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LIQUID-LIQUID EQUILIBRIA OF PROPIONIC ACID - WATER - SOLVENT (n-HEXANE, CYCLOHEXANE, CYCLOHEXANOL AND CYCLOHEXYL ACETATE) TERNARIES AT 298.15 K

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Abstract - The experimental liquid-liquid equilibrium data on propionic acid-water-solvent ternary mixtures at a temperature of 298.15 K are presented. The solvents are n-hexane, cyclohexane, cyclohexanol and cyclohexyl acetate. The distribution coefficients and separation factors are reported. The tie line data are correlated using the methods of Othmer-Tobias and Hand. The experimental results are compared with the values predicted by the UNIFAC group-contribution method.
Keywords: liquid-liquid equilibria, propionic acid, UNIFAC.

INTRODUCTION

Liquid-liquid equilibria are of interest in extraction operations and are useful for developing a thermodynamic predictive and correlative method. Liquid extraction of propionic acid from aqueous solutions with various solvents has been reviewed by several researchers (Badakhshan et al., 1985; Arce et al., 1993, 1995; Yoshizawa et al., 1994; Sólimo et al., 1997; Radwan et al., 1997; Zurita et al., 1998; Cehreli et al., 1999). To be able to choose the most suitable agent for extraction of propionic acid from aqueous solutions, experimental liquid-liquid equilibrium data were determined for propionic acid - water - solvent ternary mixtures at a temperature of 298.15 K.

The solvents used are n-hexane, cyclohexane, cyclohexanol and cyclohexyl acetate. The distribution coefficients and separation factors were obtained from experimental results and are also reported. The tie lines were determined and were correlated by the methods of Othmer-Tobias and Hand on a mass-fraction basis. The experimental results are compared with values predicted by the UNIFAC group-contribution method, using a calculating program in MATLAB.

EXPERIMENTAL

Materials

Propionic acid was furnished by Fluka. Other chemicals were used as received from Merck. The purity of the chemicals was checked on the basis of their refractive indexes at 293.15 ± 0.20 K. Refractive indexes were measured with an Abbé-Hilger refractometer with a stated accuracy of ±0.0001 n_D. The measured physical properties are listed in Table 1 along with values from the literature (Weast, 1990). Deionized water was further distilled before use.

Table 1: Physical Properties of the Chemicals.

Chemical	M [g/g-mol]*	d [kg/l]*	b.p. [^{o}C]*	Refractive Index (20 ^{o}C)	
				Lit.*	Exp.
Propionic acid	74.08	0.9930	141.00	1.3809	1.3863
n-Hexane	86.18	0.6603	69.00	1.3751	1.3753
Cyclohexane	84.16	0.7785	80.70	1.4266	1.4275
Cyclohexanol	100.16	0.9624	161.10	1.4641	1.4657
Cyclohexyl Acetate	142.20	0.9698	173.62	1.4401	1.4406

***** Weast. R.C., Handbook of Chemistry and Physics, CRC Press, Boca Raton, Florida (1989-1990).

Procedure

Data for the solubility curve of the ternary systems were determined by the cloud point method (Alders, 1959; Cehreli, 2002). Solubility curve data determinations were made in an equilibrium cell equipped with a magnetic stirrer and an isothermal fluid jacket. The temperature of the mixture was controlled by a bath within an accuracy of ±0.2 K. The inner temperature of the cell was measured within an accuracy of ±0.1 K by a certified Fischer thermometer.

The cell, designed to contain a solution of 50-200 cm^3, was filled with homogeneous water-propionic acid mixtures prepared by weighing. An electronic Sauter balance with an accuracy of ±0.1 mg was used. The solvent was added by means of an automatic microburet with an accuracy of ±0.005 cm^3. The end point was determined by observing the transition from a homogeneous to a heterogeneous mixture. This pattern was convenient for providing the water-rich side of the curves. On the other hand, data for the solvent-rich side of the curves were it became obtained by titrating homogeneous propionic acid-solvent with water until a turbid. Composition determinations were accurate to ±0.0005 mass fraction.

The solubilities of water and solvent were determined by applying a synthetic method. A weighed amount of the first substance was introduced into the cell; the second was added until permanent heterogeneity had been observed. An ultra-accurate titrator with an accuracy of ±0.001 cm^3 was used.

