



(Liquid + liquid) equilibria for ternary mixtures of (water + propionic acid + organic solvent) at $T = 303.2$ K

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ABSTRACT

Experimental tie-line results and phase diagrams were obtained for the ternary systems of {water + propionic acid + organic solvent (cyclohexane, toluene, and methylcyclohexane)} at $T = 303.2$ K and atmospheric pressure. The organic solvents were two cycloaliphatic hydrocarbons (*i.e.*, cyclohexane and methylcyclohexane) and an aromatic hydrocarbon (toluene). The experimental tie-lines values were also compared with those calculated by the UNIQUAC and NRTL models. The consistency of the values of the experimental tie-lines was determined through the Othmer–Tobias and Hands plots. Distribution coefficients and separation factors were evaluated over the immiscibility regions and a comparison of the extracting capabilities of the solvents was made with respect to distribution coefficients and separation factors. The Kamlet LSER model was applied to correlate distribution coefficients and separation factors in these ternary systems. The LSER model values showed a good regression to the experimental results.

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1. Introduction

Propionic acid is one of the most widely used carboxylic acids, which has many industrial applications. It is a clear, corrosive liquid with a pungent odor melting at 252.2 K. This acid can be produced by chemical synthetic or fermentation methods. Therefore, the extraction of this acid from aqueous mixtures using the liquid–liquid extraction technique is still an important problem.

The type of solvent is one of the most important factors which influence the equilibrium characteristics of extraction of the acid from aqueous solutions. Significant investigation has been carried out in recent years on the LLE measurements and the extraction of propionic acid from aqueous solutions by Kirbaslar and co-workers [1–3], Özmen and co-workers [4–6] and Bilgin and Arisoy [7]. Heavy alcohols, ketones and ethers have mainly been used for extraction of propionic acid from aqueous solutions [1–8].

We have recently reported LLE data for (water + propionic acid + 2-ethyl-1-hexanol) at different temperatures, where type-1 liquid–liquid phase diagram was obtained for the system [8]. In this mixture the correlated results were in good agreement with the observed results. As a continuation of that previous work, we present the LLE data for the ternary system {water + propionic acid + organic solvents (cyclohexane, toluene, and methylcyclo-

hexane)} at 303.2 K. These solvents have already been used as extractants to determination of LLE data for many ternary mixtures individually [9–15].

The temperature effect on (liquid + liquid) equilibria of the ternary systems of (propionic acid + water + cyclohexane) and (propionic acid + water + toluene) has already been reported by Badakhshan and co-workers [16]. Recently, more LLE data for the ternary system of (propionic acid + water + cyclohexane) at 298.15 K have been reported by Özmen and co-workers [6]. However, the focus of this study is placed on the phase behaviour of LLE for (water + propionic acid) with cyclohexane, toluene and methylcyclohexane at $T = 303.2$ K. The raw experimental LLE data were correlated using the universal quasi-chemical (UNIQUAC) method of Abrams and Prausnitz [17] and the non-random two-liquid (NRTL) model of Renon and Prausnitz [18]. The experimental data were then compared with the values correlated by these activity coefficient models.

For a comparison of the extracting capabilities of the solvents for the separation of (water + propionic acid) mixtures, the experimental distribution coefficients and separation factors were determined. The choice of these solvents as organic solvents was motivated by the following considerations. In spite of the structural similarity of these three organic solvents (hydrocarbons) there are, however, differences between them. Cyclohexane is a non-polar, non-associated, non-HBD solvent with very low dielectric constant ($\epsilon = 2.02$) and zero permanent dipole moment. The

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solvatochromic parameters (β , α , and π^*) values of cyclohexane are equal zero. Therefore, this hydrocarbon is a good reference solvent in the solvatochromism and solute–solvent investigations [19]. The obvious difference between cyclohexane and methylcyclohexane is that the latter has a methyl group with a weak polar nature.

Toluene is an aromatic solvent with very low dielectric constants ($\epsilon = 2.38$) has only a small permanent dipole moment ($\mu = 0.3$ D) and may be considered as a hydrophobic non-polar aromatic solvent. However, due to the polarizable character of aromatic ring, toluene shows that it is more polar solvent than its relative permittivity would lead one to predict. Toluene with a relatively high polarizability is not able to donate H-bonds but is very weak H-bond acceptor ($\alpha = 0$, $\beta = 0.11$ and $\pi^* = 0.49$), therefore, it is expected to form H-bonds in polar protic media.

