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Liquid-liquid equilibrium data in aqueous solutions of propionic and butyric acids with 1-heptanol at T=(298.15, 308.15, and 318.15) K

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Abstract–Liquid-liquid phase equilibrium (LLE) data were determined for the (water+propionic or butyric acid+1-heptanol) ternary systems at T=(298.15, 308.15, and 318.15) K and p=101.3 kPa. For both systems, a type-1 LLE phase diagram was obtained. The quality of the experimental LLE data was determined through the Othmer-Tobias and Bancroft equations. The experimental tie-lines were fitted using the UNIQUAC and NRTL correlation models. For the studied systems, a comparison was made between the experimental and correlated distribution coefficients and separation factors. The LSER model of Katritzky was applied to obtain the contributions of intermolecular interactions in these systems.

Keywords: Liquid-liquid Equilibrium, Carboxylic Acid, UNIQUAC Model, NRTL Model, LSER Model

INTRODUCTION

Carboxylic acids are scientifically and industrially important group of organic compounds produced by chemical synthetic or fermentation methods [1-4]. Due to their wide industrial applications, extraction of carboxylic acids from aqueous solutions is an important problem [5-7]. Thus, accurate equilibrium data for the ternary systems consisting of water, carboxylic acid, and various solvents are always necessary for the understanding and interpretation of phase behavior.

In this study, two carboxylic acids, propionic acid (PA) and butyric acid (BA), were used. They have just one carbon difference in their carbon chain length. These organic acids are produced mainly by biochemical methods and their efficient separation from water is an important issue [8-10]. Up to now, various investigations have been carried out on the extraction and liquid-liquid equilibrium (LLE) measurements of PA and BA from water, and several researchers have examined the extractability of these acids by various organic solvents with different chemical properties [11-17]. Heavy alcohols [18-21], hydrocarbons [22,23], and esters [24-26] were mainly used as extractants in the LLE measurements. However, further studies in this area are still important and required for various industrial goals. In this study, ternary LLE data of (water-propionic acid-1-heptanol) and (water-butyric acid-1-heptanol) systems were obtained at T=(298.15, 308.15, 318.2) K, where no such data are available in the literature.

At each temperature, the phase compositions and tie-line data were measured and ternary phase diagrams were plotted. Distribution coefficients (D) and separation factors (S) were determined from the tie-line data. The quality of the experimental data was tested by the Othmer-Tobias [27] and Bancroft [28] equations. The experimental tie lines were fitted by using the NRTL [29] and the UNIQUAC models [30]. The values for the interaction parameters were obtained and the calculated compositions compared with the experimental ones. In this work, the Katritzky LSER model [31] was applied to correlate distribution coefficients and separation factors.

EXPERIMENTAL

The supplier, purity, and their selected properties of materials used in this study are given in Table 1. Purchased materials were used as received. Deionized and redistilled water with an electrical conductivity less than 5 $\mu S\cdot cm^{-1}$ at T=298.15 K was used.

Refractive indices and densities of the pure liquids were measured at 298.15 K with a CETI Abbe Refractometer (accuracy; ±0.0002) and a Kyoto electronic DA210 density meter (accuracy; ±0.05 $kg\cdot m^{-3}$), respectively. The sample weighing involved an HR 200 AND electronic analytical balance (accuracy; ±0.0001 g). Karl-Fisher titration was carried out using a Metrohm 870 KF Titrino plus Karl-Fisher titrator. The temperature of the liquids was measured with a Lutron TM-917 precision digital thermometer (accuracy; ±0.01 K).

The detailed experimental procedure and measurements are described in our previous publication [21]. The procedure used to obtain the LLE data essentially consisted of solubility and tie line data. The solubility curves were determined by the cloud point titration method. To obtain the solubility data of the aqueous-rich and organic-rich sides of the curves, the feed homogeneous mixtures of either (water-acid) or (solvent-acid) were titrated against solvent or water. The consistency of the cloud point method depends on the accuracy of the micropipette (±0.005 ml) and restriction of

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Table 1. Source, purity, refractive index (n_D), density (ρ), and the UNIQUAC structural parameters (r and q) of the pure components at *T*=298.15 K (the literature data are included [19,36-38])[a]

Component	Source	Purity	r	q	n_D		$\rho/(kg\cdot m^{-3})$	
					Exp.	Lit.	Exp.	Lit.
Propionic acid	Chemlab	>0.99	2.88	2.61	1.3807	1.3809 [37]	987.92	988.20 [37]
Butyric acid	Merck	>0.99	3.55	3.15	1.3977	1.3975 [19]	952.68	952.80 [19]
1-Heptanol	Merck	≥0.99	5.47	4.67	1.4240	1.4249 [38]	821.41	822.46 [38]
Water	--	Deionized & bidistilled	0.92	1.40	1.3324	1.3325 [39]	997.01	997.05 [39]

[a] Standard uncertainties u are $u(n_D)=0.0002$, $u(\rho)=0.05\ kgm^{-3}$, $u(T)=0.01$ K, and $u(p)=0.4$ kPa

