

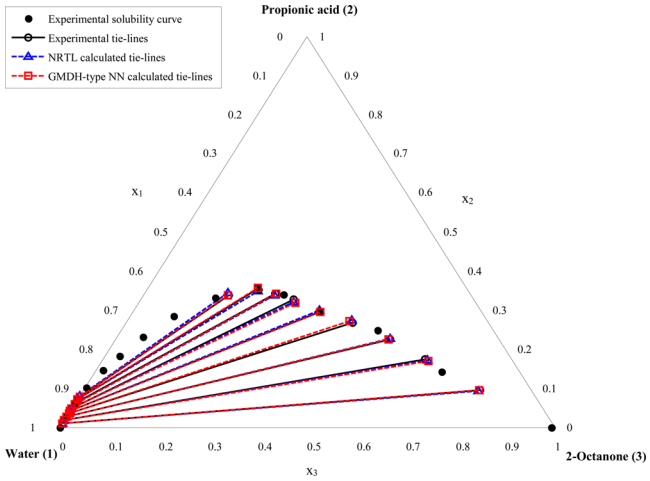

Figure 4. Liquid−liquid equilibrium phase diagram of water (1) + propionic acid (2) + 2-octanone (3) ternary system at T = 298.2 K and P = 101.3 kPa.

For this thermodynamic model, the binary interaction parameters were obtained and listed.

Furthermore, the Group Method of Data Handling (GMDH)-type neural network (NN) was also utilized to correlate and optimize the experimental tie-line data. GMDH-type NN has been recently used in the analysis of liquid−liquid equilibria. Atashrouz et al.[24] predict activity of water in glycol and ethylene glycol solutions using GMDH algorithm. Hakim et al.[25] estimate liquid−liquid phase behavior of a ternary system using two different NN-based models. A mathematical model of LLE for a ternary system using GMDH and genetic algorithms is studied by Ghanadzadeh. et al.[26] In this work, GMDH algorithm based on Kolmogorov-Gabor polynomial function is used. Experimental tie-lines and the calculated tie-lines from both NRTL model and GMDH-type NN model have been presented comparatively in graphics. In order to investigate the reliability of the models, root mean square deviation (rmsd) values were calculated for each of the ternary system.

The rmsd is an evaluation of the consistency between the experimental and calculated data. The accuracy of the correlated tie-line data was calculated using rmsd as shown in the following equation.

$$\text{rmsd} = \sqrt{\frac{\sum_{k=1}^{N} \sum_{j=1}^{2} \sum_{i=1}^{3} (x_{ijk} - \hat{x}_{ijk})^2}{6N}} \quad (2)$$

where N shows the number of the tie-lines, x represents the experimental mole fraction, $\hat{x}$ represents the calculated mole fraction, and subscript i, j, and k are indexes of components, phases, and tie-lines, respectively.

2. GMDH-TYPE NEURAL NETWORK

GMDH algorithm was first proposed as a polynomial neural network for identification and modeling complex systems by

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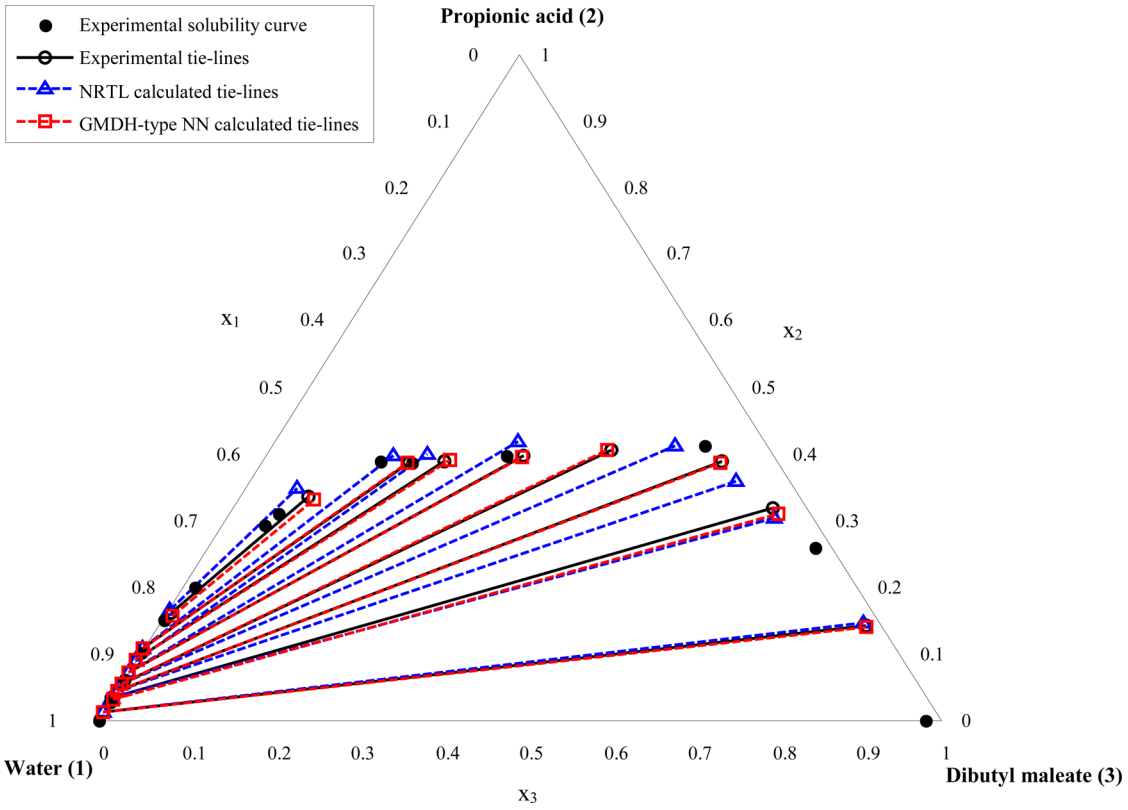