The tie line data determinations were obtained using the equilibrium apparatus described above. A variety of mixtures within the heterogeneous gap were prepared for the four systems studied. The cell was filled with each of these mixtures and vigorously stirred for 1 h under isothermal conditions. After the stirrer was turned off, the contents were immediately introduced into the vertical settler, also equipped with an isothermal jacket. After complete separation of the phases, a suitable amount of each layer was removed for analysis. The acid contents of the samples were determined by volumetric titration with 0.1 N NaOH solution by using ethanolic phenolphthalein. Several check determinations on known samples showed the accuracy of the method was within ±0.001 of the mass fraction.

RESULTS AND DISCUSSION

The measured values for solubility curves and experimental mutual solubilities for the propionic acid - water - n-hexane, propionic acid - water - cyclohexane, propionic acid - water - cyclohexanol and propionic acid - water - cyclohexyl acetate systems are reported in Tables 2-5. The tie line compositions for the these systems are given in Table 6.

Table 2:The Solubility Curve Data for the Propionic Acid (1)-Water (2)-n-Hexane (3) System at 298.15 K.

Exp. No.	W_1	W_2	W_3
1	0.00	1.38	98.62
2	9.96	1.38	88.66
3	20.57	1.29	78.14
4	31.07	1.15	67.78
5	39.74	1.85	58.41
6	57.85	3.60	38.55
7	58.47	3.59	37.94
8	66.42	5.18	28.40
9	73.57	7.89	18.54
10	71.95	9.92	18.13
11	76.20	15.37	8.43
12	68.24	30.40	1.36
13	68.37	30.45	1.18
14	59.13	40.46	0.41
15	49.75	50.08	0.17
16	39.87	59.94	0.19
17	29.97	69.84	0.19
18	20.26	79.47	0.27
19	10.25	89.46	0.29
20	0.00	99.05	0.95

Table 3: The Solubility Curve Data for the Propionic Acid (1)-Water (2)-Cyclohexane (3) System at 298.15 K.

Exp. No.	W_1	W_2	W_3
1	0.00	99.90	0.10
2	10.66	89.08	0.26
3	20.11	79.70	0.19
4	29.26	70.57	0.17
5	44.17	55.39	0.44
6	58.65	40.52	0.83
7	70.60	13.07	16.33
8	71.17	26.88	1.95
9	64.61	8.48	26.91
10	60.49	6.05	33.46
11	59.99	4.33	37.68
12	44.42	1.46	54.12
13	32.69	0.31	67.00
14	15.49	0.25	84.26
15	0.00	0.42	99.58

Table 4: The Solubility Curve Data for the Propionic Acid (1)-Water (2)-Cyclohexanol (3) System at 298.15 K.

Exp. No.	W_1	W_2	W_3
1	0.00	97.84	2.16
2	17.09	78.39	4.52
3	18.90	75.84	5.26
4	21.00	71.07	7.93
5	26.59	58.71	14.70
6	29.75	49.16	21.09
7	32.83	40.11	27.06
8	32.38	34.23	33.39
9	32.54	26.95	40.51
10	29.00	21.80	49.20
11	21.65	15.78	62.57
12	12.85	8.91	78.24
13	0.00	8.00	92.00

Table 5: The Solubility Curve Data for the Propionic Acid (1)-Water (2)-Cyclohexyl Acetate (3) System at 298.15 K.

Exp. No.	W_1	W_2	W_3
1	0.00	0.56	99.44
2	10.14	0.52	89.34
3	19.77	2.60	77.63
4	28.56	5.34	66.10
5	35.79	8.99	55.22
6	42.77	13.53	43.70
7	46.34	20.44	33.22
8	46.00	34.00	20.00
9	43.50	44.84	11.66
10	37.45	55.87	6.68
11	30.02	69.47	0.51
12	24.80	74.52	0.68
13	19.52	79.98	0.50
14	15.55	84.41	0.04
15	10.32	89.60	0.08
16	0.00	99.95	0.05

Table 6: The Tie Line Compositions for the Propionic Acid-Water-Solvent System at 298.15 K.