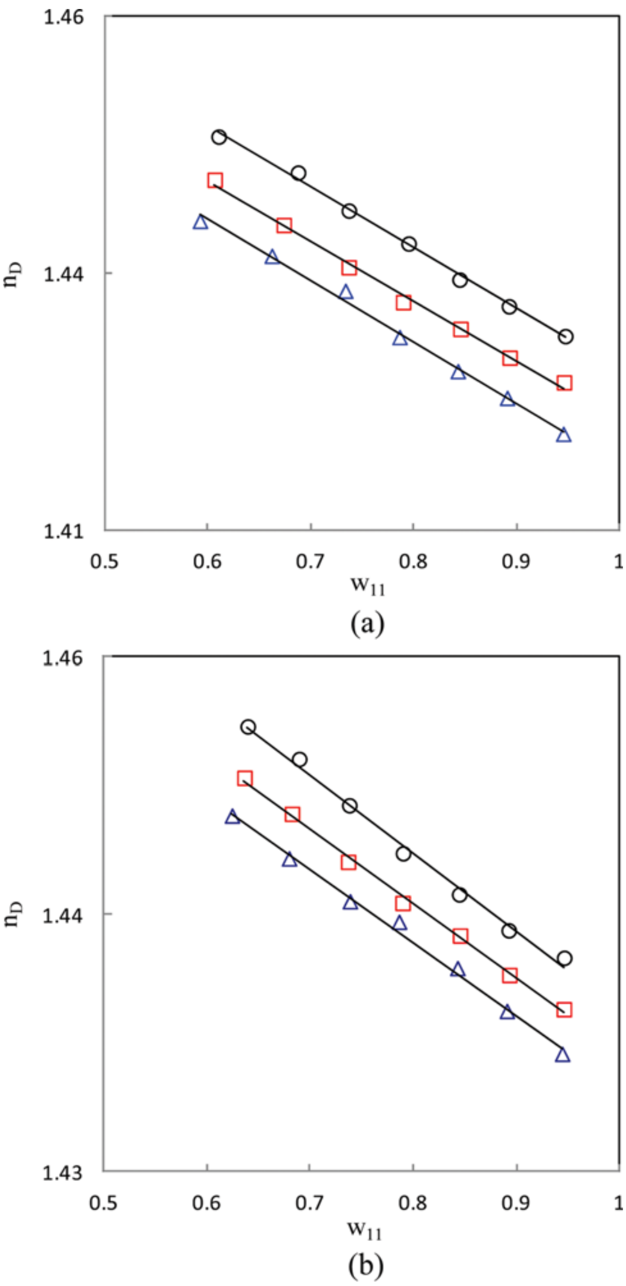


Fig. 1. Refractive index standard curves for (a) [water+propionic acid+1-heptanol], (b) [water+butyric acid+1-heptanol] in aqueous phase (w_{11}) at various temperatures; (○) *T*=298.15 K, (□) *T*=308.15 K, (△) *T*=318.15 K.

the visual examination. The standard uncertainty [32] in the mass fraction of the solubility data was estimated to be better than ±0.0009.

Tie-line measurements for the ternary systems were made at *T*=(298.15, 308.15, and 318.15) K. The prepared ternary mixtures by mass were placed in the extraction cell (250 ml glass cell) and were vigorously agitated by a magnetic stirrer for 4 h, and then left to settle for 4 h for phase separation. Preliminary tests showed that these times are adequate to achieve phase equilibrium.

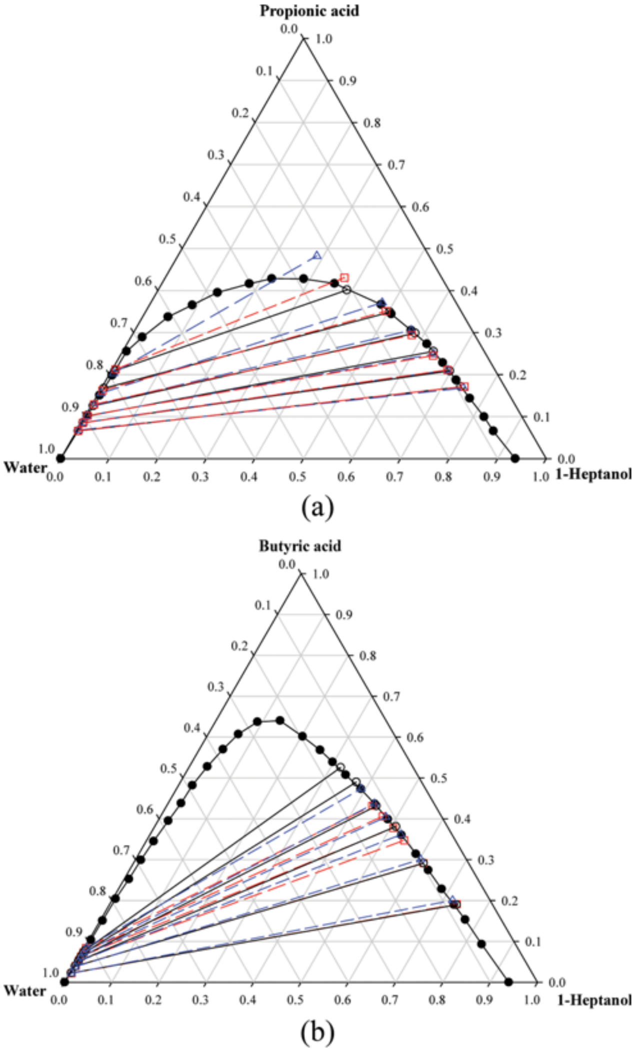
The tie lines were analyzed by acidimetric titration, the Karl-Fisher technique, and refractive index measurements. The mass fractions of the acid in the both phases (w_{21} and w_{23}) were measured by acidimetric titration using phenolphthalein as an indicator. The water content of the organic and aqueous phases (w_{11} and w_{13}) was measured by the Karl-Fisher and refractive index measurement methods, respectively. Thus, knowing the two mass fractions in each phase, the mass of the third component (w_{31} or w_{33}) was evaluated using the equation of $\{w_1+w_2+w_3=\Sigma w_i=1\}$. The standard curves at three different temperatures are shown in Fig. 1(a)-(b). The best-fit straight lines (trend lines) for refractive index (n_D) vs. w_{11} at various temperatures are presented in Supplementary data Table S1. The estimated standard uncertainty [32] of the measured compositions is better than ±0.002.

RESULTS AND DISCUSSION

1. Solubility and Tie Line Data

Experimental solubility curve data determined for the (water-PA-1-heptanol) and (water-BA-1-heptanol) ternary systems at *T*=(298.15, 308.15, and 318.15) K and *p*=101.3 kPa. Supplementary data Table S2 contains the measured solubility data for the studied systems at each temperature. For verification of the applied method, the mutual binary solubilities between water-1-heptanol obtained in this work were compared with the literature data [33], which indicates that the method used in this work is appropriate. To show the small effect of temperature on the solubility curves and biphasic region, the corresponding diagrams at three different temperatures were plotted and compared in Supplementary data Fig. S1. As a result, the immiscibility region for the system containing BA is larger than that of the other.