Figure 5. Liquid−liquid equilibrium phase diagram of water (1) + propionic acid (2) + dibutyl maleate (3) ternary system at T = 298.2 K and P = 101.3 kPa.

Table 2. Experimental and NRTL Model Predicted Tie-Line Data for Water (1) + Propionic Acid (2) + Solvent (3) Ternary Systems at T = 298.2 K and P = 101.3 kPa (with rmsd Values)[a]

water-rich phase mole fraction				solvent-rich phase mole fraction			
x_1		x_2		x_1		x_2	
exp.	NRTL	exp.	NRTL	exp.	NRTL	exp.	NRTL
Water (1) + Propionic Acid (2) + Cyclopentanol (3): rmsd value = 9×10^{-3}							
0.9782	0.9782	0.0194	0.0192	0.0058	0.0049	0.0203	0.0236
0.9582	0.9582	0.0386	0.0387	0.0058	0.0058	0.0670	0.0441
0.9334	0.9334	0.0625	0.0628	0.0097	0.0116	0.1253	0.1364
0.9133	0.9133	0.0817	0.0823	0.0152	0.0145	0.1743	0.1704
0.8822	0.8822	0.1118	0.1121	0.0225	0.0195	0.2328	0.2174
0.8492	0.8492	0.1442	0.1435	0.0275	0.0255	0.2756	0.2605
0.8052	0.8052	0.1853	0.1851	0.0302	0.0335	0.3089	0.3036
0.7421	0.7421	0.2441	0.2438	0.0360	0.0461	0.3412	0.3487
0.6860	0.6860	0.2963	0.2941	0.0852	0.0695	0.3928	0.4111
0.6029	0.6029	0.3619	0.3664	0.1261	0.1039	0.4283	0.4544
Water (1) + Propionic Acid (2) + Cyclopentanol (3): rmsd Value = 1.6×10^{-3}							
0.9780	0.9780	0.0041	0.0038	0.5173	0.5155	0.0299	0.0319
0.9766	0.9766	0.0051	0.0054	0.5391	0.5409	0.0482	0.0441
0.9680	0.9680	0.0116	0.0117	0.5675	0.5697	0.0810	0.0777
0.9597	0.9597	0.0179	0.0178	0.6024	0.6031	0.1002	0.0996
0.9491	0.9491	0.0258	0.0260	0.6662	0.6648	0.1146	0.1176
0.9471	0.9471	0.0274	0.0277	0.6856	0.6837	0.1156	0.1195
Water (1) + Propionic Acid (2) + 2-Octanone (3): rmsd Value = 2.7×10^{-3}							
0.9900	0.9900	0.0098	0.0098	0.1042	0.1070	0.0940	0.0925
0.9816	0.9816	0.0181	0.0181	0.1747	0.1711	0.1740	0.1716
0.9734	0.9734	0.0262	0.0262	0.2204	0.2185	0.2236	0.2261
0.9635	0.9635	0.0360	0.0360	0.2751	0.2718	0.2660	0.2735
0.9585	0.9585	0.0409	0.0409	0.3280	0.3258	0.2952	0.2986
0.9504	0.9504	0.0489	0.0489	0.3642	0.3672	0.3260	0.3210
0.9395	0.9395	0.0596	0.0594	0.3931	0.3964	0.3418	0.3374