Furthermore, the polarity/polarizability and hydrogen-bonding properties of the solvents used in this work, represented by the Kamlet–Taft parameters (π^* , α , and β) [19]. The properties of a solute–solvent system of hydrogen-bond formation can be estimated theoretically using a generalized solvatochromic approach with linear solvation energy relationship (LSER) [20]. The LSER model can be used to correlate distribution coefficients and separation factors, which has been previously reported by several researchers [21–23]. This model has been previously modified by Uslu [24,25]. In the present work, this modified model was used to correlate the distribution coefficients and separation factors of propionic acid in these three ternary systems.

2. Experimental

2.1. Materials

All chemicals used in this work (mass fraction purity > 0.99) were obtained from Merck. The purity of these materials was checked by gas chromatography and used without further purification. Distilled water was used throughout all experiments.

2.2. Apparatus and procedure

A 250 ml glass cell connected to a thermostat was made to measure the LLE data. The equilibrium data were determined by preparing the ternary mixtures of known compositions. The temperature of the cell was controlled by a water jacket and maintained with an accuracy of within ± 0.1 K. All mixtures were pre-

pared by weighing with an analytical balance accurate to within ± 0.0001 g.

The prepared mixtures with known compositions were located inside the cell and were vigorously agitated with a magnetic stirrer for 4 h, in order to allow a close contact between the phases. The mixtures were then settled for 4 h to completely separate in two-liquid phases and to get the equilibrium. After separation, samples of both phases were transparent and carefully collected from each phase and analyzed to determine their compositions. The homogeneity of the samples of both phases was maintained by adding an auxiliary solvent to the samples.

2.3. Analysis

The sample analysis was performed by using a Varian CP-3800 gas chromatography (GC) equipped with a thermal conductivity detector (TCD) and Star integrator. A 4 m \times 4 mm stainless steel column packed with CHROMOSORB T 40–60 Mesh was used to separate the components. The injection and the detector temperatures for cyclohexane and toluene mixtures were 523.2 K, and for methylcyclohexane mixtures were 473.2 K. High purity helium was used as a carrier gas at a flow rate of 40 cm³ · min⁻¹.

The TCD's response was calibrated with 1-butanol (for cyclohexane and methylcyclohexane mixtures) or methanol (for toluene mixtures) as an internal standard. The area fraction was converted into mole fraction by the calibration equations. Calibration coefficients were obtained by fitting a straight line to the calibration results for each composition range. The estimated uncertainties in the mole fraction were about 0.0005.

3. Results and discussion

3.1. Experimental tie-line measurements

The LLE measurements were made at $T = 303.2$ K and under atmospheric pressure. Table 1 contains the compositions of two coexistence liquid phases for the ternary systems of (water + propionic acid + cyclohexane), (water + propionic acid + toluene), and (water + propionic acid + methylcyclohexane). The estimated uncertainties in the mole fraction were about 0.0005. The corresponding experimental and calculated LLE diagrams for these three ternary systems (water + propionic acid + organic solvent) at $T = 303.2$ K are presented in figures 1 to 3. Since (water + organic

TABLE 1
Experimental tie-line results in mole fraction for ternary systems {water (1) + propionic acid (2) + organic solvent (3)} at $T = 303.2$ K.

Water-rich phase (aqueous phase)			Solvent-rich phase (organic phase)		
x_1 (water)	x_2 (propionic acid)	x_3 (solvent)	x_1 (water)	x_2 (propionic acid)	x_3 (solvent)
(Water + propionic acid + cyclohexane)					
0.8280	0.1716	0.0004	0.0013	0.0461	0.9526
0.7777	0.2218	0.0005	0.0014	0.0650	0.9336
0.6953	0.3038	0.0009	0.0015	0.1022	0.8963
0.6237	0.3742	0.0021	0.0017	0.1370	0.8613
0.5532	0.4425	0.0043	0.0020	0.1702	0.8278
(Water + propionic acid + toluene)					
0.8758	0.1240	0.0002	0.0058	0.1244	0.8698
0.8262	0.1735	0.0003	0.0069	0.1791	0.8140
0.7744	0.2252	0.0004	0.0087	0.2350	0.7563
0.6704	0.3290	0.0006	0.0107	0.3101	0.6792
0.5933	0.4059	0.0008	0.0119	0.3528	0.6353
(Water + propionic acid + methylcyclohexane)					
0.7956	0.2041	0.0003	0.0030	0.0305	0.9665
0.7005	0.2991	0.0004	0.0032	0.0458	0.9510
0.5949	0.4046	0.0005	0.0036	0.0696	0.9268
0.5008	0.4986	0.0006	0.0039	0.1093	0.8868
0.4483	0.5507	0.0010	0.0044	0.1443	0.8513

