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Experimental Investigation and Thermodynamic Modeling in Liquid-Liquid Equilibrium of Water + Propionic Acid + Cyclic Alcohols at T= 303.2, 313.2, and 323.2 K

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ABSTRACT

Propionic acid extraction is of economic and environmental importance. In the present study, the liquid-liquid equilibrium data of the ternary system of water + propionic acid + cyclic alcohols (cyclopentanol and cyclohexanol) was obtained at 303.2, 313.2, and 323.2 K temperatures. Phase behavior of type-1 has been observed for studied systems. The Hand and Bachman equations confirm the validity of the measured data. For correlation of liquid-liquid equilibrium data, the NRTL and UNIQUAC thermodynamic models have been used and the coefficients of the inter-molecular interaction have been determined. RMSD values for NRTL and UNIQUAC models in cyclopentanol-containing systems were 0.0107 and 0.0057, respectively, and for cyclohexanol 0.0108 and 0.0076 respectively, which showed the accuracy of these models in correlation liquid-liquid equilibrium data. The values of the selectivity factor for both solvents larger than the unit are obtained, which indicates the ability of the solvents to extract propionic acid.

Introduction

Liquid extraction is an effective method of separating organic compounds [1, 2]. This method is widely used in industry because it costs less energy than distillation [3]. In fermentation process or synthesis methods, carboxylic acids are obtained in water solution, their separation is of scientific, economic, and industrial significance [4]. Carboxylic acids are the main contaminants in wastewater discharged by various industries and are recovered by liquid extraction [5, 6].

Propionic acid one of the most important carboxylic acids is widely used in chemical and biochemical industries. Propionic acid and its salts form a wide range of preservatives because they have antiviral, antibacterial, and fungal effects [7, 8]. Due to the characteristic of the fragrance, various esters of propionate are used in the seasoning and perfume. Propionic acid is used to produce herbicides, drugs, paints, textile products, plastics, cosmetics, and leather [9].

The most important factor affecting the extraction of propionic acid is the choice of solvent. Various solvents have been used for this goal [10].

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Liquid-liquid equilibrium (LLE) data is required to predict thermodynamic properties and study the phase behavior of multicomponent systems [11]. In recent years, many studies have been performed to measure propionic acid LLE data [12]. LLE data is obtained from direct measurements for an effective separation [13].

In the study of propionic acid extraction by Özmen et al., due to the two-phase region and high distribution coefficient, cyclohexyl acetate solvent has been introduced as the most suitable extractant. The results of the thermodynamic model of UNIFAC showed the correlation of the experimental data for the system containing cyclohexyl acetate [14]. In one research, the effect of temperature on the liquid-liquid equilibrium (water + propionic acid + diethyl phthalate) was insignificant [15]. Dibasic ester solvents have been considered environmentally friendly solvents for the extraction of propionic acid. The results indicate that the solubility of water of these solvents depends on the number of carbon atoms, and as the carbon chain length increases, their solubility in water decreases [16]. Research by Chen et al. has shown that separation factors in polar solvents such as cyclohexanone are much higher than in nonpolar alkanes [17].

In this study, two cyclic alcohols (cyclopentanol and cyclohexanol) are considered solvents for propionic acid extraction. In the previous study by Özmen et al. [14] cyclohexanol was used as the solvent. In the present work, in addition to cyclohexanol, cyclopentanol was used as a solvent at different temperatures. These solvents are suitable for extracting propionic acid due to their high boiling point and partial solubility in water.

Liquid-liquid equilibrium and thermodynamic modeling of water + propionic acid + cyclic alcohols (cyclopentanol and cyclohexanol) ternary system have been investigated. LLE data was determined at atmospheric pressure at 303.2, 313.2, and 323.2 K, respectively.

The simulation of LLE data was done by MATLAB software using NRTL and UNIQUAC thermodynamic models.

Materials and Methods

Materials

Propionic acid (99%), cyclohexanol (99%), and cyclopentanol (99%) have been purchased from Merck and Sigma Aldrich Company, respectively. Deionized water was used in all of the experiments. The purity percentage of the materials was studied based on their refractive index at 293.2 ±0.1 K. The refractive index is measured by the ATAGO CO, LTO refractometer with an accuracy of ± 0.001n_D. In Table 1, the physical properties of the material and the measured refractive index, along with the values found in the reference, have been reported.

Experiments

The binodal curve experiments for the studied systems at 303.2, 313.2, and 323.2 K were performed by the cloud point method [14,15,17-19]. The temperature is kept constant by the water bath with temperature control at ± 0.1 K accuracy. The water-rich branch in the binodal curves was obtained by titration of the homogeneous mixture (water + propionic acid) with organic solvent and conversion to a heterogeneous mixture. The solvent-rich branch was obtained by continuing titration and disappearing the turbidity mixture. To increase accuracy, each test is repeated 3 times, and the mean of data is considered as the final result.

The study of Kirbaslar et al. [16] was used to determine the tie lines data. To determine the mass fraction of acid in water-rich and solvent-rich phases, volumetric titration with 0.1 N

NaOH was used in the presence of a phenolphthalein detector. The water mass fraction in the solvent-rich phase was determined by Karl-Fisher (Metrohm 870) method.

Table 1. Physical properties of chemicals at 101.3 kPa [a]

Chemicals	Source	Molecular Formula	CAS number	Initial Mole Fraction Purity	M (g/mol)	d (g/cm^3)	T_b (C)	Refractive index (n_D) at 20 (C)		Ref
								Literature	Experiment	
Water	Merck	H_2O	7732-18-5	-	18.01	0.998	100.0	1.333	1.330	[16]
Propionic Acid	Merck	$C_3H_6O_2$	79-09-4	0.99	74.08	0.993	141.0	1.386	1.388	[20]
Cyclopentanol	Aldrich	$C_5H_{10}O$	96-41-3	0.99	86.13	0.949	139.0	1.453	1.456	[21,22]
Cyclohexanol	Aldrich	$C_6H_{12}O$	108-93-0	0.99	100.16	0.948	161.1	1.465	1.465	[14]

[a] The standard uncertainties, u, of T and n_D are $u(T) = 0.1$ ℃, $u(n_D) = 0.001$ and $u(P) = 0.5$ kPa.
[b] Analysis method

Thermodynamic modeling

Equilibrium data for the studied systems containing cyclic alcohols (cyclopentanol and cyclohexanol), water, and propionic acid were modeled with the NRTL [23] and UNIQUAC [24] thermodynamic models. In these relationships, the intermolecular parameters were a function of temperature [23-26]. Structural parameters r_i, q_i and q_i' in UNIQUAC equation for the materials are reported in Table 2 [6, 27].