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Table 2. continued

water-rich phase mole fraction				solvent-rich phase mole fraction			
x_1		x_2		x_1		x_2	
exp.	NRTL	exp.	NRTL	exp.	NRTL	exp.	NRTL
Water (1) + Propionic Acid (2) + 2-Octanone (3): rmsd Value = 2.7×10^{-3}							
0.9282	0.9282	0.0704	0.0705	0.4217	0.4256	0.3542	0.3483
0.9193	0.9193	0.0785	0.0790	0.4899	0.4878	0.3368	0.3439
Water (1) + Propionic Acid (2) + Dibutyl Maleate (3): rmsd Value = 1.89×10^{-2}							
0.9886	0.9886	0.0114	0.0114	0.0180	0.0187	0.1405	0.1460
0.9667	0.9667	0.0332	0.0332	0.0408	0.0457	0.3176	0.3025
0.9555	0.9555	0.0444	0.0444	0.0661	0.0628	0.3876	0.3594
0.9460	0.9460	0.0539	0.0539	0.1887	0.1092	0.4043	0.4109
0.9285	0.9285	0.0714	0.0714	0.2969	0.2931	0.3973	0.4176
0.9104	0.9104	0.0894	0.0894	0.3937	0.4086	0.3891	0.3998
0.8931	0.8931	0.1064	0.1066	0.4381	0.4514	0.3869	0.3972
0.8331	0.8331	0.1602	0.1653	0.5829	0.5897	0.3342	0.3480

[a]Standard uncertainties u are $u(x) = 0.005$, $u(T) = 0.2$ K, and $u(P) = 0.7$ kPa.

Ivakhnenko.[27] GMDH-type NN has been widely used in many engineering applications.[28−32]

A GMDH model with multiple input and one output is defined as follows

$$y(x_1, ..., x_n) = a_0 + \sum_{i=1}^{m} a_i f_i \tag{3}$$

where f_1, f_2,... f_m, functions are called as base functions and depend on the inputs x. Coefficients a_0, a_1,... a_m are the weight coefficients and m is the number of the base functions. In this work, Kolmogorov-Gabor polynomial, also known as polynomial neural network, is used as a base function as follows

$$y(x_1, ..., x_n) = a_0 + \sum_{i=1}^{n} a_i x_i + \sum_{i=1}^{n}\sum_{j=i}^{n} a_{ij} x_i x_j \sum_{i=1}^{n}\sum_{j=i}^{n}\sum_{k=j}^{n} a_{ijk} x_i x_j x_k + \cdots \tag{4}$$

2.1. Proposed GMDH Model. The GMDH-type NN is used to estimate the activity coefficient model of the ternary LLE data. The experimental data is applied to the proposed NN system and activity coefficients are selected as outputs as shown in the Figure 1.

In this figure, x_1, x_2 and x_3 show the experimental data and γ_1, γ_2, γ_3 show the activity coefficients. Each box of the figure represents Kolmogorov-Gabor polynomial with three inputs and one output. By using eq 4, the activity coefficients are obtained as follows

$$\gamma(x_1, x_2, x_3) = a_0 + \sum_{i=1}^{3} a_i x_i + \sum_{i=1}^{3}\sum_{j=i}^{3} a_{ij} x_i x_j + \sum_{i=1}^{3}\sum_{j=i}^{3}\sum_{k=j}^{3} a_{ijk} x_i x_j x_k \tag{5}$$

In this model, 60 coefficients (20 coefficients for each gamma value) were used. At the first step, by using genetic algorithm[33] the following objective function is minimized and optimum coefficients are obtained for the given experimental data.

$$\mathrm{OF1} = \sum_{j=1}^{N}\sum_{i=1}^{3} \frac{(x_{ij}^{\mathrm{I}}\gamma_{ij}^{\mathrm{I}} - x_{ij}^{\mathrm{II}}\gamma_{ij}^{\mathrm{II}})^2}{(x_{ij}^{\mathrm{I}}\gamma_{ij}^{\mathrm{I}} + x_{ij}^{\mathrm{II}}\gamma_{ij}^{\mathrm{II}})^2} \tag{6}$$

where x^{I}_{ij} and x^{II}_{ij} refer to the experimental mole fraction of component i of water-rich and solvent-rich phase, respectively, along tie-line j, γ^{I}_{ij} and $\gamma^{\mathrm{II}}_{ij}$ are the corresponding activity coefficients.

Table 3. Optimized NRTL Binary Interaction Parameters for the Water (1) + Propionic Acid Acid (2) + Solvent (3) Ternary Systems at T = 298.2 K and P = 101.3 kPa[a]