The experimental tie lines for the systems studied here were determined at the same range of temperatures. Typical phase diagrams for the ternary systems at *T*=298.15 K are plotted and shown in Fig. 2(a)-(b). The tie line data for the studied ternary systems at



(a)

(b)

Fig. 2. Phase diagram for the ternary systems at T=298.15 K; (●) experimental cloud points, (○) experimental tie-line points, (□) UNIQUAC calculated points; (△) NRTL calculated points; (a) [water+propionic acid+1-heptanol], (b) [water+butyric acid+1-heptanol].

Table 2. Experimental tie-line data in mass fraction for [water (1)+carboxylic acid (2)+1-heptanol (3)] at T=(298.15, 308.15, and 318.15) K and p=101.3 kPa[a]

Aqueous phase mass fraction		Organic phase mass fraction	
w_1 (water)	w_2 (PA)	w_1 (water)	w_2 (PA)
Water (1)+propionic acid (2)+1-heptanol (3)			
T=298.15 K			
0.931	0.066	0.090	0.171
0.911	0.086	0.095	0.209
0.895	0.101	0.105	0.255
0.870	0.126	0.121	0.299
0.828	0.167	0.148	0.349
0.784	0.209	0.210	0.401
T=308.15 K			
0.928	0.068	0.092	0.175
0.908	0.087	0.100	0.213
0.888	0.107	0.108	0.243
0.873	0.122	0.115	0.280
0.837	0.156	0.137	0.314
0.792	0.201	0.192	0.370
T=318.15 K			
0.920	0.075	0.097	0.169
0.907	0.088	0.105	0.199
0.881	0.112	0.111	0.239
0.857	0.136	0.123	0.278
0.849	0.145	0.139	0.303
0.797	0.195	0.194	0.361
Water (1)+butyric acid (2)+1-heptanol (3)			
T=298.15 K			
0.974	0.022	0.077	0.190
0.958	0.039	0.096	0.291
0.945	0.052	0.109	0.381
0.935	0.061	0.125	0.432
0.926	0.070	0.138	0.490
0.916	0.079	0.154	0.525
T=308.15 K			
0.974	0.022	0.078	0.174
0.957	0.039	0.096	0.283
0.946	0.050	0.121	0.369
0.935	0.061	0.125	0.424
0.926	0.069	0.136	0.463
0.921	0.074	0.150	0.491
T=318.15 K			
0.974	0.021	0.081	0.167
0.956	0.038	0.097	0.275
0.945	0.049	0.115	0.340
0.935	0.059	0.127	0.386
0.926	0.068	0.143	0.445
0.921	0.073	0.151	0.465

[a] Standard uncertainties u are u(T)=0.01 K, u(p)=0.4 kPa, and u(w)=0.002

various temperatures are given in Table 2. Since the water-1-heptanol mixture is the only liquid pair that is partially miscible, both the ternary systems present as the Treybal's type-1 LLE phase behavior [34], as expected for systems containing primary alcohols. The slope of the tie lines shows that both the acids are more soluble in the organic phase than the aqueous phase.

For the studied systems, the quality of the experimental tie lines was validated by using the Othmer-Tobias [27] (Eq. (1)) and Bancroft [28] (Eq. (2)) correlation equations.

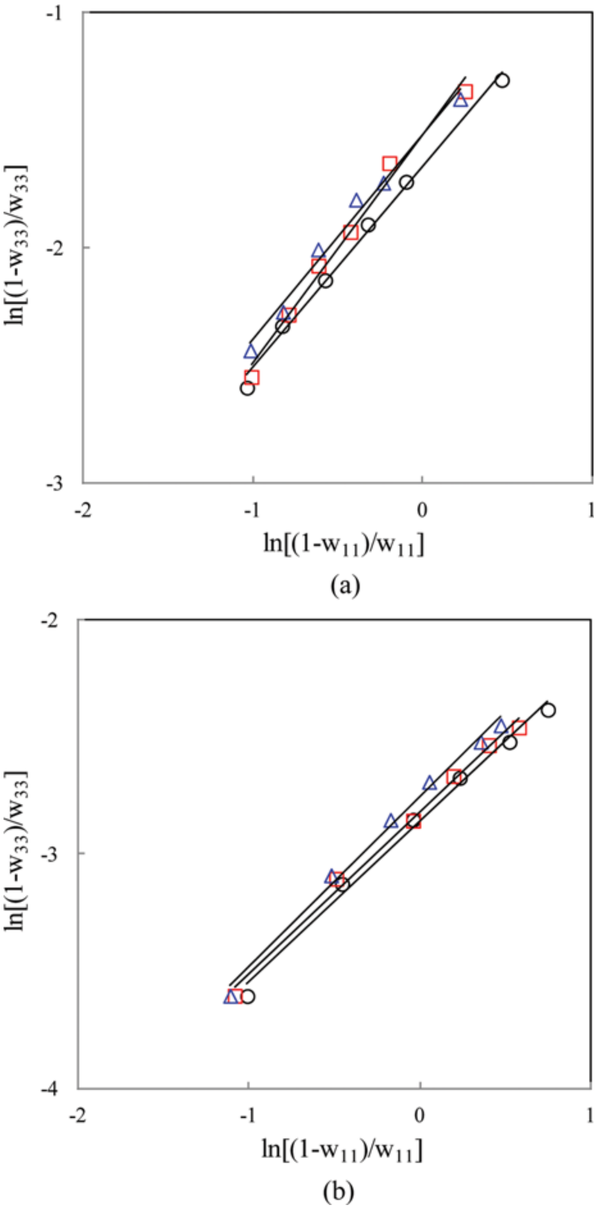
$$\ln\left(\frac{1-w_{33}}{w_{33}}\right)=A+B\ln\left(\frac{1-w_{11}}{w_{11}}\right) \tag{1}$$

$$\ln\left(\frac{1-w_{33}}{w_{23}}\right)=A'+B'\ln\left(\frac{1-w_{31}}{w_{11}}\right) \tag{2}$$

Here w_{23} and w_{33} are the mass fractions of the acid and solvent in the organic phase, respectively; w_{11} and w_{31} are the mass fractions of water and solvent in the aqueous phase. The Othmer-Tobias and Bancroft correlation parameters of [A(A′) and B(B′)] are given