Table 2. Parameters r_i, q_i and q_i' the materials used

Component	r_i	q_i	q_i'
Water	0.9200	1.4000	1.0000
Propionic acid	2.8768	2.6120	2.6120
Cyclopentanol	4.1445	3.5880	1.1500
Cyclohexanol	4.8189	4.1280	1.7800

Results and Discussion

Experimental data of LLE

The binodal curve data for the studied systems containing cyclic alcohols (cyclopentanol and cyclohexanol), water, and propionic acid at 303.2, 313.2, and 323.2 K are calculated and shown in Table 3. These data show the mass fraction of the components. The triangular phase diagrams for the studied systems at 303.2, 313.2, and 323.2 K, are plotted in Figs. 1, 2, and 3, respectively. For both ternary systems, the bimodal curves show the type-1 phase behavior [28]; That is, the pairs of (water and propionic acid) and (solvent and propionic acid) are fully miscible, and the (solvent, water) pair is partially dissolved. It is also observed in these Figures that the two-phase region is smaller at 323.2 K. From the comparison of the two-phase region for solvents, it is concluded that in cyclic alcohols such as linear alcohols [16] with the increasing number of carbon, their solubility in water decreases and the two-phase region will be larger. For cyclohexanol, a larger two-phase region is obtained.

Table 3. LLE data of systems containing cyclic alcohols (cyclopentanol and cyclohexanol), water, and propionic acid at a temperature of 303.2, 313.2, and 323.2 K and pressure of 101.3 kPa [a]

T, K	Water-rich phase			Solvent-rich phase		
	w_1^{aq}	w_2^{aq}	w_3^{aq}	w_1^{O}	w_2^{O}	w_3^{O}
water (1) + propionic acid (2) + cyclopentanol (3)						
303.2	0.9723	0.0000	0.0277	0.1360	0.0000	0.8640
	0.9154	0.0479	0.0367	0.1306	0.0068	0.8626
	0.8222	0.0909	0.0869	0.1244	0.0137	0.8619
	0.7635	0.1341	0.1025	0.1297	0.0228	0.8475
	0.6950	0.1729	0.1322	0.1288	0.0320	0.8391
	0.6113	0.2027	0.1860	0.1348	0.0447	0.8205
	0.5535	0.2360	0.2105	0.1376	0.0587	0.8037
	0.4715	0.2526	0.2759	0.1579	0.0846	0.7575
	0.4020	0.2667	0.3313	0.1574	0.1044	0.7382
	0.3639	0.2963	0.3398	0.1457	0.1186	0.7357
313.2	0.9813	0.0000	0.0187	0.1147	0.0000	0.8853
	0.9154	0.0479	0.0367	0.1177	0.0062	0.8762
	0.8518	0.0942	0.0540	0.1193	0.0132	0.8675
	0.7767	0.1364	0.0869	0.1144	0.0201	0.8655
	0.7187	0.1788	0.1025	0.1381	0.0344	0.8275
	0.6411	0.2126	0.1463	0.1308	0.0434	0.8258
	0.5706	0.2433	0.1860	0.1294	0.0552	0.8155
	0.4715	0.2526	0.2759	0.1322	0.0708	0.7969
	0.4236	0.2810	0.2954	0.1334	0.0885	0.7781
	0.3686	0.3001	0.3314	0.1255	0.1022	0.7724
	0.2835	0.2604	0.4562	0.1704	0.1565	0.6731
	0.2670	0.2657	0.4672	0.1680	0.1672	0.6647
323.2	0.9293	0.0000	0.0707	0.1300	0.0000	0.8700
	0.8529	0.0447	0.1024	0.1266	0.0066	0.8668
	0.7815	0.0864	0.1321	0.1231	0.0136	0.8633
	0.7262	0.1275	0.1462	0.1226	0.0215	0.8559
	0.6727	0.1673	0.1599	0.1173	0.0292	0.8535
	0.6113	0.2027	0.1860	0.1254	0.0416	0.8330
	0.5077	0.2165	0.2759	0.1233	0.0526	0.8241
	0.4354	0.2333	0.3313	0.1445	0.0774	0.7780
	0.3735	0.2477	0.3788	0.1357	0.0900	0.7743
	0.3465	0.2821	0.3714	0.1249	0.1017	0.7733
water (1) + propionic acid (2) + cyclohexanol (3)						
303.2	0.9814	0.0000	0.0186	0.1245	0.0000	0.8755
	0.9154	0.0479	0.0366	0.1206	0.0063	0.8731
	0.8519	0.0942	0.0539	0.1299	0.0144	0.8557
	0.7905	0.1388	0.0707	0.1283	0.0225	0.8491
	0.7313	0.1819	0.0868	0.1365	0.0339	0.8296
	0.6309	0.2093	0.1598	0.1300	0.0431	0.8268
	0.5536	0.2361	0.2103	0.1447	0.0617	0.7935
	0.4991	0.2674	0.2334	0.1595	0.0854	0.7551
	0.4073	0.2702	0.3224	0.1658	0.1100	0.7243
	0.3687	0.3002	0.3311	0.1528	0.1244	0.7229
313.2	0.9937	0.0000	0.0063	0.0977	0.0000	0.9023
	0.9384	0.0491	0.0125	0.1043	0.0055	0.8902
	0.8782	0.0971	0.0247	0.1221	0.0135	0.8644
	0.8296	0.1457	0.0247	0.1216	0.0214	0.8570
	0.7668	0.1907	0.0425	0.1332	0.0331	0.8337