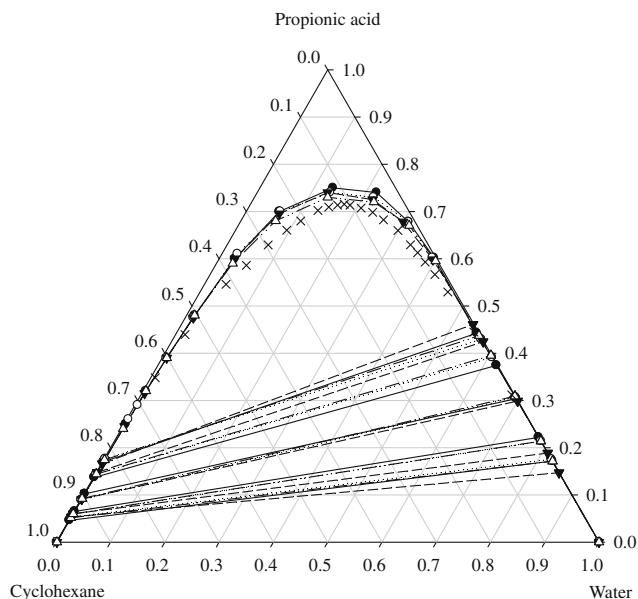


FIGURE 1. Ternary phase diagram for LLE of {water (1) + propionic acid (2) + cyclohexane (3)} at $T = 303.2$ K. (●) Experimental points; (○) UNIQUAC calculated points, (▼) NRTL calculated points ($\alpha = 0.3$), (Δ) NRTL calculated points (regressed α), (×) Lit. data [15].

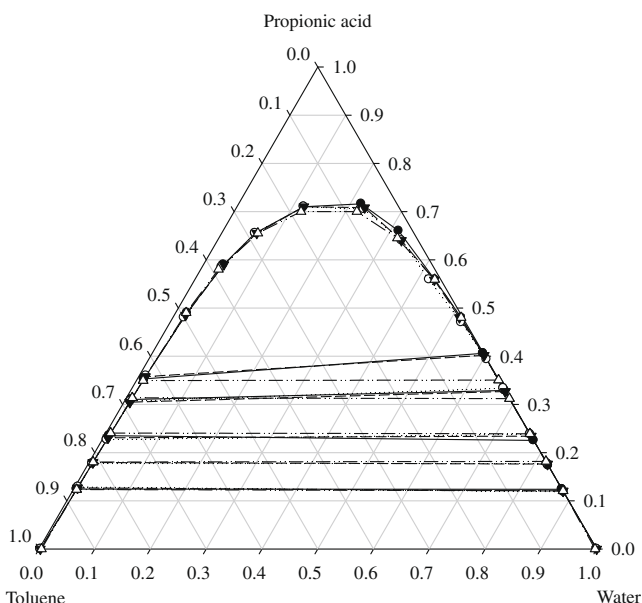


FIGURE 2. Ternary phase diagram for LLE of {water (1) + propionic acid (2) + toluene (3)} at $T = 303.2$ K. (●) Experimental points, (○) UNIQUAC calculated points, (▼) NRTL calculated points ($\alpha = 0.3$), (Δ) NRTL calculated points (regressed α).

solvent) system is the only pair that is partially miscible, these three investigated ternary systems behave as a Type 1 LLE.

The type of organic solvent (hydrocarbon) is one of the most important factors which influence the equilibrium characteristics and the immiscibility region of these investigated systems. The areas of the two-phase region primarily depend on the mutual solubility of water and the organic solvent. As seen from the LLE phase diagrams, the immiscibility region decreases in the order of the mixtures containing methylcyclohexane < toluene < cyclohexane. This suggests that, in the ternary systems, water is most soluble in the system containing methylcyclohexane, but least soluble in

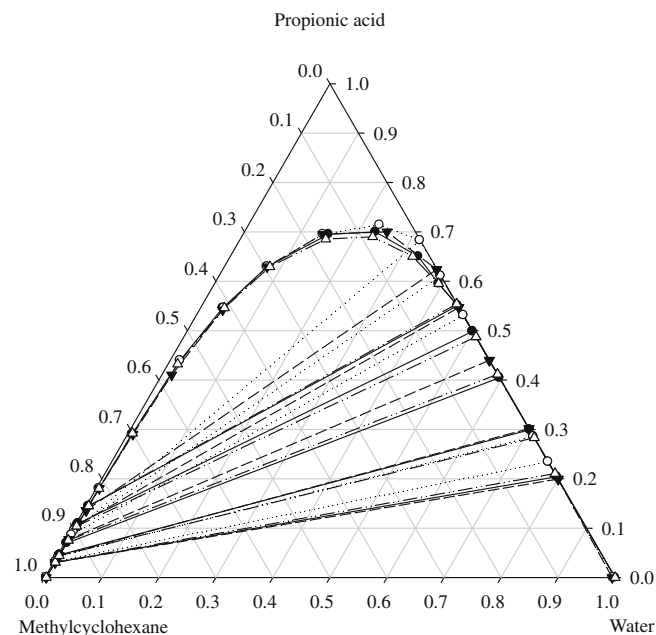


FIGURE 3. Ternary phase diagram for LLE of {water (1) + propionic acid (2) + methylcyclohexane (3)} at $T = 303.2$ K. (●) Experimental points, (○) UNIQUAC calculated points, (▼) NRTL calculated points ($\alpha = 0.3$), (Δ) NRTL calculated points (regressed α).