Table 3. Othmer-Tobias and Bancroft equations coefficients for (water+carboxylic acid+1-heptanol) at *T*=(298.15, 308.15, and 318.15) K and *p*=101.3 kPa

	Othmer-Tobias correlation			Bancroft correlation		
T/K	A	B	R^2	A′	B′	R^2
			Water+propionic acid+1-heptanol			
298.15	−1.6515	0.8560	0.994	−7.5585	−1.5674	0.993
308.15	−1.5167	0.9685	0.987	−8.5648	−1.8562	0.995
318.15	−1.5159	0.8709	0.986	−8.4600	−1.9017	0.992
			Water+butyric acid+1-heptanol			
298.15	−2.8589	0.6854	0.992	−20.0160	−3.6793	0.993
308.15	−2.8195	0.6889	0.993	−24.5901	−4.6187	0.992
318.15	−2.7556	0.7235	0.993	−23.6180	−4.6787	0.994



(a)

(b)

Fig. 3. Othmer-Tobias plot for the system containing (a) propionic acid, and (b) butyric acid, at various temperatures; (○) *T*=298.15 K, (□) *T*=308.15 K, (△) *T*=318.15 K.

in Table 3. As can be seen from Fig. 3(a)-(b), the Othmer-Tobias plots exhibit good linear fit and indicate the reliability of the experimental data. The same trends were observed for the Bancroft plots.

Separation factor ($S=D_2/D_1$), which is a measure of ability of a solvent to separate a solute (acid in the present case) from water, is given by the following equation:

$$S=\frac{\text{distribution coefficient of solute}}{\text{distribution coefficient of water}}=\frac{w_{23}/w_{21}}{w_{13}/w_{11}} \tag{3}$$

where w_{21} is the mass fraction of the acid in the aqueous-rich phase. The distribution coefficients and separation factors are given in Table 4. The variations of experimental separation factor of the acids as a function of the mass fraction of the acid in aqueous phase for the systems are shown in Fig. 4(a)-(b). 1-Heptanol as a solvent is more successful for the extraction of BA than PA and could separate BA more effectively. Both systems have high separation factors at *T*=298.15 K.

2. Thermodynamic Modeling

For each ternary system, the experimental tie lies were satisfactorily fitted using the NRTL and the UNIQUAC correlation models. In the present work, the value of the non-randomness was fixed at α=0.3. The UNIQUAC structural parameters (r and q) [30] are presented in Table 1. The correlated data for the ternary systems at each temperature are listed in Supplementary data Table S3. The same data at *T*=298.15 K are also shown in Fig. 2(a)-(b). The experimental data were then compared by the thermodynamic models, which indicate the validity and reliability of the models. Also, the comparison between the experimental and correlated distribution coefficients and separation factors exhibits a good agreement between them (Table 4).

The temperature-dependent binary interaction parameters were achieved in order to fit the correlation models of UNIQUAC and NRTL to experimental tie line data. The goodness of the correlation is tested by the root mean square error (rmse) according to the following equation:

$$\text{rmse}=\frac{1}{6n}\left\{\sum_{k=1}^{n}\sum_{j=1}^{2}\sum_{i=1}^{3}(w_{ijk}^{exp}-w_{ijk}^{cal})^2\right\}^{-2} \tag{3}$$

where w^{exp} and w^{cal} indicate the experimental and calculated mass fraction, n is the number of tie lines, and the subscripts i, j, and k are indexes components, phases, and number of tie lines, respec-

Table 4. Experimental and correlated separation factors (S) and distribution coefficients of the acid (D_2) at different temperatures and atmospheric pressure[a]

T/K	D_2 (Exp.)	S (Exp.)	D_2 (UNIQ.)	S (UNIQ.)	D_2 (NRTL)	S (NRTL)
Water (1)+propionic acid (2)+1-heptanol (3)						
298.15	2.59	26.7	2.48	26.4	2.59	29.1
	2.44	23.4	2.46	22.9	2.49	23.3
	2.52	21.5	2.44	20.2	2.41	19.5
	2.38	17.2	2.41	16.7	2.28	15.2
	2.09	11.7	2.39	13.2	2.17	11.6
	1.92	7.2	2.37	8.1	2.03	7.9
308.15	2.56	25.8	2.53	25.3	2.58	27.8
	2.44	22.3	2.40	20.9	2.37	21.2
	2.28	18.7	2.31	17.9	2.25	17.5
	2.30	17.5	2.24	16.2	2.18	15.4
	2.01	12.3	2.09	12.7	2.06	11.7
	1.84	7.6	1.98	10.6	2.00	9.4
318.15	2.27	21.5	2.26	20.5	2.21	21.7
	2.27	19.6	2.23	19.0	2.20	19.6
	2.13	16.9	2.14	15.5	2.05	15.0
	2.05	14.2	2.09	13.7	2.05	13.6
	2.09	12.7	1.95	12.7	2.21	13.3
	1.86	7.6	1.96	10.2	1.77	8.4
Water (1)+butyric acid (2)+1-heptanol (3)						
298.15	8.43	106.8	8.71	112.3	9.25	113.4
	7.50	75.2	7.41	74.5	8.01	79.3
	7.39	63.9	6.49	56.5	7.12	61.8
	7.03	52.5	5.97	47.9	6.46	50.9
	6.95	46.5	5.55	41.1	6.06	44.3
	6.67	39.8	5.16	35.3	5.60	37.5
308.15	7.77	96.8	7.60	96.8	8.11	100.9
	7.26	72.2	7.23	70.5	7.56	71.7
	7.37	57.8	6.57	56.1	6.96	58.4
	6.99	52.2	6.05	46.6	6.48	49.5
	6.67	45.6	5.72	41.2	6.08	43.1
	6.64	40.7	5.52	38.1	5.90	40.4
318.15	7.91	95.3	7.41	96.9	7.83	96.6
	7.17	70.6	6.81	68.6	7.35	68.0
	6.87	60.0	6.50	55.4	6.81	55.8
	6.57	48.4	6.26	46.3	6.38	47.8
	6.59	45.3	6.06	39.1	6.02	41.7
	6.44	40.8	5.96	35.9	5.85	39.0

[a] Standard uncertainties u are u(T)=0.01 K, u(p)=0.4 kPa, and u(S)=0.2

tively. The NRTL and UNIQUAC binary interaction parameters with dependence of temperature together with values for the studied systems are shown in Table 5. As can be seen, both the thermodynamic models present fairly good results for the systems.