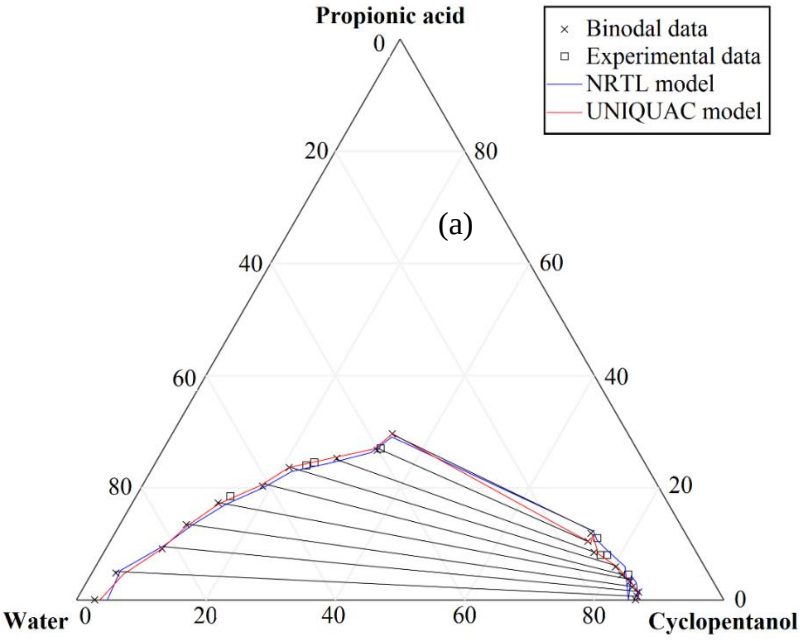
	0.6779	0.2248	0.0973	0.1336	0.0443	0.8221
	0.6051	0.2580	0.1369	0.1245	0.0531	0.8224
	0.5529	0.2962	0.1508	0.1288	0.0690	0.8021
	0.4795	0.3181	0.2024	0.1358	0.0901	0.7741
	0.4164	0.3390	0.2445	0.1466	0.1193	0.7341
	0.3709	0.3339	0.2953	0.1514	0.1363	0.7123
	0.3324	0.3308	0.3368	0.1494	0.1486	0.7020
	0.2836	0.3119	0.4045	0.2081	0.2288	0.5631
	0.2430	0.2955	0.4616	0.2016	0.2452	0.5532
323.2	0.9723	0.0000	0.0277	0.1383	0.0000	0.8617
	0.8990	0.0471	0.0539	0.1434	0.0075	0.8491
	0.8223	0.0909	0.0868	0.1442	0.0159	0.8399
	0.7507	0.1318	0.1175	0.1396	0.0245	0.8359
	0.6838	0.1701	0.1461	0.1449	0.0360	0.8190
	0.6518	0.2162	0.1321	0.1387	0.0460	0.8153
	0.5707	0.2434	0.1859	0.1519	0.0648	0.7833
	0.4850	0.2598	0.2552	0.1566	0.0839	0.7596
	0.3922	0.2601	0.3477	0.1607	0.1066	0.7327
	0.3551	0.2891	0.3557	0.1488	0.1212	0.7300

[a] Standard uncertainties, u, of T and w are $u(T) = 0.1$ ℃, $u(w) = 0.01$ and $u(P) = 0.5$ kPa.

The Hand and Bachman equations have been used to validate binodal data [25]. Eqs. 1 and 2 represent the Hand [29, 30] and Bachman equations [31], respectively.

$$\text{Hand: } \ln\left(\frac{w_2^O}{w_3^O}\right) = a_H \ln\left(\frac{w_2^{aq}}{w_1^{aq}}\right) + b_H \quad (1)$$

$$\text{Bachman: } w_2^O = a_B \left(\frac{w_2^{aq}}{w_1^{aq}}\right) + b_B \quad (2)$$



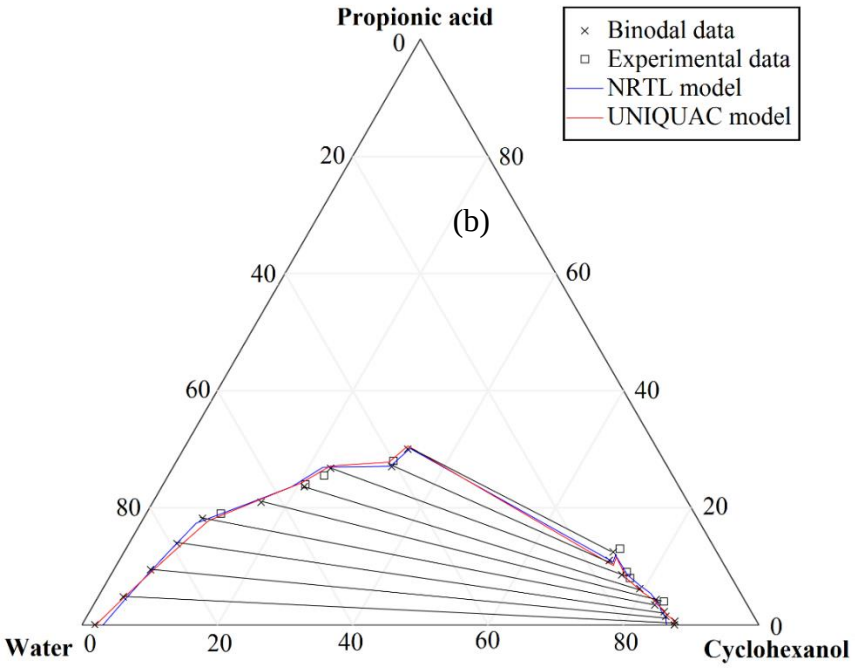
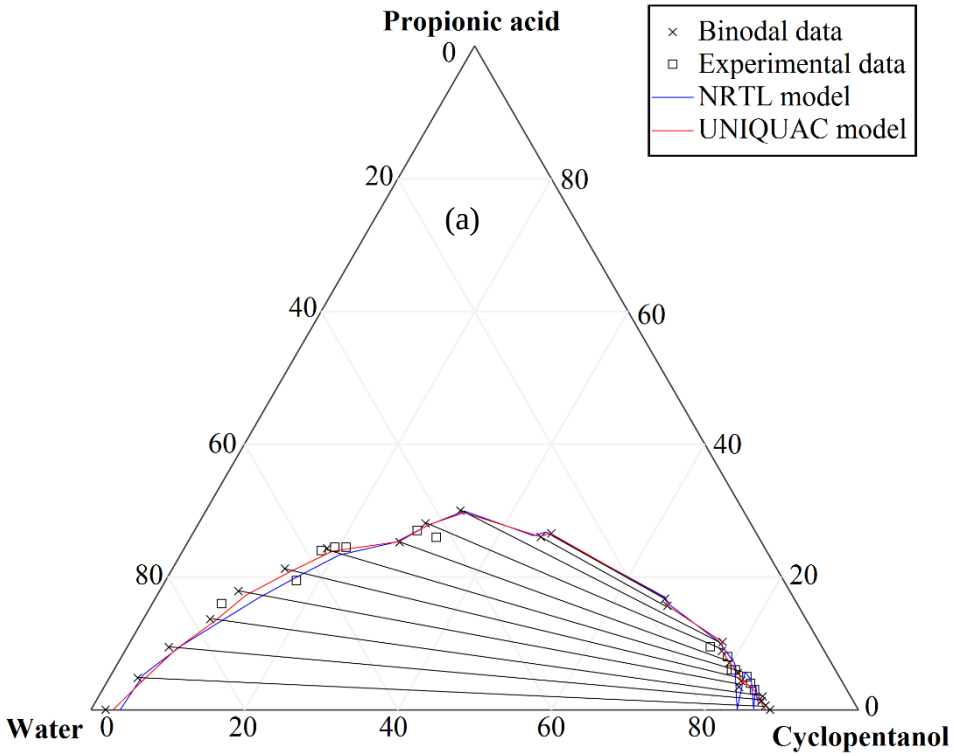