cyclohexane or toluene. The experimental results show that the solubility of water in the organic solvent increases with increasing of the third component (i.e., propionic acid).

3.2. Correlation models and evaluation of the parameters

The UNIQUAC and NRTL models were used to correlate the raw experimental LLE values. The UNIQUAC structural parameters r (the number of segments per molecules) and q (the relative surface area per molecules) were computed from the number of molecular groups and the individual values of the van der Waals volume and area of the molecule by the Bondi method [26,27]. The detailed description of the meaning of parameters and equations is widely defined in the current literature [28]. The values r and q used for these ternary systems are presented in table 2.

The correlated tie-lines for each ternary system are presented in table 3. In the present work, the value of the non-randomness parameter of the NRTL equation, α , was fixed at 0.3. On the other hand, in the NRTL equation α was regressed (correlated α) and was also used for the three systems.

The objective function developed by Sørensen [29] was used to optimize the equilibrium models. The objective function is the sum of the squares of the difference between the experimental and calculated mole fractions. The correlated results together with the experimental values for this ternary system of (water + propionic acid + organic solvent) were plotted and are shown in figures 1 to 3. The observed results were also used to determine the opti-

TABLE 2
The UNIQUAC structural parameters (r and q) for pure components.

Components	r	q
Water	0.9200	1.4000
Propionic acid	2.8768	2.6120
Cyclohexane	4.0464	3.2400
Toluene	3.9228	2.9680
Methylcyclohexane	4.7200	3.7760

TABLE 3
Calculated UNIQUAC and NRTL ($\alpha = 0.3$ and regressed α) tie-line values in mole fraction for {water (1) + propionic acid (2) + organic solvent (3)} at $T = 303.2$ K.

Aqueous phase						Organic phase					
x_1 (water)			x_2 (propionic acid)			x_1 (water)			x_2 (propionic acid)		
UNIQU.	NRTL ($\alpha = 0.3$)	NRTL (regr. α)	UNIQU.	NRTL ($\alpha = 0.3$)	NRTL (regr. α)	UNIQU.	NRTL ($\alpha = 0.3$)	NRTL (regr. α)	UNIQU.	NRTL ($\alpha = 0.3$)	NRTL (regr. α)
(Water + propionic acid + cyclohexane)											
0.8241	0.8525	0.8282	0.1755	0.1470	0.1713	0.0013	0.0013	0.0013	0.0531	0.0532	0.0513
0.7858	0.8109	0.7857	0.2137	0.1885	0.2137	0.0014	0.0014	0.0014	0.0593	0.0599	0.0598
0.6924	0.7003	0.6901	0.3067	0.2987	0.3089	0.0016	0.0015	0.0015	0.0892	0.0909	0.0921
0.6069	0.5739	0.6029	0.3911	0.4244	0.3951	0.0018	0.0018	0.0018	0.1441	0.1475	0.1441
0.5677	0.5371	0.5601	0.4297	0.4610	0.4370	0.0020	0.0019	0.0020	0.1762	0.1659	0.1740
(Water + propionic acid + toluene)											
0.8813	0.8795	0.8791	0.1185	0.1203	0.1207	0.0059	0.0057	0.0060	0.1287	0.1267	0.1232
0.8224	0.8236	0.8180	0.1773	0.1761	0.1817	0.0070	0.0071	0.0070	0.1773	0.1794	0.1803
0.7615	0.7655	0.7607	0.2381	0.2341	0.2389	0.0083	0.0085	0.0082	0.2268	0.2305	0.2405
0.6660	0.6727	0.6876	0.3334	0.3267	0.3118	0.0106	0.0106	0.0105	0.3070	0.3045	0.3135
0.6058	0.5973	0.6487	0.3934	0.4018	0.3505	0.0122	0.0120	0.0121	0.3594	0.3575	0.3492
(Water + propionic acid + methylcyclohexane)											
0.7654	0.8005	0.7892	0.2344	0.1993	0.2104	0.0031	0.0030	0.0030	0.0322	0.0303	0.0308
0.7140	0.6982	0.7166	0.2856	0.3015	0.2830	0.0032	0.0032	0.0032	0.0428	0.0441	0.0440
0.4685	0.5596	0.5880	0.5310	0.4399	0.4115	0.0038	0.0037	0.0036	0.0862	0.0773	0.0752
0.3882	0.4526	0.5123	0.6112	0.5468	0.4871	0.0040	0.0041	0.0039	0.0994	0.1061	0.1038
0.3163	0.3753	0.4453	0.6827	0.6236	0.5537	0.0041	0.0047	0.0045	0.0956	0.1358	0.1449