ternary systems	$\alpha_{ij} = \alpha_{ji}$	i,j[b]	A_{ij}[c] $= \Delta g_{ij}/R$	$\tau_{ij} = A_{ij}/T$
water (1) + propionic acid (2) + cylopentane (3)	0.2	1,2	1349.3963	4.5259
	0.2	2,1	−0.6915	−0.0023
	0.2	1,3	1305.7274	4.3794
	0.2	3,1	1122.1714	3.7638
	0.2	2,3	306.2884	1.0273
	0.2	3,2	1020.7838	3.4237
water (1) + propionic acid (2) + cylopentanol (3)	0.2	1,2	1753.2066	5.8803
	0.2	2,1	−697.5850	−2.3397
	0.2	1,3	1496.3028	5.0186
	0.2	3,1	−273.4570	−0.9172
	0.2	2,3	976.0033	3.2735
	0.2	3,2	−395.2164	−1.3256
water (1) + propionic acid (2) + 2-octanone (3)	0.2	1,2	1240.7037	4.1613
	0.2	2,1	−469.8402	−1.5759
	0.2	1,3	2291.8307	7.6868
	0.2	3,1	412.7915	1.3845
	0.2	2,3	−245.1177	−0.8221
	0.2	3,2	300.7383	1.0087
water (1) + propionic acid (2) + dibutyl maleate (3)	0.2	1,2	361.5664	1.2127
	0.2	2,1	−31.8547	−0.1068
	0.2	1,3	2735.2411	9.1740
	0.2	3,1	1089.7964	3.6552
	0.2	2,3	191.9588	0.6438
	0.2	3,2	−673.5961	−2.2593

[a]Standard uncertainty u is $u(P) = 0.7$ kPa. [b]i−j pair of components: water (1), propionic acid (2), solvent (3). [c]$A_{ij} = (g_{ij} - g_{jj})/R$.

After minimizing the first objective function, the obtained coefficients are used for testing. At the test step, polynomial coefficients that are obtained by minimizing OF1 are used to correlate experimental tie lines. For this purpose, only mole fractions of water obtained from the water-rich phase are given to the proposed system and then the other mole fractions were determined. The following objective function are minimized

$$\mathrm{OF2} = \sum_{i=1}^{3} \frac{(x_{ik}^{\mathrm{I}}\gamma_{ik}^{\mathrm{I}} - x_{ik}^{\mathrm{II}}\gamma_{ik}^{\mathrm{II}})^2}{(x_{ik}^{\mathrm{I}}\gamma_{ik}^{\mathrm{I}} + x_{ik}^{\mathrm{II}}\gamma_{ik}^{\mathrm{II}})^2} \tag{7}$$

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Table 4. Experimental and GMDH Estimated Tie-Line Data for Water (1) + Propionic Acid (2) + Solvent (3) Ternary Systems at T = 298.2 K and P = 101.3 kPa (with rmsd Values)[a]

water-rich phase mole fraction				solvent-rich phase mole fraction			
x_1		x_2		x_1		x_2	
exp.	GMDH	exp.	GMDH	exp.	GMDH	exp.	GMDH
Water (1) + Propionic Acid (2) + Cyclopentane (3): rmsd Value = 2.7×10^{-3}							
0.9782	0.9782	0.0194	0.0194	0.0058	0.0053	0.0203	0.0213
0.9582	0.9582	0.0386	0.0388	0.0058	0.0070	0.0670	0.0598
0.9334	0.9334	0.0625	0.0624	0.0097	0.0104	0.1253	0.1299
0.9133	0.9133	0.0817	0.0817	0.0152	0.0138	0.1743	0.1781
0.8822	0.8822	0.1118	0.1118	0.0225	0.0197	0.2328	0.2308
0.8492	0.8492	0.1442	0.1437	0.0275	0.0265	0.2756	0.2717
0.8052	0.8052	0.1853	0.1858	0.0302	0.0353	0.3089	0.3108
0.7421	0.7421	0.2441	0.2442	0.0360	0.0402	0.3412	0.3435
0.6860	0.6860	0.2963	0.2971	0.0852	0.0839	0.3928	0.3974
0.6029	0.6029	0.3619	0.3616	0.1261	0.1275	0.4283	0.4276
Water (1) + Propionic Acid (2) + Cyclopentanol (3): rmsd Value = 8.5×10^{-5}							
0.9780	0.9780	0.0041	0.0041	0.5173	0.5173	0.0299	0.0298
0.9766	0.9766	0.0051	0.0051	0.5391	0.5392	0.0482	0.0481
0.9680	0.9680	0.0116	0.0116	0.5675	0.5674	0.0810	0.0811
0.9597	0.9597	0.0179	0.0178	0.6024	0.6024	0.1002	0.1001
0.9491	0.9491	0.0258	0.0260	0.6662	0.6662	0.1146	0.1147
0.9471	0.9471	0.0274	0.0273	0.6856	0.6856	0.1156	0.1156
Water (1) + Propionic Acid (2) + 2-Octanone (3): rmsd Value = 2.8×10^{-3}							
0.9900	0.9900	0.0098	0.0098	0.1042	0.1054	0.0940	0.0950
0.9816	0.9816	0.0181	0.0180	0.1747	0.1696	0.1740	0.1701
0.9734	0.9734	0.0262	0.0262	0.2204	0.2234	0.2236	0.2243
0.9635	0.9635	0.0360	0.0359	0.2751	0.2782	0.2660	0.2721
0.9585	0.9585	0.0409	0.0409	0.3280	0.3255	0.2952	0.2948
0.9504	0.9504	0.0489	0.0488	0.3642	0.3635	0.3260	0.3191
0.9395	0.9395	0.0596	0.0595	0.3931	0.3924	0.3418	0.3412
0.9282	0.9282	0.0704	0.0707	0.4217	0.4214	0.3542	0.3569
0.9193	0.9193	0.0785	0.0782	0.4899	0.4912	0.3368	0.3366
Water (1) + Propionic Acid (2) + Dibutyl Maleate (3): rmsd Value = 3.1×10^{-3}							
0.9886	0.9886	0.0114	0.0113	0.018	0.0184	0.1405	0.1403
0.9667	0.9667	0.0332	0.0313	0.0408	0.0381	0.3176	0.3089
0.9555	0.9555	0.0444	0.0443	0.0661	0.0686	0.3876	0.3858
0.9460	0.9460	0.0539	0.0540	0.1887	0.1929	0.4043	0.4048
0.9285	0.9285	0.0714	0.0711	0.2969	0.2993	0.3973	0.3953
0.9104	0.9104	0.0894	0.0894	0.3937	0.3879	0.3891	0.3904
0.8931	0.8931	0.1064	0.1065	0.4381	0.4405	0.3869	0.3862
0.8331	0.8331	0.1602	0.1557	0.5829	0.5782	0.3342	0.3315