Fig. 1. Binodal curve data, tie lines and thermodynamic models (NRTL and UNIQUAC) for studied systems: a) water, propionic acid, cyclopentanol and b) water, propionic acid, cyclohexanol at 303.2 K



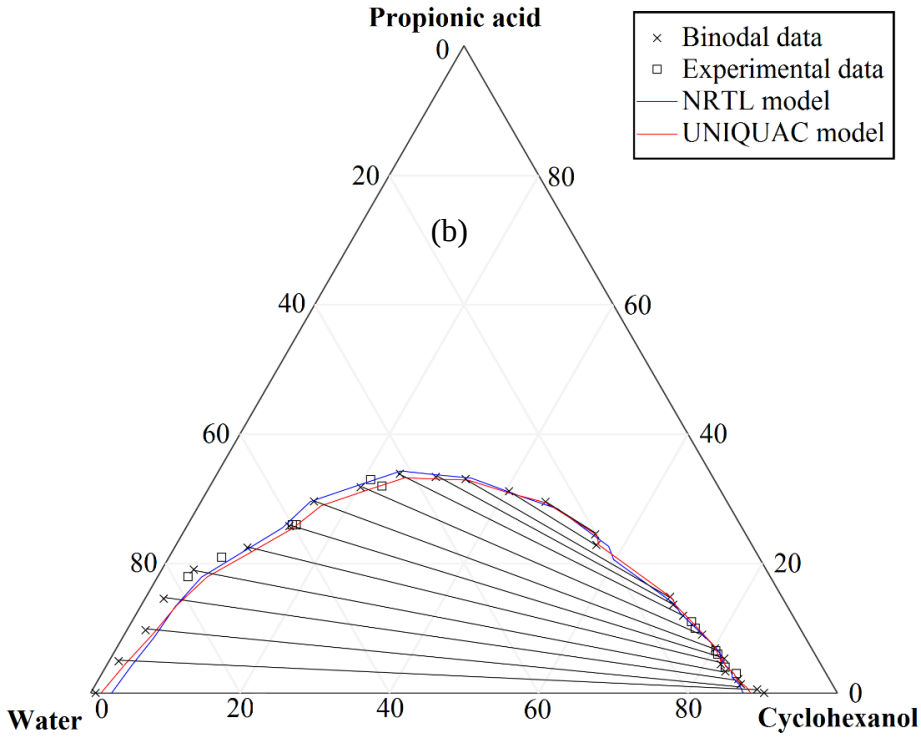
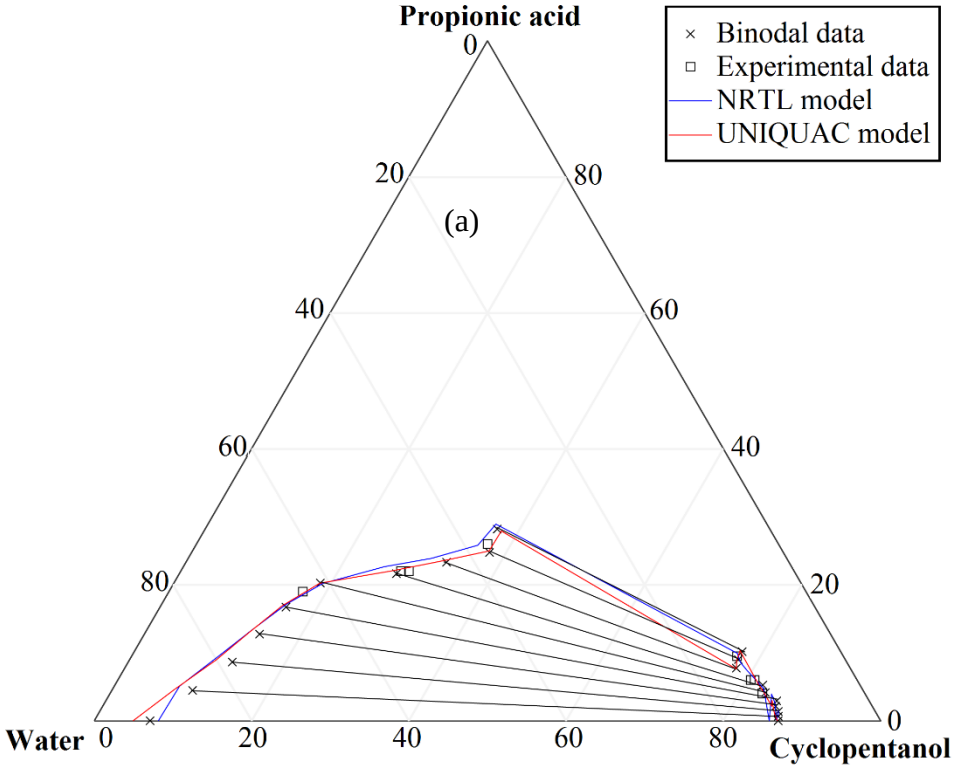