imum UNIQUAC (Δu_{ij}) and NRTL (Δg_{ij}) binary interaction energy between an i - j pair of molecules or between each pair of compounds (tables 4 and 5).

The quality of the correlation is measured by the root-mean square deviation (RMSD). The RMSD value was calculated from the difference between the experimental and calculated mole fractions according to the following equation:

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

where n is the number of tie-lines, x indicates the experimental mole fraction, \hat{x} is the calculated mole fraction, and the subscript i indexes components, j indexes phases and $k = 1, 2, \dots, n$ (tie-lines). The RMSD values in the correlation by UNIQUAC and NRTL models for the systems studied at $T = 303.2$ K are also listed in tables 4 and 5.

3.3. Othmer–Tobias and Hand correlations

In this study, the Othmer–Tobias [30] (equation (2)) and the Hand [31] (equation (3)) equations were used to ensure the consistency with the experimental tie-line results, where x_{11} , mole fraction of water in the aqueous phase; x_{23} and x_{21} , mole fraction of

TABLE 4
UNIQUAC binary interaction parameters (Δu_{ij} and Δu_{ji}) and root-mean square deviation (RMSD) values for LLE data of the ternary systems at $T = 303.2$ K.

i - j	$\Delta u_{ij}/(\text{J} \cdot \text{mol}^{-1})$	$\Delta u_{ji}/(\text{J} \cdot \text{mol}^{-1})$	$100 \times \text{RMSD}$
(Water (1) + propionic acid (2) + cyclohexane (3))			
1-2	-8335.50	5366.97	0.77
1-3	4555.61	9336.59	
2-3	1708.89	-4814.75	
(Water (1) + propionic acid (2) + toluene (3))			
1-2	-2875.85	3674.91	0.60
1-3	3317.84	7350.26	
2-3	8018.96	-2929.77	
(Water (1) + propionic acid (2) + methylcyclohexane (3))			
1-2	29007.50	-2735.63	5.77
1-3	-14787.78	-13379.36	
2-3	-26391.73	23367.79	

TABLE 5
NRTL ($\alpha = 0.3$ and regressed α) binary interaction parameters (Δg_{ij} and Δg_{ji}) and RMSD values for LLE data of the ternary systems at $T = 303.2$ K.

α_{ij}	i - j	$\Delta g_{ij}/(\text{J} \cdot \text{mol}^{-1})$	$\Delta g_{ji}/(\text{J} \cdot \text{mol}^{-1})$	$100 \times \text{RMSD}$
(Water (1) + propionic acid (2) + cyclohexane (3))				
0.3	1-2	-3191.90	9647.06	1.80
0.3	1-3	26429.19	16345.17	
0.3	2-3	10706.52	793.18	
Regressed α				
0.469	1-2	2595.36	-3469.41	0.72
0.031	1-3	27149.59	-2783.66	
0.062	2-3	8077.60	-4323.64	
(Water (1) + propionic acid(2) + toluene(3))				
0.3	1-2	-1345.76	6449.97	0.37
0.3	1-3	21172.65	13341.73	
0.3	2-3	12313.73	-1474.47	
Regressed α				
0.155	1-2	8164.67	50958.40	1.57
0.010	1-3	64193.11	-35933.22	
0.232	2-3	18956.44	7193.90	
(Water (1) + propionic acid(2) + methylcyclohexane (3))				
0.3	1-2	-29007.50	2735.63	2.46
0.3	1-3	14787.78	13379.36	
0.3	2-3	26391.73	-23367.79	
Regressed α				
0.2994	1-2	840.82	2326.03	0.61
0.3076	1-3	13087.57	12952.73	
0.2469	2-3	50991.17	6050.40	

TABLE 6
NRTL ($\alpha = 0.3$ and regressed α) binary interaction parameters (Δg_{ij} and Δg_{ji}) and RMSD values for LLE data of the ternary systems at $T = 303.2$ K.