[a]Standard uncertainties u are $u(x)$ = 0.005, $u(T)$ = 0.2 K, $u(P)$ = 0.7 kPa.

with constraints

$$\sum_{i=1}^{3} x_{ik}^{\mathrm{I}} = 1 \quad \text{and} \quad \sum_{i=1}^{3} x_{ik}^{\mathrm{II}} = 1 \tag{8}$$

$$x_{ik}^{\mathrm{I}} \geq 1, \quad i = 1, 2, 3$$

$$x_{ik}^{\mathrm{II}} \geq 1, \quad i = 1, 2, 3$$

For both objective functions, minimization process was achived using genetic algorithm to obtain the solution that gives minimum rmsd error.[34]

3. EXPERIMENTAL SECTION

3.1. Chemicals. All chemicals used in this work were commercial analytical grade. The chemicals were supplied by Merck and used without any further purification. During the experiments, distilled water was utilized for the preparation of all solutions. Physical properties of the chemicals stated by the supplier and literature[35,36] were given in the Table 1. The experimental densities were measured using a temperature controlled Anton Paar DMA 4500 density meter in an accuracy of $\pm 4 \times 10^{-3}$ g·cm^{-3}. It was calibrated with double distilled water and dry air. The refractive indices were measured with an Abbé-Hilger refractometer with an accuracy of $\pm 5 \times 10^{-4}$.

3.2. Apparatus and Procedure. The apparatus, measurements, and experimental and analysis method were described in our previous publication.[9,10] The experimental solubility curves for each ternary system were determined by the cloud point method.[37] The experiments were carried out at T = 298.2 K and atmospheric pressure. The liquid samples were analyzed using a gas chromatography (HP 6890), equipped with flame ionization (FI) and thermal conductivity (TC) detectors. Ethanol was used as an internal standard. The precision of the compositions of the tie-lines was within 1×10^{-4} mole fraction.

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Table 5. Kolmogorov-Gabor Polynomial Coefficients of the GMDH Model for the Water (1) + Propionic Acid (2) + Solvent (3) Ternary Systems