Fig. 2. Binodal curve data, tie lines and thermodynamic models (NRTL and UNIQUAC) for studied systems: a) water, propionic acid, cyclopentanol and b) water, propionic acid, cyclohexanol at 313.2 K



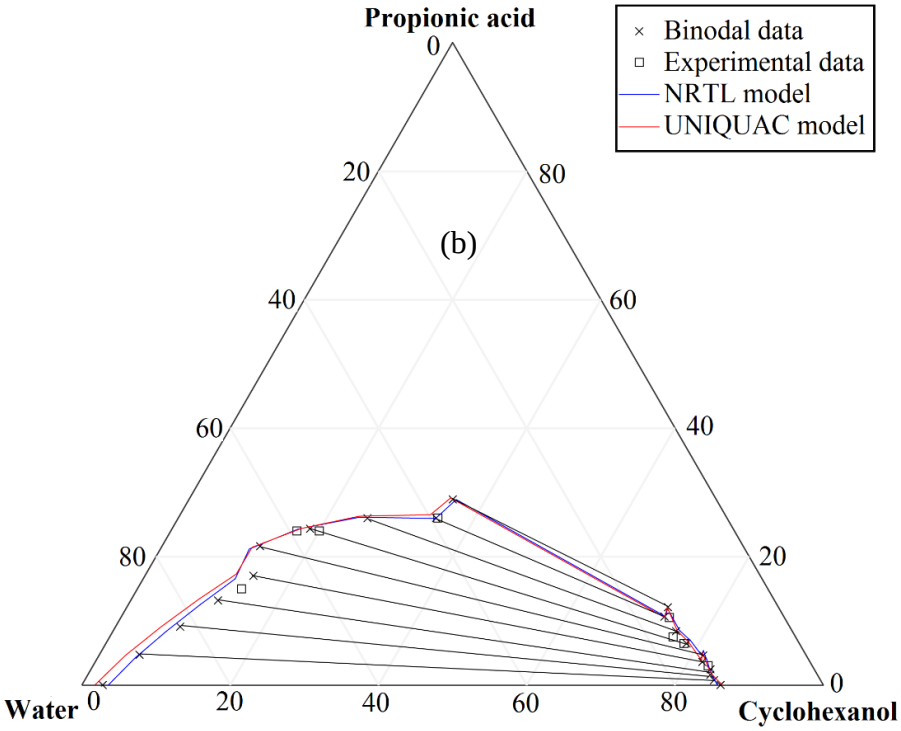


Fig. 3. Binodal curve data, tie lines and thermodynamic models (NRTL and UNIQUAC) for studied systems: a) Water, Propionic acid, cyclopentanol and b) Water, Propionic acid, cyclohexanol at 323.2K

where w_2^O is the mass fraction of the acid and w_3^O is the solvent mass fraction in the solvent-rich phase, w_2^{aq} is the mass fraction of the acid and w_1^{aq} is the mass fraction of water in the water-rich phase. The constants of the Hand equation are a_H and b_H, a_B and b_B are the constants of the Bachman equation. This stability was obtained through the experimental data regression [32], and with the correlation coefficient (R^2) have been presented for the studied systems in Table 4. The correlation coefficient values in both the equation of Hand and Bachman are close to the unit, which shows the reliability of the experimental data [33]. Also, in Figs. 4 and 5, the Hand and Bachman equations (Eqs. 1 and 2) for ternary systems containing cyclopentanol and cyclohexanol solvents are shown. In these figures, good correlation between these equations and experimental data can be observed. It also shows that measuring LLE data for both systems has high accuracy [29-32].

Table 4. Coefficients of Hand and Bachman equations and correlation coefficient (R^2) for the studied systems [a]

T, K	Hand			Bachman		
	a_H	b_H	R^2	a_B	b_B	R^2
water (1) + propionic acid (2) + cyclopentanol (3)						
303.2	1.1396	-1.5862	0.9936	0.3605	0.0110	0.9669
313.2	1.1818	-1.5919	0.9844	0.2573	0.0186	0.9529
323.2	1.0742	-1.7765	0.9937	0.3385	0.0102	0.9650
water (1) + propionic acid (2) + cyclohexanol (3)						
303.2	1.1805	-1.5135	0.9946	0.3655	0.0115	0.9649
313.2	1.2879	-1.4324	0.9740	0.2467	0.0251	0.9516
323.2	1.0937	-1.5650	0.9962	0.3490	0.0128	0.9546

[a] Standard uncertainties, u, of T, a, b and R^2 are $u(T) = 0.1$ ℃ , $u(a) = u(b) = u(R^2) = 0.0001$.

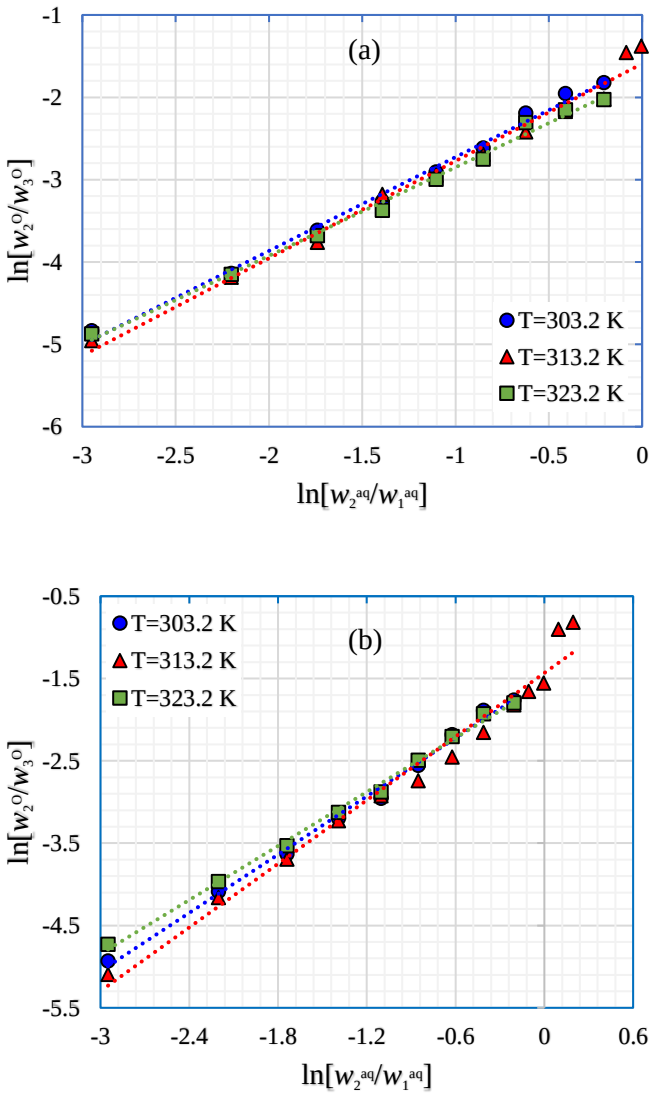


Fig. 4. Hand plot of the ternary system of a) water + Propionic acid+ cyclopentanol, b) water + propionic acid+ cyclohexanol at the studied temperature