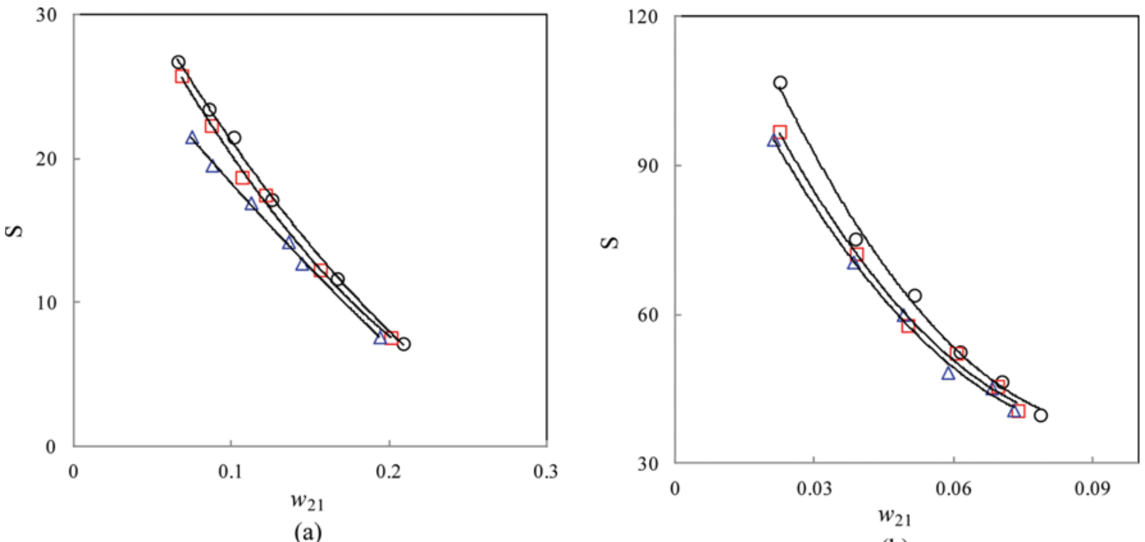
The Katritzky LSER multi-parameter equation [31] was used to correlate the separation factors and distribution coefficients according to the following equation:

$$\log D_2 = \log D_2^0 + a \cdot E_T^N + b \cdot \left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) + c \cdot \left(\frac{n_D^2 - 1}{2n_D^2 + 1}\right) \tag{4a}$$

$$\log S = \log S^0 + a \cdot E_T^N + b \cdot \left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) + c \cdot \left(\frac{n_D^2 - 1}{2n_D^2 + 1}\right) \tag{4b}$$

where ε, n_D and E_T^N are the relative permittivity, refractive index of solvent, and Reichardt polarity function, respectively. The coefficients a, b and c contain the solute properties, which come from regression [31].

The experimental distribution coefficients and separation factors were regressed by a computer program (Excel data solver). The permittivity (ε) and E_T^N values for 1-heptanol is 0.549 [35] and



(a)

(b)

Fig. 4. Plot of the separation factor (S) as a function of mass fraction of the acid in the aqueous phase for the system containing (a) propionic acid, and (b) butyric acid, at various temperatures; (○) T=298.15 K, (□) T=308.15 K, (△) T=318.15 K.

Table 5. The optimized UNIQUAC and NRTL (α=0.3) binary interaction parameters (a_{ij} or b_{ij})/K with dependence of temperature and the root mean square error (rmse) values for the ternary systems

Model	i-j	a_{ij} (b_{ij})	a_{ji} (b_{ji})	rmse%
		Water (1)+propionic acid (2)+1-heptanol (3)		
UNIQUAC	1-2	6.86 T−620.57	−1.97 T+234.29	
	1-3	0.86 T−322.19	1.63 T−159.09	1.69
	2-3	0.81 T+5.21	2.51 T−161.70	
NRTL	1-2	18.10 T+631.55	−0.05 T−311.51	
	1-3	−3.53 T+2122.30	−14.53 T+1399.30	0.91
	2-3	23.12 T−110.30	12.08 T−479.77	
		Water (1)+butyric acid (2)+1-heptanol (3)		
UNIQUAC	1-2	0.34 T−242.80	−3.21 T+164.98	
	1-3	−1.43 T−135.04	6.80 T−524.95	2.53
	2-3	−159.57 T+4881.01	331.24 T−14572.01	
NRTL	1-2	4.52 T+915.65	−0.69 T−73.01	
	1-3	−1.12 T+2044.10	−5.17 T+760.88	1.71
	2-3	−0.66 T−513.21	18.99 T+2331.8	

11.32 [36], respectively. That means this solvent exhibits 54.9% of the solvent polarity of water. Typically, the comparison of experimental and correlated data for S and D_2 at T=298.15 K is shown in Supplementary data Table S4. The regression coefficients a, b, and c were obtained and are presented in Table 6. As a result, different types of specific and non-specific interactions are involved to some extent for the studied systems. It means that the solvent effect is closely related to the nature and degree of intermolecular interactions, which arises from either non-specific interactions (polar and van der Waals interactions) or specific interactions (hydrogen bonding interactions).

Table 6. Results of the regression coefficients for the LSER equations at T=298.15 K

	log S^o	a	b	c	R^2
	Water (1)+propionic acid (2)+1-heptanol (3)				
$\log S_{LSER}$	0.025	3.313	2.634	1.229	0.981
$\log D_{LSER}$	0.095	0.960	0.764	0.356	0.926
	Water (1)+butyric acid (2)+1-heptanol (3)				
$\log S_{LSER}$	0.852	4.702	3.739	1.744	0.988
$\log D_{LSER}$	0.656	2.146	1.706	0.796	0.930

Supplementary data Fig. S2 shows correlation of experimental values of separation factor (S) and those correlated with different theoretical models at T=(298.15, 308.15, and 318.15) K. As can be seen from the plot, the diagonal line represents a good correlation of experimental and correlated values.