	water (1) + propionic acid (2) + cyclopentane (3)			water (1) + propionic acid (2) + cyclopentanol (3)		
	x_1	x_2	x_3	x_1	x_2	x_3
a_0	0.4174	0.1150	0.3634	3.9329	−1.6549	−0.1838
a_1	0.3383	0.7643	0.4878	0.0198	−1.3329	−0.3234
a_2	0.1263	0.0085	0.2388	3.7648	−1.8464	0.0869
a_3	0.1797	−1.4981	−0.7636	0.5245	0.9759	−0.8285
a_{11}	−1.1104	−0.1723	13.9243	−2.2397	4.9641	2.4024
a_{12}	−0.7300	−10.6327	−0.7867	1.3691	0.9713	−1.7009
a_{13}	−0.0810	13.2396	−1.7629	0.1300	−0.7819	−2.4353
a_{22}	−0.3161	4.3101	−0.7272	5.5744	48.6011	−6.7768
a_{23}	−0.6263	1.0038	−1.9635	5.2746	11.9690	5.9464
a_{33}	0.1645	0.0201	0.4056	−3.1011	0.9794	5.1011
a_{111}	0.1058	1.4591	17.7330	−1.3707	1.8768	2.0855
a_{112}	−0.3957	23.2444	−63.2656	−4.3893	−11.1021	−8.1968
a_{113}	0.2244	−0.3980	42.3735	−5.2298	0.2097	−0.6171
a_{122}	−1.1306	−2.1003	−6.9455	−1.2901	−3.2599	−10.1616
a_{123}	−4.8554	−37.5235	1.2723	3.8223	45.6404	11.7644
a_{133}	−11.0926	4.6104	0.0486	−0.0543	2.0812	2.6773
a_{222}	−4.4675	−1.5842	0.6441	−5.3087	59.4564	152.8101
a_{223}	−16.4847	12.0201	2.4477	28.9040	8.3533	42.2382
a_{233}	0.1836	−2.2392	1.2585	48.5689	5.6487	−2.5096
a_{333}	14.1246	1.4070	−0.6715	24.9318	20.2089	−3.4316
	water (1) + propionic acid (2) + 2-octanone (3)			water (1) + propionic acid (2) + dibutyl maleate (3)		
	x_1	x_2	x_3	x_1	x_2	x_3
a_0	−76.1852	357.8391	2.9103	3.3394	534.3366	1.5325
a_1	217.9941	−138.6647	0.2502	−3.0165	−515.9869	−0.6826
a_2	95.2605	691.2288	−2.2301	−0.7310	300.2141	−1.9105
a_3	95.7039	214.1584	−1.6246	3.3055	−164.0239	1.9259
a_{11}	−17.7079	3633.6693	2.1363	−0.6889	2458.7821	3.3044
a_{12}	−4662.9466	−5429.5958	−6.1197	−122.2229	4651.3911	−1.8100
a_{13}	1140.3566	−11.1652	1.2934	321.8979	−15176.7700	3.3471
a_{22}	2508.2981	2724.8192	3.9711	−229.8537	−5070.8208	0.5027
a_{23}	2437.7577	−2398.2705	−0.4647	−57.6573	−1304.7416	−0.2231
a_{33}	8879.2488	−354.7361	−0.4180	−9.8092	29.3259	−0.7807
a_{111}	42.4641	1250.4476	12.4932	7.2960	11345.6047	22.1745
a_{112}	3952.8941	−3562.3339	−16.9760	85.5463	1186.5371	−41.9248
a_{113}	−1364.9194	−5215.1705	7.1171	−334.5926	30646.3670	18.6530
a_{122}	−637.4520	27.0043	−4.6114	235.0970	−7976.3764	−6.4216
a_{123}	10161.0677	550.6287	−1.7776	1419.3413	41372.1365	0.3981
a_{133}	−2110.6225	−305.8025	−0.6764	−1421.8947	1257.3138	−2.3731
a_{222}	−1557.2374	3365.6040	17.7486	−99.1655	4455.6478	−5.8365
a_{223}	139.5879	−351.4837	−0.5303	225.9892	14423.2331	−1.5342
a_{233}	−22496.1448	838.8649	5.2072	−87.5384	4509.1288	−0.9262
a_{333}	−3045.6989	−225.9658	1.1149	849.9563	982.1430	−0.3019

4. RESULTS AND DISCUSSIONS

The experimental solubility curves and experimental tie-lines for the studied ternary systems were determined at atmospheric pressure and 298.2 K. The ternary LLE phase diagrams for the (water + propionic acid + cyclopentane), (water + propionic acid + cyclopentanol), (water + propionic acid + 2-octanone) and (water + propionic acid + dibutyl maleate) ternary systems were plotted with solubility curve data and shown in Figures 2−5. The experimental and calculated tie-line data and the optimized NRTL binary interaction parameters of the researched ternary systems are reported in Tables 2 and 3, for which x_{i1} and x_{i3} denotes the mole fractions of component i in the water-rich and solvent-rich phases, respectively. Experimental and GMDH estimated tie-line data are reported in the Table 4. Kolmogorov-Gabor polynomial coefficients are also reported in the Table 5. The correlated tie-lines for the NRTL and the proposed method are shown in Figures 2−5. As can be seen, the obtained ternary LLE phase diagrams which are showed in these figures are the type-1 ternary systems. Because only one liquid pair (water + solvent) is partially miscible and the (propionic acid + water or solvent) are the two liquid pairs that are exactly miscible.