Exp. No.	Overall			Water-rich phase			Solvent-rich phase		
	W_1	W_2	W_3	W_{12}	W_{22}	W_{32}	W_{13}	W_{23}	W_{33}
Propionic Acid (1)-Water (2)-n-Hexane (3) System									
1	4.97	55.09	39.94	6.74	92.95	0.31	1.32	1.41	97.27
2	10.33	50.41	39.26	13.78	86.08	0.14	4.17	1.38	94.45
3	15.20	45.07	39.73	19.58	80.19	0.23	8.12	1.32	90.56
4	20.15	40.21	39.64	26.32	73.33	0.35	12.55	1.25	86.20
5	25.35	35.00	39.65	34.04	65.62	0.34	16.42	1.22	82.36
6	30.05	30.38	39.57	39.01	60.73	0.26	21.35	1.22	77.43
7	39.81	30.43	29.76	49.22	50.71	0.07	22.56	1.08	76.36
8	49.42	26.52	24.06	57.86	41.98	0.16	27.77	1.32	70.91
9	59.87	20.27	19.86	66.80	32.14	1.06	38.16	1.71	60.13
10	69.67	15.12	15.21	73.83	22.37	3.80	51.35	2.66	45.99
Propionic Acid (1)-Water (2)-Cyclohexane (3) System									
1	10.11	45.35	44.54	15.64	84.16	0.20	3.66	0.52	95.82
2	19.98	40.09	39.93	28.87	70.80	0.33	10.13	0.41	89.46
3	30.09	34.96	34.95	42.00	57.74	0.26	16.36	0.22	83.42
4	36.36	36.14	27.50	46.90	52.78	0.32	17.96	0.18	81.86
5	49.81	25.15	25.04	64.60	32.62	2.78	27.51	0.12	72.37
6	59.88	19.92	20.20	70.17	22.63	7.20	36.92	0.57	62.51
Propionic Acid (1)-Water (2)-Cyclohexanol (3) System									
1	5.25	57.66	37.09	2.83	95.09	2.08	8.76	9.14	82.10
2	10.35	52.25	37.40	5.85	91.90	2.25	15.39	11.03	73.58
3	16.10	47.96	35.94	9.01	88.35	2.64	22.34	14.35	63.31
4	20.77	41.90	37.33	11.13	85.84	3.03	26.44	17.68	55.88
5	25.98	35.93	38.09	13.66	82.65	3.69	30.24	23.36	46.40
Propionic Acid (1)-Water (2)-Cyclohexyl Acetate (3) System									
1	5.11	54.72	40.17	4.55	95.29	0.16	6.69	0.25	93.06
2	10.19	49.99	39.82	7.75	92.13	0.12	11.71	0.67	87.62
3	14.94	45.83	39.23	11.35	88.59	0.06	18.24	2.11	79.65
4	19.88	41.05	39.07	14.55	85.41	0.04	24.73	4.20	71.07
5	24.92	36.00	39.08	17.42	82.51	0.07	30.76	6.45	62.79
6	29.82	31.03	39.15	20.84	78.95	0.21	35.10	8.36	56.54
7	35.00	25.38	39.62	24.10	75.42	0.48	39.40	10.82	49.78
8	40.01	20.31	39.68	27.56	71.44	1.00	43.79	14.87	41.34
9	38.43	46.66	14.91	34.68	61.98	3.34	46.92	23.84	29.24

Distribution Coefficients and Separation Factors

Distribution coefficients, D_i, for propionic acid (i = 1) and water (i = 2) and separation factors, S, were determined (where 3 = solvent) as follows:

$$D_i = W_{i3}/W_{i2} \quad (1)$$

$$S = D_1/D_2 \quad (2)$$

Results are listed in Table 7.

Table 7: Experimental Distribution Coefficients (D_i) of the Propionic Acid and Water and Separation Factors (S) at 298.15 K.

a) Propionic Acid (1)-Water (2)-n-Hexane (3) System

Exp. No.	D_1 W_{13}/W_{12}	D_2 W_{23}/W_{22}	S D_1/D_2
1	0.20	0.02	12.87
2	0.30	0.02	18.89
3	0.41	0.02	25.26
4	0.48	0.02	27.91
5	0.48	0.02	25.94
6	0.55	0.02	27.17
7	0.46	0.02	21.51
8	0.48	0.03	15.27
9	0.57	0.05	10.74
10	0.70	0.12	5.85

b) Propionic Acid (1)-Water (2)-Cyclohexanol (3) System

Exp. No.	D_1 W_{13}/W_{12}	D_2 W_{23}/W_{22}	S D_1/D_2
1	3.10	0.10	32.20
2	2.63	0.12	21.92
3	2.48	0.16	15.27
4	2.38	0.21	11.53
5	2.21	0.28	7.83
-	-	-	-

c) Propionic Acid (1)-Water (2)-Cyclohexyl Acetate (3) System

Exp. No.	D_1 W_{13}/W_{12}	D_2 W_{23}/W_{22}	S D_1/D_2
1	1.47	0.00	558.21
2	1.51	0.01	208.52
3	1.61	0.02	67.41
4	1.70	0.05	34.56
5	1.77	0.08	22.58
6	1.68	0.11	15.90
7	1.63	0.14	11.39
8	1.59	0.21	7.63
9	1.35	0.38	3.52
-	-	-	-

d) Propionic Acid (1)-Water (2)-Cyclohexane (3) System

Exp. No.	D_1 W_{13}/W_{12}	D_2 W_{23}/W_{22}	S D_1/D_2
1	0.23	0.00	98.52
2	0.35	0.00	75.17
3	0.39	0.00	87.52
4	0.38	0.01	64.13
5	0.43	0.09	5.00
6	0.53	0.32	1.65