For comparison purposes, the average values of the separation factor obtained in this work and some previously reported in the literature for similar ternary mixtures are summarized in Table 7.

Table 7. The average values of separation factors for the (water+carboxylic acid+solvents) ternary systems

System	Solvent type	S	Literature
Water+PA+1-heptanol	$C_7H_{15}OH$	18.0	This study
Water+BA+1-heptanol	$C_7H_{15}OH$	64.1	This study
Water+PA+1-octanol	$C_8H_{17}OH$	22.2	[18]
Water+BA+1-octanol	$C_8H_{17}OH$	69.6	[21]
Water+PA+2-ethyl-1-hexanol	$C_8H_{17}OH$	7.5	[40]
Water+BA+2-ethyl-1-hexanol	$C_8H_{17}OH$	109.4	[21]
Water+PA+1-decanol	$C_{10}H_{21}OH$	24.4	[18]
Water+BA+1-decanol	$C_{10}H_{21}OH$	95.6	[41]
Water+PA+undecanol	$C_{11}H_{23}OH$	15.3	[42]
Water+BA+undecanol	$C_{11}H_{23}OH$	52.4	[42]
Water+PA+oleyl alcohol	$C_{18}H_{35}OH$	121.0	[43]
Water+BA+oleyl alcohol	$C_{18}H_{35}OH$	383.5	[44]

As can be seen, it is possible to show how the alcohol chain length affects the separation factor values of the investigated systems. Clearly, there is a relatively regular relation between the data, as the heavier alcohols offer a higher separation factor compared to others. In addition, the separation factor values of BA are greater than PA.

CONCLUSIONS

1-Heptanol was chosen as a solvent for recovery of PA and BA from aqueous solutions at T=(298.15, 308.15, and 318.15) K and p=101.3 kPa. Since only one liquid pair (water+solvent) is partially miscible, both ternary systems exhibit type-1 behavior of the LLE. The immiscibility region was found to be larger in the system containing BA. The distribution coefficients and separation factors were calculated for each system. The obtained separation factors confirm the capability of the solvent for extraction of the acids from water. However, these factors display larger values at T= 298.15 K for both the systems. It is obvious that the system containing BA gives higher separation factors compared to the other system. The Othmer-Tobias and Bancroft equation were applied for the investigated systems. The linearity of the plots indicates the consistency of the experimental data.

The UNIQUAC and NRTL (α=0.3) equilibrium models were satisfactorily used to correlate the experimental data. The corresponding temperature-dependent binary interaction parameters were presented. Moreover, the average values between the measured and calculated mass fractions were calculated and show that both models give acceptable results for the investigated systems. Moreover, the distribution coefficients and separation factors were adequately correlated with the LSER of Katritzky model. These results are in good agreement with contributions of different type of interactions (specific and non-specific interactions) for the systems studied here.

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Liquid-liquid equilibrium data in aqueous solutions of propionic and butyric acids with 1-heptanol at T=(298.15, 308.15, and 318.15) K

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Table S1. Equations for refractive index (n_D) as a function of water mass fractions (w_{11}) in the aqueous phase at T=(298.15, 308.15, and 318.15) K and atmospheric pressure[a]

System	T/K	Equation[b]	R^2
Water (1)+propionic acid (2)+1-heptanol (3)	298.15	$n_D=-0.0593\,w_{11}+1.4849$	0.997
	308.15	$n_D=-0.0582\,w_{11}+1.4789$	0.996
	318.15	$n_D=-0.0598\,w_{11}+1.4761$	0.995
Water (1)+butyric acid (2)+1-heptanol (3)	298.15	$n_D=-0.0458\,w_{11}+1.4802$	0.994
	308.15	$n_D=-0.0436\,w_{11}+1.4755$	0.997
	318.15	$n_D=-0.0426\,w_{11}+1.4725$	0.995

[a] Standard uncertainties u are u(T)=0.01 K, u(p)=0.4 kPa, u(n_D)=0.0002, and u(w)=0.001

[b] Standard uncertainty in the slope and intercept coefficients of the linear plot are 0.0015 and 0.0012, respectively

Table S2. Solubility curve data in mass fraction for [water (1)+carboxylic acid (2)+1-heptanol (3)] at T=(298.15, 308.15, and 318.15) K and p=101.3 kPa[a]

T=298.15 K		T=308.15 K		T=318.15 K	
w_1 (water)	w_2 (acid)	w_1 (water)	w_2 (acid)	w_1 (water)	w_2 (acid)
Water (1)+propionic acid (2)+1-heptanol (3)					
0.9997	0.0000	0.9998	0.0000	0.9998	0.0000
0.9471	0.0499	0.9459	0.0501	0.9451	0.0498
0.8923	0.1036	0.8930	0.1019	0.8905	0.1034
0.8443	0.1507	0.8452	0.1488	0.8426	0.1503
0.7948	0.1983	0.7894	0.2036	0.7860	0.2051
0.7367	0.2554	0.7366	0.2513	0.7333	0.2470
0.6873	0.2891	0.6735	0.2971	0.6618	0.2924
0.6101	0.3372	0.6064	0.3268	0.5920	0.3256
0.5462	0.3655	0.5292	0.3545	0.5170	0.3524
0.4795	0.3953	0.4645	0.3800	0.4542	0.3744
0.4034	0.4163	0.4048	0.4016	0.3940	0.3914
0.3509	0.4284	0.3315	0.4049	0.3241	0.3955
0.2855	0.4279	0.2747	0.4044	0.2570	0.3877
0.2275	0.4168	0.2045	0.3792	0.1952	0.3620
0.1570	0.3666	0.1485	0.3466	0.1393	0.3182
0.1471	0.3443	0.1533	0.3399	0.1622	0.3350
0.1258	0.3052	0.1303	0.3045	0.1383	0.3015
0.1094	0.2728	0.1139	0.2690	0.1196	0.2644
0.0991	0.2283	0.1050	0.2239	0.1096	0.2316