Tie line data

In Table 5, the data of the tie lines are presented for ternary systems of water + propionic acid + cyclic alcohols (cyclopentanol and cyclohexanol) at 303.2, 313.2, and 323.2 K. These data are plotted in triangular diagrams in Figs. 1 to 3.

Distribution coefficient and selectivity factor are essential parameters for liquid-liquid extraction and are shown respectively with D and S and are defined according to Eqs. 3 and 4 [34, 35].

$$D_i = \frac{w_i^O}{w_i^{aq}} \tag{3}$$

$$S = \frac{D_2}{D_1} \tag{4}$$

where w_i^O and w_i^{aq} are the mass fraction of component i in rich-solvent and rich-water phases. D_2 and D_1show the distribution coefficients for propionic acid and water. The distribution coefficient and selectivity factor for both cyclopentanol and cyclohexanol solvents are calculated at 303.2, 313.2, and 323.2 K, and are presented in Table 5. The selectivity factor shows the solvent ability to extract propionic acid from an aqueous solution. For effective separation, the selectivity factor should be greater than one so that the solvent for acid extraction is used [34, 35].

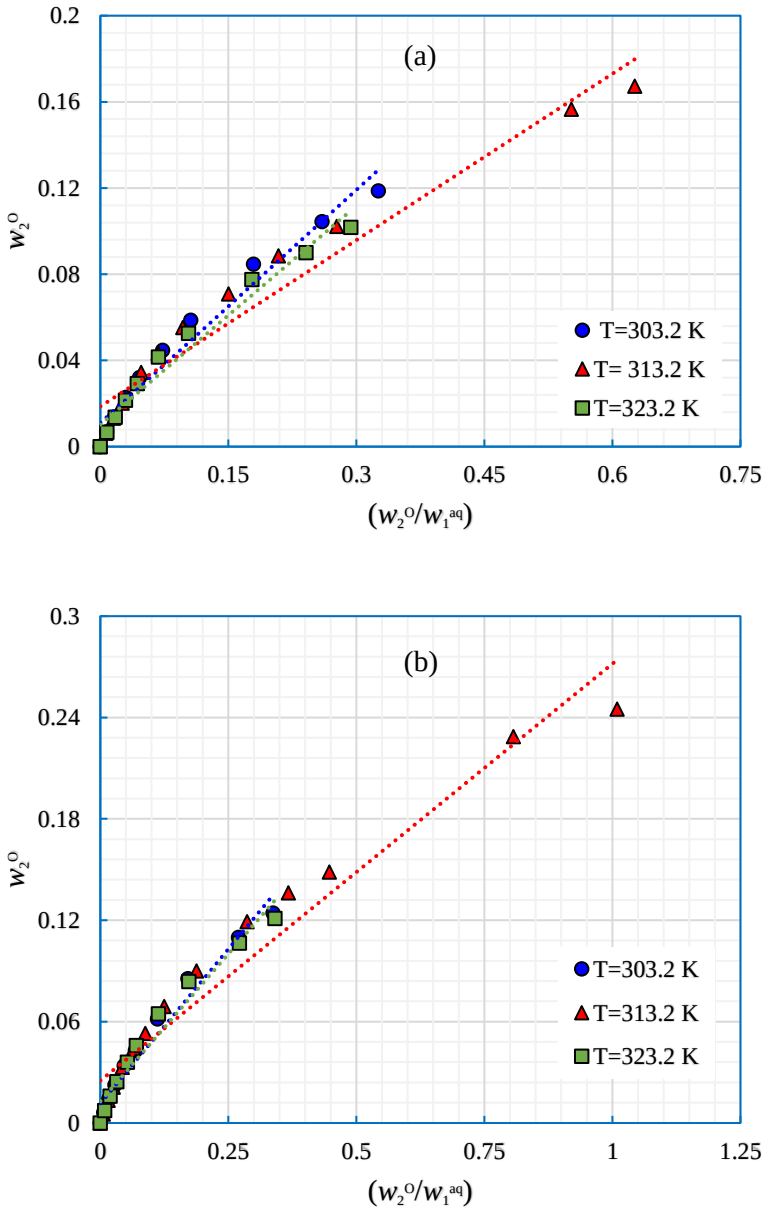


Fig. 5. Bachman plot of the ternary system of a) water + propionic acid+ cyclopentanol, b) water + propionic acid + cyclohexanol at the studied temperature

Table 5. Experimental tie-line data, distribution coefficient of propionic acid, and selectivity factor for the ternary systems of water + propionic acid + cyclic alcohols (cyclopentanol and cyclohexanol) at the temperature of 303.2, 313.2, and 323.2 K and pressure of 101.3 kPa [a]