Solvents	Othmer–Tobias correlation			Hand correlation		
	A	B	R^2	A'	B'	R^2
Cyclohexane	-1.3092	1.0648	0.9979	1.2025	0.9219	0.9979
Toluene	-0.1701	0.8507	0.9855	0.2091	1.1479	0.9850
Methylcyclohexane	-2.0453	1.0230	0.9848	1.9218	0.9272	0.9866

propionic acid in organic and aqueous phases, respectively; x_{33} , mole fraction of hydrocarbon in organic phase; A, B, A', and B', the parameters of the Othmer–Tobias correlation and the Hand correlation, respectively,

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

$$\ln\left(\frac{x_{21}}{x_{11}}\right) = A' + B' \ln\left(\frac{x_{23}}{x_{33}}\right). \quad (3)$$

The parameters of the Othmer–Tobias and Hand correlations are listed in table 6 at $T = 303.2$ K. For these three systems, the Othmer–Tobias and Hand plots are also shown in figures 4 and 5, respectively. The correlation factor (R^2) being approximately unity and the linearity of the plots indicate the degree of consistency of the measured LLE values in this study.

3.4. Distribution coefficient and separation factor

The efficient separation of propionic acid from aqueous solutions is an important concept in the chemical industries. In order to evaluate the extracting capability of the solvents (cyclohexane, toluene, and methylcyclohexane) for the separation of propionic acid from aqueous solutions with liquid–liquid extraction, the separation factor (S) was calculated.

The separation factor is defined as the ratio of distribution coefficients of propionic acid (D_2) to water (D_1), $S = D_2/D_1$. The distribution coefficients ($D_1 = x_{13}/x_{11}$) and ($D_2 = x_{23}/x_{21}$) were calculated from the tie-line data for each system. The x_{13} and x_{23} are the mole fractions of water and propionic acid in the organic phase, respectively; x_{11} and x_{21} are the mole fractions of water and propionic acid in aqueous phase, respectively.

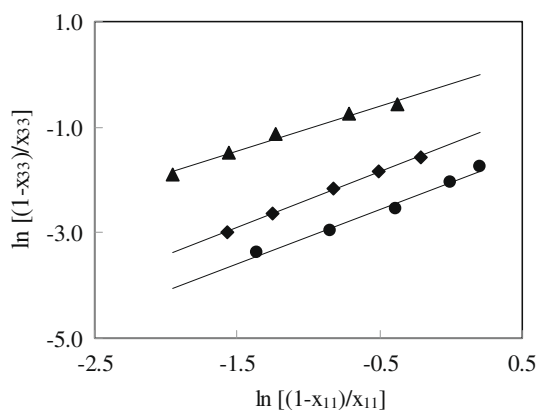


FIGURE 4. Othmer–Tobias plots of {water (1) + propionic acid (2) + hydrocarbon (3)} ternary systems at $T = 303.2$ K; (▲) cyclohexane, (●) toluene, (◆) methylcyclohexane.

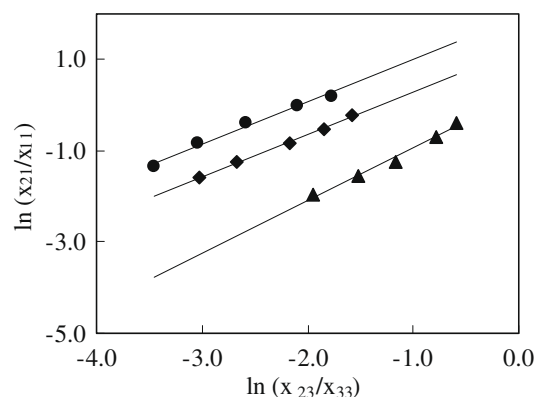


FIGURE 5. Hand plots of {water (1) + propionic acid (2) + hydrocarbon (3)} ternary systems at $T = 303.2$ K; (▲) cyclohexane, (●) toluene, (◆) methylcyclohexane.

TABLE 7

Experimental separation factors (S), distribution coefficients of propionic acid (D_2) and limiting distribution coefficients of propionic acid at infinite dilution ($D_{2\infty}$) at $T = 303.2$ K.

S	D_2	$D_{2\infty}$
<i>(Water (1) + propionic acid (2) + cyclohexane (3))</i>		
171.1081	0.2686	0.2247
168.3924	0.2932	
155.9352	0.3364	
134.3209	0.3661	
106.3894	0.3846	
<i>(Water (1) + propionic acid (2) + toluene (3))</i>		
151.4871	1.0032	0.6226
122.8571	1.0321	
92.8850	1.0435	
59.0549	0.9426	
43.3348	0.8692	
<i>(Water (1) + propionic acid (2) + methylcyclohexane (3))</i>		
39.3681	0.1494	0.116
33.5202	0.1531	
28.2305	0.1718	
28.1493	0.2192	
26.6973	0.2620	

The experimental values of distribution coefficient and separation factor for each solvent are listed in table 7. The $D_{2\infty}$ in this table shows the propionic acid distribution coefficient at infinite dilution at aqueous phase. A comparison of the extracting capabilities of the solvents was made with respect to separation factor values. This factor is found to be greater than 1 ($S > 1$) for the systems investigated, which means that extraction of propionic acid by these solvents is possible.