Table S2. Continued

T=298.15 K		T=308.15 K		T=318.15 K	
w_1 (water)	w_2 (acid)	w_1 (water)	w_2 (acid)	w_1 (water)	w_2 (acid)
Water (1)+propionic acid (2)+1-heptanol (3)					
0.0921	0.1870	0.0935	0.1850	0.1002	0.1791
0.0861	0.1434	0.0909	0.1365	0.0949	0.1359
0.0787	0.0994	0.0825	0.0922	0.0867	0.0916
0.0673	0.0423	0.0721	0.0452	0.0750	0.0427
0.0584	0.0000	0.0610	0.0000	0.0637	0.0000
Water (1)+butyric acid (2)+1-heptanol (3)					
0.9997	0.0000	0.9998	0.0000	0.9998	0.0000
0.9461	0.0498	0.9459	0.0501	0.9442	0.0497
0.8923	0.1036	0.8930	0.1019	0.8905	0.1034
0.7899	0.2041	0.7894	0.2036	0.7860	0.2051
0.7377	0.2523	0.7366	0.2513	0.7384	0.2487
0.6892	0.2989	0.6822	0.3009	0.6793	0.3001
0.6393	0.3448	0.6361	0.3429	0.6240	0.3432
0.5832	0.3951	0.5835	0.3909	0.5729	0.3905
0.5346	0.4381	0.5310	0.4345	0.5247	0.4326
0.4888	0.4818	0.4808	0.4771	0.4761	0.4730
0.4346	0.5276	0.4253	0.5196	0.4222	0.5151
0.3802	0.5698	0.3779	0.5563	0.3714	0.5604
0.3292	0.6070	0.3239	0.6007	0.3191	0.5918
0.2737	0.6371	0.2648	0.6181	0.2664	0.6087
0.2242	0.6401	0.2056	0.6059	0.2152	0.5820
0.1962	0.6016	0.1858	0.5687	0.1952	0.5610
0.1758	0.5682	0.1692	0.5355	0.1801	0.5323
0.1519	0.5076	0.1594	0.5051	0.1520	0.4654
0.1371	0.4732	0.1293	0.4358	0.1365	0.4338
0.1264	0.4363	0.1167	0.3545	0.1272	0.3916
0.1174	0.3990	0.0940	0.2750	0.1191	0.3522
0.0940	0.2744	0.0866	0.2285	0.0960	0.2714
0.0819	0.1898	0.0771	0.1883	0.0839	0.1824
0.0719	0.0929	0.0729	0.0932	0.0762	0.0926
0.0584	0.0000	0.0610	0.0000	0.0637	0.0000

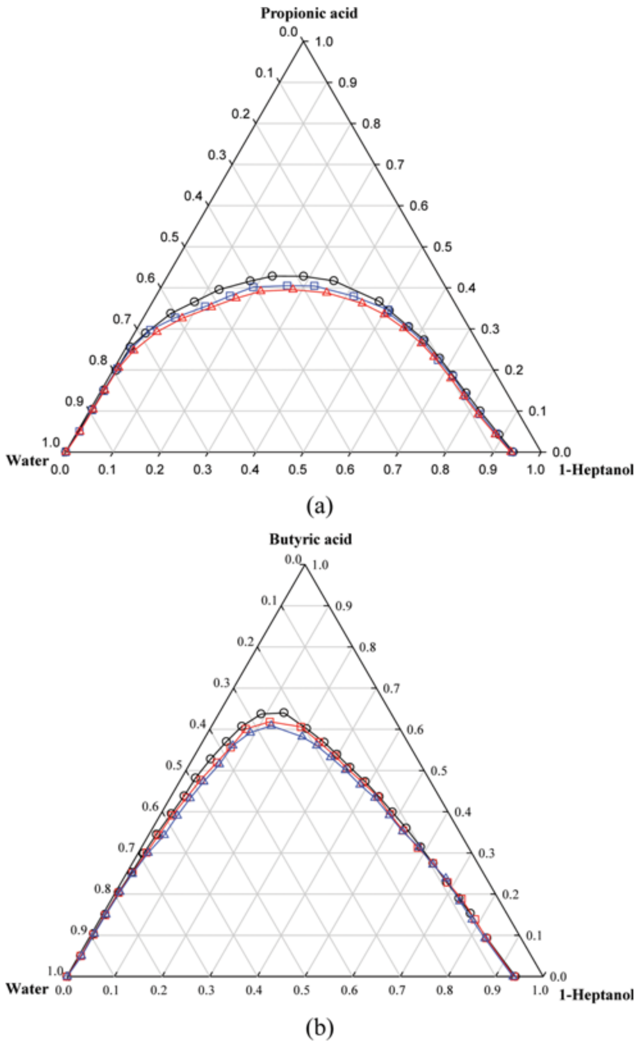
[a] Standard uncertainties u are u(T)=0.01 K, u(p)=0.4 kPa, and u(w)=0.0010

Table S3. Calculated the UNIQUAC and NRTL (α=0.3) tie line data in mass fraction for [water (1)+carboxylic acid (2)+1-heptanol (3)] at different temperatures