Separation factors (S), distribution coefficients (D_i) for water (i = 1) and propionic acid (i = 2) were calculated to estimate the acid extraction efficiency by the solvents. The distribution coefficients and separation factors are calculated from the following equations shown below

$$D_i = \frac{x_{i3}}{x_{i1}} \tag{9}$$

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Table 6. Experimental Values of the Distribution Coefficients (D_i) for the Water (1) and Propionic Acid (2) and the Separation Factors (S) at T = 298.2 K and P = 101.3 kPa[a]

D_1	D_2	S
Water (1) + Propionic Acid (2) + Cyclopentane (3)		
0.01	1.04	175
0.01	1.73	284
0.01	2.01	192
0.02	2.13	128
0.03	2.08	82
0.03	1.91	59
0.04	1.67	44
0.05	1.40	29
0.12	1.33	11
0.21	1.18	6
Water (1) + Propionic Acid (2) + Cyclopentanol (3)		
0.53	7.25	14
0.55	9.37	17
0.59	6.69	12
0.63	5.60	9
0.70	4.43	6
0.72	4.22	6
Water (1) + Propionic Acid (2) + 2-Octanone (3)		
0.11	9.64	92
0.18	9.63	54
0.23	8.52	38
0.29	7.39	26
0.34	7.21	21
0.38	6.66	17
0.42	5.74	14
0.45	5.03	11
0.53	4.29	8
Water (1) + Propionic Acid (2) + Dibutyl Maleate (3)		
0.02	12.37	679
0.04	9.56	227
0.07	8.73	126
0.20	7.49	38
0.32	5.56	17
0.43	4.35	10
0.49	3.64	7
0.70	2.09	3

[a]Standard uncertainties u are $u(T)$ = 0.2 K, $u(P)$ = 0.7 kPa.

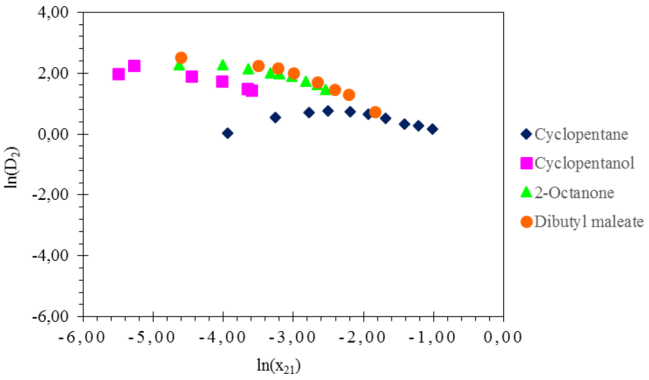

Figure 6. Distribution coefficients of propionic acid (D_2) as a function of the mole fraction of propionic acid in water-rich phase (x_{21}).

$$S = \frac{D_2}{D_1} \tag{10}$$

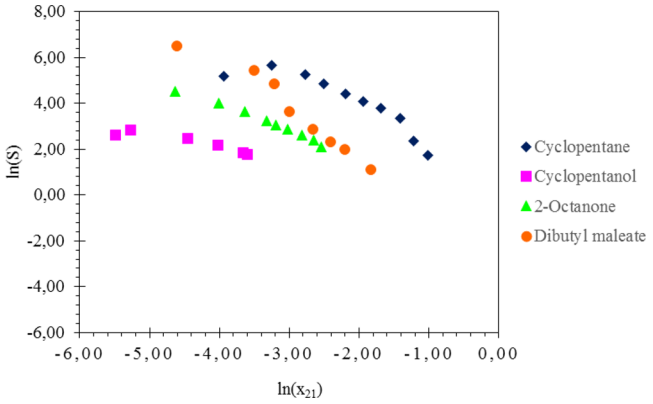

Figure 7. Separation factors (S) as a function of the mole fraction of propionic acid in water-rich phase (x_{21}).

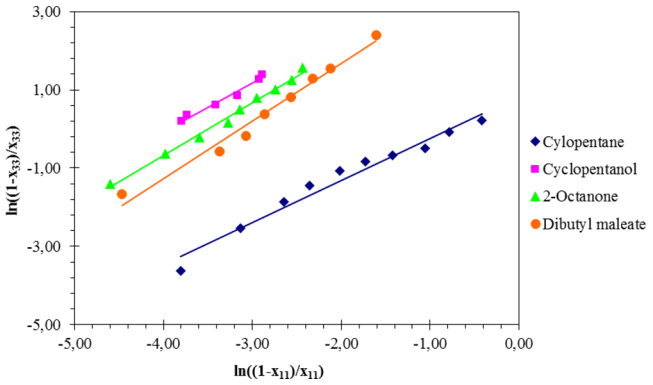

Figure 8. Othmer-Tobias plot for LLE data of the (water + propionic acid + solvent) ternary systems at T = 298.2 K and P = 101.3 kPa.

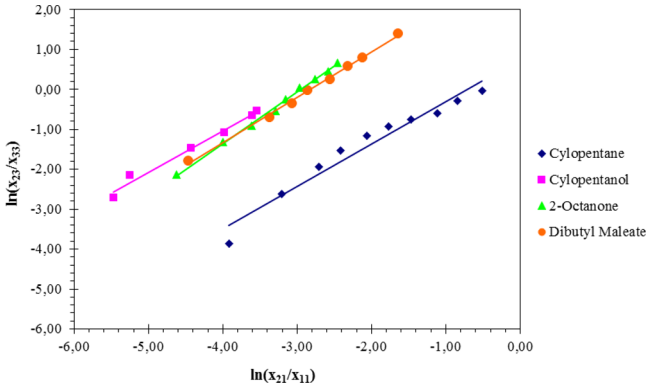

Figure 9. Hand plot for LLE data of the (water + propionic acid + solvent) ternary systems at T = 298.2 K and P = 101.3 kPa.