As seen from table 7 for these ternary systems, the separation factor changes in the order of the mixtures containing methylcyclohexane < toluene < cyclohexane. From the experimental results, it can be concluded that cyclohexane is the most appropriate solvent for the separation of a mixture of water and propionic acid. It is also apparent from table 7 that methylcyclohexane is a less favourable solvating agent for propionic acid. Based on the differences in the chemical nature of the three solvents used, it is known that the aromatic ring has a much stronger hydrophobic character than a saturated cyclic ring. This may lead to a stronger interaction between propionic acid molecule with cyclohexane. This suggests that the aromaticity or existence of $-\text{CH}_3$ group in toluene or methylcyclohexane decreases the power of these solvents in extraction of propionic acid with respect to cyclohexane.

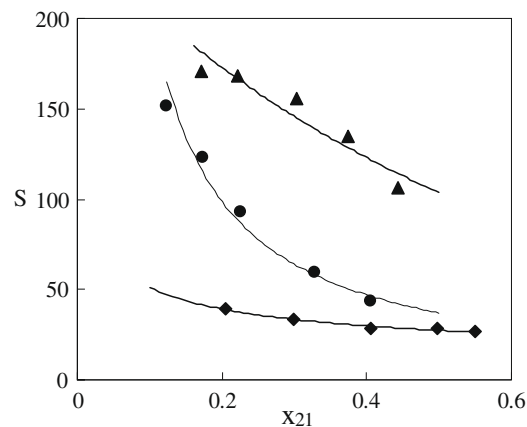


FIGURE 6. Experimental separation factor, S , plotted against the mole fraction of propionic acid in the aqueous phase, x_{21} , at $T = 303.2$ K. (▲) cyclohexane, (●) toluene, (◆) methylcyclohexane.

TABLE 8
Kamlet–Taft solvatochromic parameters (π^* , α , and β) for the organic solvents [16,29].

Solvents	α	β	δ	π^*
Cyclohexane	0.0	0.00	0	0.00
Toluene	0.0	0.11	1	0.49
Methylcyclohexane	0.0	0.00	0	-0.02

TABLE 9
Comparison of values between observed and correlated (LSER) for distribution coefficients (D_2) and separation factors (S).

Solvents	x (mole fraction)	$\lg(D_{2,LSER})$	$\lg(D_{2,exp})$	$\lg(S_{LSER})$	$\lg(S_{exp})$
Cyclohexane	0.1631	-0.4593	-0.5708	2.1222	2.2333
	0.1574	-0.4593	-0.4731	2.1222	2.1929
	0.1518	-0.4593	-0.4364	2.1222	2.1281
	0.1468	-0.4593	-0.4150	2.1222	2.0269
Toluene	0.2334	0.0600	0.0014	1.9971	2.1804
	0.2245	0.0447	0.0185	2.0136	1.9679
	0.1405	-0.1648	-0.0257	2.0023	1.7713
Methylcyclohexane	0.1432	-0.7356	-0.8255	1.4649	1.5951
	0.1381	-0.7261	-0.8150	1.4875	1.5253
	0.1330	-0.7165	-0.6591	1.5102	1.4495
	0.1286	-0.7070	-0.5816	1.5329	1.4265

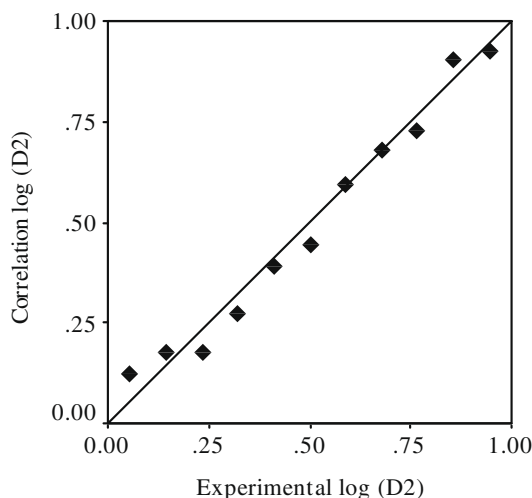


FIGURE 7. Correlation of experimental values of $\lg D_2$ (distribution coefficient) and those correlated with equation (5) for {water (1) + propionic acid (2) + hydrocarbon (3)} ternary systems at $T = 303.2$ K. The diagonal line represents a good correlation of experimental and correlated values.