T	Overall composition			Water-rich phase			Solvent-rich phase			D_2	S
(K)	w_1	w_2	w_3	w_1^{aq}	w_2^{aq}	w_3^{aq}	w_1^{O}	w_2^{O}	w_3^{O}		
water (1) + propionic acid (2) + cyclopentanol (3)											
303.2	0.4700	0.2000	0.3300	0.5250	0.2400	0.2350	0.1400	0.0800	0.7800	0.333	1.250
	0.2300	0.1000	0.6700	0.5100	0.2450	0.2450	0.1500	0.0800	0.7700	0.327	1.110
	0.3000	0.2000	0.5000	0.3950	0.2700	0.3350	0.1400	0.1100	0.7500	0.407	1.149
	0.4000	0.1000	0.5000	0.6700	0.1850	0.1450	0.1250	0.0450	0.8300	0.243	1.304
313.2	0.3500	0.1500	0.5000	0.5450	0.2450	0.2100	0.1300	0.0600	0.8100	0.245	1.027
	0.2000	0.1300	0.6700	0.4400	0.2700	0.2900	0.1300	0.0800	0.7900	0.296	1.003
	0.5400	0.1300	0.3300	0.7500	0.1600	0.0900	0.1200	0.0300	0.8500	0.188	1.172
	0.2600	0.0700	0.6700	0.6350	0.1950	0.1700	0.1200	0.0400	0.8400	0.205	1.085
	0.4000	0.2700	0.3300	0.4200	0.2600	0.3200	0.1450	0.0950	0.7600	0.365	1.058
	0.3500	0.1500	0.5000	0.5800	0.2400	0.1800	0.1200	0.0500	0.8300	0.208	1.007
	0.3500	0.1500	0.5000	0.5600	0.2450	0.1950	0.1350	0.0600	0.8050	0.245	1.016
323.2	0.2300	0.1000	0.6700	0.5000	0.2200	0.2800	0.1350	0.0600	0.8050	0.273	1.010
	0.4000	0.1000	0.5000	0.6400	0.1900	0.1700	0.1300	0.0400	0.8300	0.211	1.036
	0.3000	0.2000	0.5000	0.3700	0.2600	0.3700	0.1350	0.0950	0.7700	0.365	1.001
	0.4700	0.2000	0.3300	0.4900	0.2200	0.2900	0.1300	0.0600	0.8100	0.273	1.028
water (1) + propionic acid (2) + cyclohexanol (3)											
303.2	0.4700	0.2000	0.3300	0.5500	0.2400	0.2100	0.1500	0.0800	0.7700	0.333	1.222
	0.2300	0.1000	0.6700	0.5150	0.2550	0.2300	0.1500	0.0900	0.7600	0.353	1.212
	0.3000	0.2000	0.5000	0.4000	0.2800	0.3200	0.1400	0.1300	0.7300	0.464	1.327
	0.4000	0.1000	0.5000	0.7000	0.1900	0.1100	0.1200	0.0400	0.8400	0.211	1.228
313.2	0.3500	0.1500	0.5000	0.5950	0.2600	0.1450	0.1300	0.0600	0.8100	0.231	1.056
	0.2000	0.1300	0.6700	0.4500	0.3200	0.2300	0.1400	0.1000	0.7600	0.313	1.004
	0.5400	0.1300	0.3300	0.7800	0.1800	0.0400	0.1200	0.0300	0.8500	0.167	1.083
	0.2600	0.0700	0.6700	0.7200	0.2100	0.0700	0.1300	0.0400	0.8300	0.190	1.055
	0.4000	0.2700	0.3300	0.4600	0.3300	0.2100	0.1400	0.1100	0.7500	0.333	1.095
	0.3500	0.1500	0.5000	0.6000	0.2600	0.1400	0.1300	0.0650	0.8050	0.250	1.154
	0.3500	0.1500	0.5000	0.6000	0.2600	0.1400	0.1300	0.0600	0.8100	0.231	1.065
323.2	0.2300	0.1000	0.6700	0.5600	0.2400	0.2000	0.1650	0.0750	0.7600	0.313	1.061
	0.4000	0.1000	0.5000	0.7100	0.1500	0.1400	0.1400	0.0300	0.8300	0.200	1.014
	0.3000	0.2000	0.5000	0.3900	0.2600	0.3500	0.1550	0.1050	0.7400	0.404	1.016
	0.4700	0.2000	0.3300	0.5900	0.2400	0.1700	0.1550	0.0650	0.7800	0.271	1.031

[a] Standard uncertainties, u, of T, w, D, and S are $u(T) = 0.1$ ℃, $u(w) = 0.01$, $u(D) = 0.001$, $u(S) = 0.001$ and $u(P) = 0.5$ kPa.

In this study, the selectivity factor values for both solvents are more significant than one, and it can be shown that both cyclopentanol and cyclohexanol solvents can be used to separate propionic acid from aqueous solution. The results also show that in both systems, with increasing temperature, the selectivity factor decreased, which is due to increased propionic acid solubility in water with increasing temperature [6].

Thermodynamic Modeling of LLE Data

Experimental data of binodal curves for the studied systems have been correlated with thermodynamic equations (NRTL and UNIQUAC) and binary interacting parameters are determined. For this purpose, an objective function is defined according to Eq. 5 and, by minimizing it, the binary interaction parameters are computed. This function shows the mean square of the difference between the measured and calculated mass fraction values for all

components in water-rich, and solvent-rich phases for the root mean square deviation (RMSD) [30] using Eq. 6.

$$OF = 100 \times \frac{1}{6n} \sum_{k} \left(\sum_{j} \left(\sum_{i} \left(w_i^{exp} - w_i^{cal} \right)^2 \right) \right) \quad (5)$$

$$RMSD = \sqrt{\frac{\sum_k \left(\sum_j \left(\sum_i \left(w_i^{exp} - w_i^{cal} \right)^2 \right) \right)}{6n}} \quad (6)$$

In these equations, w_i^{exp} is the experimental or measured mass fraction, w_i^{cal} is the calculated mass fraction, k is the number of data ($k = 1.2.3. \ldots . n$), i and j show the number of components and the rich water or solvent phases, respectively.

The binary interaction parameters are obtained by optimizing the data by the objective function according to Table 6 for the studied systems. After calculating the molecular interactions, LLE data are correlated by NRTL and UNIQUAC thermodynamic models. The activity coefficient (γ_i) is used to predict the mass fraction of components in both aqueous and organic phases. The mass fraction of component i is calculated [36] by using Eq. 7.

$$\gamma_i^{aq} \, x_i^{aq} = \gamma_i^{O} \, x_i^{O} \quad (7)$$

where γ_i^{aq} and γ_i^{O} are the activity coefficients of component i in the rich-water and rich-solvent phases. x_i^{aq} and x_i^{O} are also mole fractions of component i, in the rich-water and rich-solvent phases, respectively.