Correlations

The reliability of experimentally measured tie line data is ascertained by applying the Othmer-Tobias (Eq. 3) and Hand (Eq. 4) equations (Othmer and Tobias, 1942; Brandani and Ross, 1985).

$$\ln\frac{\left[(1-W_{33})\right]}{W_{33}} = a_1 + b_1 \ln\frac{\left[(1-W_{22})\right]}{W_{22}} \quad (3)$$

$$\ln\left(W_{13}/W_{33}\right) = a_2 + b_2 \ln\left(W_{12}/W_{22}\right) \quad (4)$$

The correlations are shown in Figures 1 and 2. The correlation coefficients and correlation factor (r^2) values were determined by the least-squares method and are given in Table 8.

The liquid-liquid equilibria of the ternary mixtures were also predicted using the UNIFAC

method (Fredenslund et al., 1975). For this purpose, the MATLAB program is used. The group-interaction parameters used for estimating the activity coefficients in the liquid phases were those obtained from experimental equilibrium results. The predicted liquid-liquid equilibria data are plotted in Figures 3-6 along with the experimental values.

Group volumes (R_k) and surface areas (Q_k) needed by UNIFAC are shown in Table 9. UNIFAC liquid-liquid equilibrium parameters (a_{mn}) representing interactions between 7 groups are shown in Table 10 (Reid, 1987).

The deviations shown in the figures are presented numerically by applying the root mean square (RMSD). RMSDs are calculated from the difference between the experimental data and the predictions of each system according to the following formula:

$$\mathrm{RMSD} = \left\{ \sum_{k} \left[\sum_{j} \left(\sum_{i} \left(W_{i,\mathrm{exp}} - W_{i,\mathrm{calc}} \right)^2 \right) \right] / 6n \right\}^{1/2} \qquad (5)$$

where $W_{i,\,exp}$ is the experimental mass fraction of the tie lines; $W_{i,\,calc}$ is the calculated mass fraction of the tie lines; k = 1, 2, 3,...,n (tie lines); j is the water-rich or solvent-rich phase and i is the number of components (Fandary et al., 1999).

The root mean square deviation values for the systems studied are presented in Table 11.

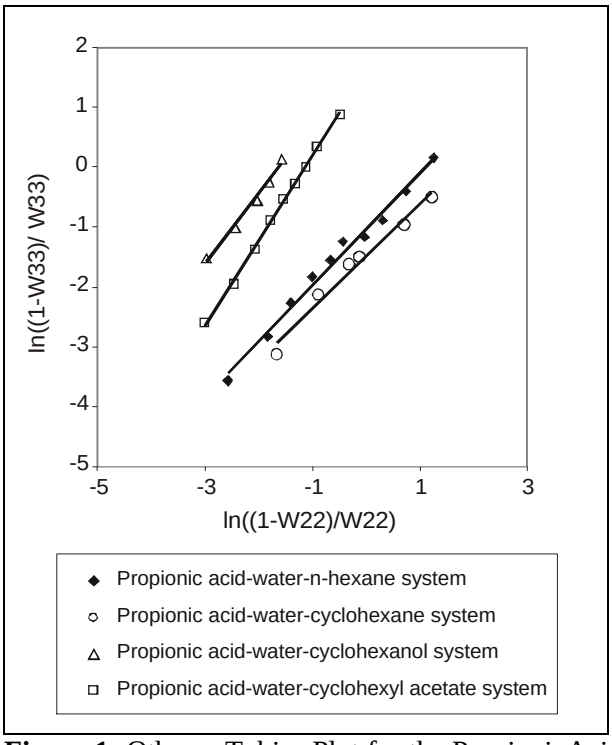

Figure 1: Othmer-Tobias Plot for the PropionicAcid (1)-Water (2)-Solvent (3) System at 298.15 K