These separation factors and distribution coefficients for each ternary system are reported in Table 6. Also, the extracting performance of cyclopentane, cyclopentanol, 2-octanone, and dibutyl maleate for propionic acid is shown in Figures 6 and 7. The extracting performance of the solvents can be achieved with respect to their separation factor values. For a feasible extraction process, this value is required to be as large as possible to 1. According to obtained results, dibutyl maleate's performance in terms of distribution coefficient and separation factor values is even higher than the other solvents. The quality of the experimentally obtained tie-line data was determined by the

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Table 7. Constants of the Othmer-Tobias and Hand Equations for the (Water + Propionic Acid + Solvent) Ternary Systems at T = 298.2 K and the Correlation Factors (R^2)

	Othmer-Tobias correlation			Hand correlation		
ternary system	A	B	R^2	A'	B'	R^2
water + propionic acid + cyclopentane	0.8372	1.0743	0.9683	0.7445	1.0586	0.9546
water + propionic acid + cyclopentanol	4.8465	1.2251	0.9775	3.0851	1.0327	0.9828
water + propionic acid +2-octanone	4.7377	1.3527	0.9924	3.8248	1.2965	0.9965
water + propionic acid + dibutyl maleate	4.6154	1.4716	0.9784	3.2106	1.1365	0.9966

Othmer-Tobias and Hand correlations, which were given by eqs 11 and 12, respectively:

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

$$\ln\left(\frac{x_{23}}{x_{33}}\right) = A' + B'\ln\left(\frac{x_{21}}{x_{11}}\right) \quad (12)$$

where x_{11} is mole fraction of water in water-rich phase; x_{21} and x_{23} are mole fractions of the propionic acid in water-rich and solvent-rich-phases, respectively; x_{33} is mole fraction of the solvent in solvent-rich phase; A, B and A', B' are parameters for Othmer-Tobias and Hand equations, respectively. For investigated ternary systems, the Othmer-Tobias and Hand plots are shown in Figures 8 and 9. Also, the fitting equation parameters and the linear correlation factors (R^2) are listed in Table 7. The linearity of the lines in Figure 8 and 9 and the R^2 values close to 1 given in Table 7 indicate the consistency of the experimental data. The whole R^2 values indicate a good reliability of our experimental tie-line data.

In this work, the experimental tie-line data were correlated using NRTL. Furthermore, a GMDH-type NN model was proposed using experimental equilibria data and the tie-line data were predicted by using this model. The value of the nonrandomness parameter of the NRTL model (α) was selected at 0.2. Also the experimental LLE data were applied to obtain the NRTL binary interaction parameters.

The rmsd values for NRTL and GMDH-type NN models are also listed in Tables 2 and 3 nearby the tie-line data.

5. CONCLUSION

Ternary LLE data for the four investigated systems (water + propionic acid + solvent) were measured at atmospheric pressure and at 298.2 K. Each ternary system exhibits type-1 behavior of the LLE. Results from the separation factor and distribution coefficients show that 2-octanone and dibutyl maleate are more appropriate solvents for extracting propionic acid from water. The experimental tie-line data indicate great reliability, as assessed by the Othmer-Tobias and Hand correlations. The NRTL and GMDH-type NN models were used to predict the experimental tie-lines. Although both models give good agreement results when compared with the experimental data, the GMDH-type NN model generally gives better rmsd values than the NRTL model. Thus, the GMDH-type NN model is convenient for predicting the LLE data.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.6b00985.

Additional table (PDF)

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Notes

The authors declare no competing financial interest.

■ NOMENCLATURE

A_{ij}	NRTL interaction parameter ($A_{ij} = \Delta g_{ij}/R$)
a_i	Kolmogorov-Gabor polynomial coefficient
A, B	The Othmer-Tobias equation constants
A', B'	The Hand equation constants
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
N	number of tie-lines
n_D	refractive index
R	the universal gas constant
R^2	correlation factor for Othmer-Tobias and Hand equations
rmsd	root-mean-square deviation
S	separation factor
T	temperature (K)
T_b	boiling temperature (K)
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
$\hat{x}_{ijk}$	the calculated mole fraction of component i in the phase j along tie-line k

Greek Letters

ρ	density (g·cm^{-3})
α_{ij}	NRTL parameter for component i and j
γ_{ij}	activity coefficient of component i in phase j
τ_{ij}	NRTL interaction parameters ($\tau_{ij} = A_{ij}/T$)

Subscripts

Mol wt	mole weight (g/mol-g)
Exp	experimental value

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