Table 6. Intermolecular interaction parameters between water + propionic acid + cyclic alcohols (cyclopentanol and cyclohexanol) [a]

Model	Component		Binary interaction parameter			
	i	j	A_{ij}	B_{ij}, K	A_{ji}	B_{ji}, K
NRTL	water	propionic acid	18.8077	-122.8437	190.0296	-340.3225
		cyclopentanol	-3.6440	241.4096	11.2430	734.8774
	propionic acid	cyclopentanol	-3.3318	144.4347	2.9111	-382.4924
	water	propionic acid	-2.7730	848.4598	1.4137	-301.2937
		cyclohexanol	0.0397	259.7456	2.7718	-371.7907
	propionic acid	cyclohexanol	1.7208	-380.2637	-2.5019	911.8005
UNIQUAC	water	propionic acid	2.0496	-914.4564	-2.8165	683.5497
		cyclopentanol	-0.7261	185.3686	-1.6357	-193.8862
	propionic acid	cyclopentanol	14.3086	3.7980	-2.4411	-126.2708
	water	propionic acid	0.6879	-234.8668	-2.0890	838.9592
		cyclohexanol	-0.5083	432.9955	2.8514	-488.4418
	propionic acid	cyclohexanol	-2.0074	829.4668	1.7180	-514.4932

[a] Standard uncertainties, u, of A and B are $u(A) = 0.0001$ and $u(B) = 0.0001$ K

In Figs. 1 to 3, the results of calculating the mass fraction of components for ternary systems (water + propionic acid + cyclopentanol) and (water + propionic acid + cyclohexanol) are plotted by the NRTL and UNIQUAC equations at 303.2, 313.2, and 323.2 K. The results show the agreement of the experimental data with the NRTL and UNIQUAC thermodynamic models.

RMSD values for ternary systems of water + propionic acid + cyclic alcohols (cyclopentanol and cyclohexanol) are calculated separately and are presented in Table 7. Total RMSD values

for cyclopentanol for NRTL and UNIQUAC models were 0.0107 and 0.0057, respectively, and were 0.0108 and 0.0076 for cyclohexanol. RMSD values in both systems containing cyclopentanol and cyclohexanol have been less for the UNIQUAC model than NRTL. The UNIQUAC model has higher accuracy in correlation LLE data in the studied system.

Table 7. Accuracy of NRTL and UNIQUAC models for correlating the composition of water + propionic acid + cyclic alcohols (cyclopentanol and cyclohexanol) ternary systems [a]

System	T (K)	RSMD	
		NRTL	UNIQUAC
water + propionic acid + cyclopentanol	303.2	0.0092	0.0037
	313.2	0.0128	0.0046
	323.2	0.0092	0.0079
total	-	0.0107	0.0057
water + propionic acid + cyclohexanol	303.2	0.0091	0.0047
	313.2	0.0125	0.0075
	323.2	0.0095	0.0099
total	-	0.0108	0.0076

[a] Standard uncertainties, u, of T and RSMD are $u(T) = 0.1$ ℃, $u(\text{RSMD}) = 0.0001$

In a study by Özmen et al. [14], the solvent of cyclohexanol was used to extract propionic acid at 298.15 K. In the present study, two cyclic alcohols of cyclopentanol and cyclohexanol were investigated at 303.2, 313.2 and 323.2 K.

In the present study, the liquid-liquid phase equilibrium of ternary systems water + propionic acid + cyclopentanol or cyclohexanol at temperatures of 303.2, 313.2, and 323.2 K is investigated. In the studies by Özmen et al. [14], and Bekri et al. [22], solvents of cyclohexanol and cyclopentanol were used at a temperature of 298.2 K, respectively. In the present study and Özmen et al. [14], and Bekri et al. [22] research, the type-1 phase behavior in the LLE of the studied systems has been observed [14, 22].

For the solvent of cyclopentanol in this study and the research by Bekri et al. [22], the LLE data were simulated using the NRT thermodynamic model. In the present work, the UNIQUAC model is also investigated, and the results show higher accuracy of this model than the NRTL model for cyclopentanol solvent.

Özmen et al. [14] correlated the LLE data for cyclohexanol with the UNIFAC equation and reported an RMSD value of 2.65, but in the present work, the NRTL and UNIQUAC equations are applied and the RMSD values are 0.0108 and 0.0076, respectively, which show higher accuracy for the studied system.

The Hand equation is used to check the validity of binodal data. In the present study, the correlation coefficient for cyclopentanol was 0.9936 at 303.2 K and in the Bekri et al. [33] study was 0.9828 at 298.2 K. The correlation coefficient for cyclohexanol was 0.9946 at 303.2 K and in the Özmen et al. [14] study was 0.9932 at 298.2 K. The values of the correlation coefficient are close to the unit, which shows the reliability of the experimental data.

Comparing the binodal data of the system containing cyclohexanol solvent in the present study and the research conducted by Özmen et al. [14] shows that the data are almost close to each other but there is also a slight difference that may be due to differences in working temperatures.

Comparing triangular diagrams of LLE of Water + Propionic acid + Cyclic Alcohols in the present study and studies conducted by Özmen et al. [14] and Bekri et al. [22] shows the difference in the slope of the tie lines. The present study was performed at temperatures of 303.2, 313.2, and 323.2 K, and similar works were performed at 298.2 K.

The difference in slope of the tie lines may be related to the working temperature, because in the research conducted by Ghanadzadeh et al. [28], at a temperature of 303.2 K, the slope of the lines is similar to the present work.

Conclusion

The extraction of propionic acid from an aqueous solution due to its many applications in the industry has economic and environmental significance. Binodal curves and tie lines data for ternary systems (water + propionic acid + cyclopentanol) and (water + propionic acid + cyclohexanol) at 303.2, 313.2, and 323.2 K have been calculated. In both ternary systems, the type-1 phase behavior is observed. The reliability and coordination of liquid-liquid equilibrium data have been confirmed by the equations of Hand and Bachman in both systems. The selectivity factor values for both solvents are greater than one which indicates the ability of solvents to extract propionic acid from an aqueous solution. The distribution coefficients for two solvents (cyclopentanol and cyclohexanol) are lower than the unit which means for this extraction a huge amount of solvent will be needed. Regarding this fact, the extracted propionic acid in the solvent phase will be another environmental issue. Liquid-liquid equilibrium data are correlated using the NRTL and UNIQUAC thermodynamic models. The results show the high accuracy of these models and their compatibility with experimental data.

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