Aqueous phase mass fraction				Organic phase mass fraction			
w_{11}		w_{21}		w_{13}		w_{23}	
UNIQ.	NRTL	UNIQ.	NRTL	UNIQ.	NRTL	UNIQ.	NRTL
Water (1)+propionic acid (2)+1-heptanol (3)							
T=298.15 K							
0.929	0.931	0.068	0.066	0.087	0.083	0.168	0.172
0.911	0.912	0.086	0.085	0.097	0.098	0.211	0.211
0.894	0.894	0.102	0.102	0.108	0.110	0.249	0.245
0.869	0.867	0.127	0.129	0.126	0.130	0.305	0.294
0.839	0.833	0.156	0.162	0.152	0.155	0.371	0.351
0.789	0.781	0.203	0.212	0.231	0.200	0.482	0.431
T=308.15 K							
0.929	0.929	0.068	0.067	0.093	0.086	0.171	0.172
0.905	0.906	0.090	0.090	0.104	0.101	0.217	0.212
0.886	0.885	0.109	0.110	0.114	0.114	0.252	0.246
0.872	0.871	0.123	0.124	0.121	0.123	0.275	0.270
0.838	0.836	0.155	0.158	0.138	0.147	0.325	0.326
0.811	0.805	0.181	0.187	0.152	0.171	0.359	0.375
T=318.15 K							
0.919	0.919	0.076	0.076	0.101	0.094	0.171	0.168
0.907	0.905	0.088	0.090	0.106	0.102	0.195	0.198
0.875	0.878	0.119	0.115	0.121	0.120	0.254	0.236
0.856	0.856	0.138	0.137	0.130	0.129	0.287	0.281
0.846	0.852	0.147	0.142	0.130	0.142	0.286	0.315
0.809	0.801	0.182	0.191	0.155	0.168	0.357	0.338
Water (1)+butyric acid (2)+1-heptanol (3)							
T=298.15 K							
0.974	0.975	0.022	0.022	0.076	0.079	0.191	0.200
0.957	0.959	0.039	0.038	0.095	0.097	0.292	0.301
0.943	0.946	0.054	0.051	0.108	0.109	0.347	0.361
0.933	0.934	0.063	0.063	0.116	0.119	0.377	0.404
0.923	0.924	0.073	0.072	0.125	0.126	0.406	0.437
0.913	0.911	0.084	0.085	0.134	0.136	0.432	0.473
T=308.15 K							
0.973	0.974	0.022	0.022	0.076	0.078	0.170	0.177
0.956	0.957	0.039	0.038	0.098	0.101	0.283	0.290
0.944	0.945	0.052	0.050	0.111	0.113	0.339	0.350
0.933	0.934	0.063	0.061	0.121	0.122	0.381	0.398
0.925	0.924	0.071	0.071	0.128	0.130	0.405	0.434
0.920	0.919	0.076	0.077	0.133	0.134	0.421	0.452
T=318.15 K							
0.973	0.973	0.022	0.021	0.074	0.079	0.159	0.165
0.955	0.956	0.039	0.038	0.095	0.103	0.264	0.279
0.944	0.945	0.050	0.049	0.111	0.115	0.325	0.336
0.935	0.935	0.060	0.059	0.126	0.125	0.373	0.379
0.926	0.925	0.069	0.069	0.144	0.134	0.415	0.417
0.921	0.920	0.073	0.074	0.153	0.138	0.435	0.435

Table S4. Comparison between experimental and correlated values obtained from Katritzky model for distribution coefficients (D_2) and separation factors (S) at *T*=298.15 K

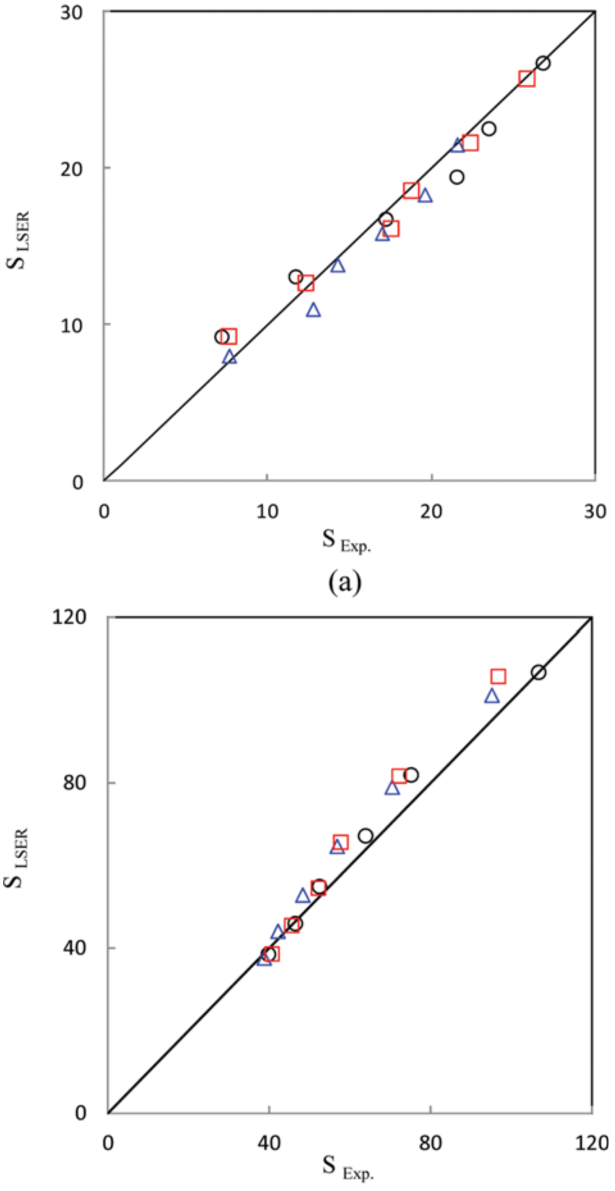
w_2 (feed)	$\log S_{LSER}$	$\log S_{Exp.}$	$\log D_{LSER}$	$\log D_{Exp.}$
Water (1)+propionic acid (2)+1-heptanol (3)				
0.4434	1.427	1.427	0.414	0.414
0.4000	1.288	1.370	0.373	0.386
0.3640	1.172	1.332	0.340	0.401
0.3334	1.073	1.235	0.311	0.376
0.3076	0.990	1.067	0.287	0.320
0.2854	0.919	0.855	0.266	0.283
Water (1)+butyric acid (2)+1-heptanol (3)				
0.4440	2.029	2.029	0.926	0.414
0.3997	1.826	1.876	0.833	0.386
0.3636	1.661	1.806	0.758	0.401
0.3332	1.522	1.720	0.695	0.376
0.3079	1.407	1.667	0.642	0.320
0.2860	1.307	1.600	0.596	0.283



(a)

(b)

Fig. S1. Phase diagram for (a) [water+propionic acid+1-heptanol], (b) [water+butyric acid+1-heptanol] at various temperatures; (○) *T*=298.15 K, (□) *T*=308.15 K, (△) *T*=318.15 K.



(a)

(b)

Fig. S2. Correlation of experimental values of separation factor (S) of (a) propionic acid, (b) butyric acid and those correlated with LSER model at various temperatures; (○) *T*=298.15 K, (□) *T*=308.15 K, (△) *T*=318.15 K.