The separation factors are not constant over the whole two-phase region. The variation of experimental separation factor of propionic acid as a function of the mole fraction of the solute in aqueous phase for the ternary systems is shown in figure 6.

A comparison of the extracting capabilities of the solvents can be made with those of other solvents such as alcohols [3,6]. For example, it is apparent that cyclohexane, toluene, and methylcyclohexane give higher separation factors comparing to 2-ethyl-1-hexanol [8] but lower separation factor comparing to oleyl alcohol [7].

TABLE 10
Results of the regression coefficient for the LSER equation.

Coefficients	$\lg D_2$ or $\lg S$	s	d	b	a	R^2
For distribution coefficients	-0.459	95.279	0	-403.913	0	0.923
For separation factors	2.122	226.653	0	-1013.781	0	0.853

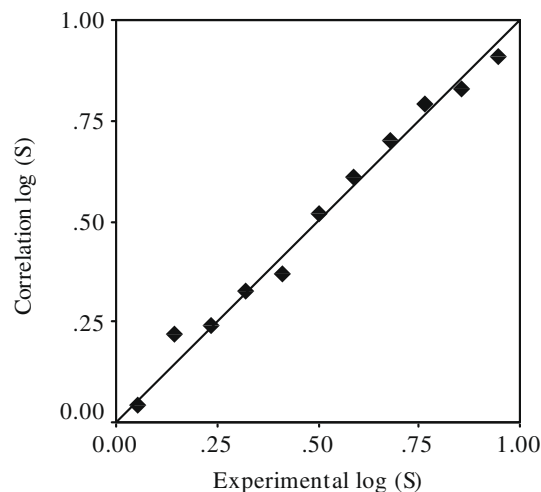


FIGURE 8. Correlation of experimental values of $\lg S$ (separation factor) and those correlated with equation (6) for {water (1) + propionic acid (2) + hydrocarbon (3)} ternary systems at $T = 303.2$ K. The diagonal line represents a very good correlation of experimental and correlated values.

3.5. LSER calculation

According to Kamlet *et al.* [32], the linear solvation energy relationship (LSER) that measures the property A in terms of solvent properties is

$$A = A_0 + s(\pi^* + d\delta) + \alpha x + b\beta. \quad (4)$$

The π^* is a measure of solvent dipolarity/polarizability, which is a measure of the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect and correlated with the solvatochromic behavior values. The δ is a discontinuous polarizability correction term and α is a measure of the solvent hydrogen-bond donor (HBD) acidity. It describes the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond. The β is a measure of the hydrogen-bond acceptor (HBA) basicity. The coefficients A_0 , s , d , a and b include the properties of solute and are derived from regression.

In the present work, the LSER model was applied to correlate distribution coefficients and separation factors. The values of distribution coefficients can be correlated with the solvatochromic parameters of the solvents according to the following equations:

$$\lg D_2 = \lg D_2^0 + s(\pi^* + d\delta) + \alpha x + b\beta, \quad (5)$$

$$\lg S = \lg S_0 + s(\pi^* + d\delta) + \alpha x + b\beta. \quad (6)$$

In this study, a modified version of LSER model [24] was applied to correlate distribution coefficients (D_2) and separation factor (S) for LLE of propionic acid in two phase system. The values of Kamlet–Taft solvatochromic parameters (α , β , and π^*) of the solvent used in this work were taken from references [19,32] and are summarized in table 8.

The experimental distribution coefficients and separation factors were regressed by the computer program SPSS v15.0. The comparison of experimental and correlated data for the distribution coefficients and separation factor is given in table 9. Figures

7 and 8 also indicate good agreement between the experimental and correlated distribution coefficients and separation factor, respectively. The LSER model values showed a good regression of the experimental data. The values of LSER model parameters are presented in table 10.

4. Conclusions

The LLE values for the ternary systems of (water + propionic acid + cyclohexane), (water + propionic acid + toluene) and (water + propionic acid + methylcyclohexane) were studied at $T = 303.2$ K and atmospheric pressure. Each ternary system exhibits type-1 behaviour for the LLE.

The UNIQUAC and NRTL solution models were used to correlate the experimental LLE results and to calculate the phase compositions of the mixtures studied. The corresponding optimized binary interaction parameters were also calculated. In general, the NRTL method gives better results than the UNIQUAC model for the three systems investigated.

The separation factor and distribution coefficient for each of organic solvent used in this work were calculated and compared. In extraction of propionic acid from water, the solvent with the higher selectivity and distribution coefficient is preferred. The experimental results indicate the superiority of cyclohexane as the preferred solvent for the extraction of propionic acid from its aqueous solutions. The immiscibility region was found to be larger when the cyclohexane was used as an organic solvent.

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