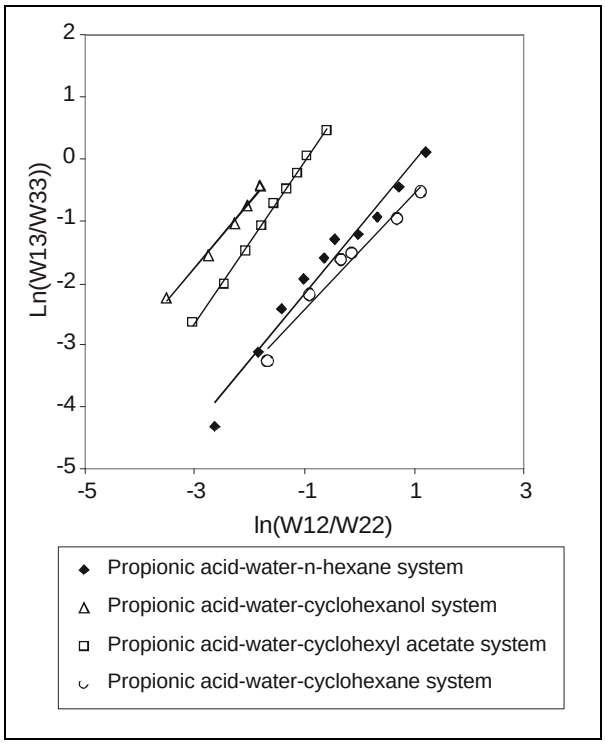

Figure 2: Hand Plot for the Propionic Acid (1)-Water (2)-Solvent (3) System at 298.15 K

Table 8: The Correlation Coefficients and Correlation Factors for the Othmer-Tobias and Hand Correlations.

	Othmer-Tobias coefficients			Hand coefficients		
Systems	a_1	b_1	r^2	a_2	b_2	r^2
Propionic Acid-Water-n-Hexane	-1.0336	0.9364	0.9865	-1.0935	1.0785	0.9704
Propionic Acid-Water-Cyclohexane	-1.4974	0.8632	0.9770	-1.4951	0.9261	0.9746
Propionic Acid-Water-Cyclohexanol	1.8999	1.1764	0.9888	1.3953	1.0486	0.9932
Propionic Acid-Water-Cyclohexyl Acetate	1.6079	1.4186	0.9978	1.2472	1.2946	0.9981

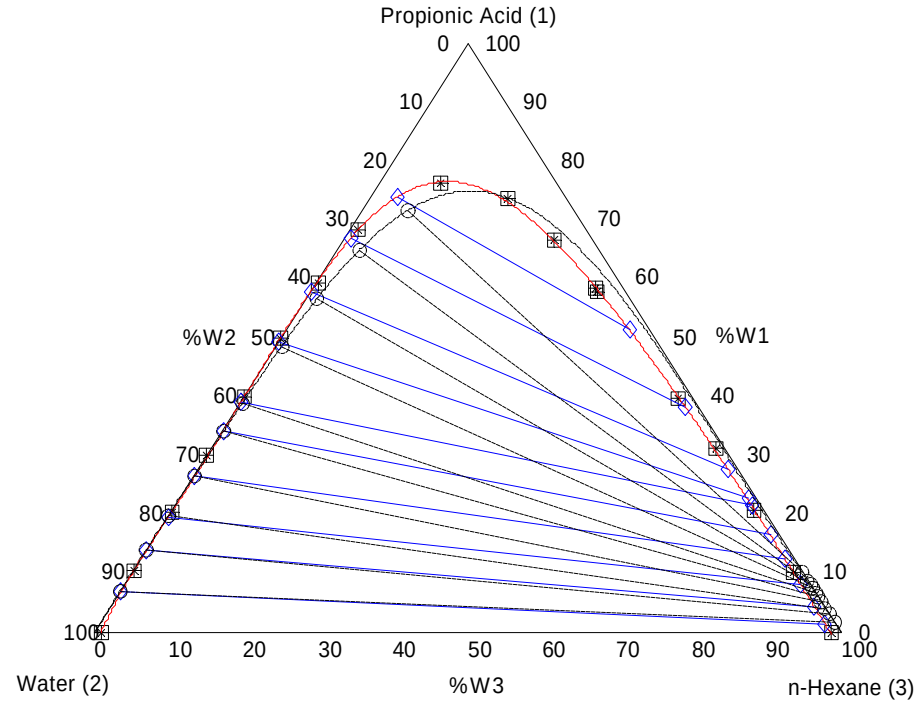

Figure 3: Experimental and Predicted Ternary Diagram for the Propionic Acid (1)-Water (2) - n-Hexane (3) System at 298.15 K

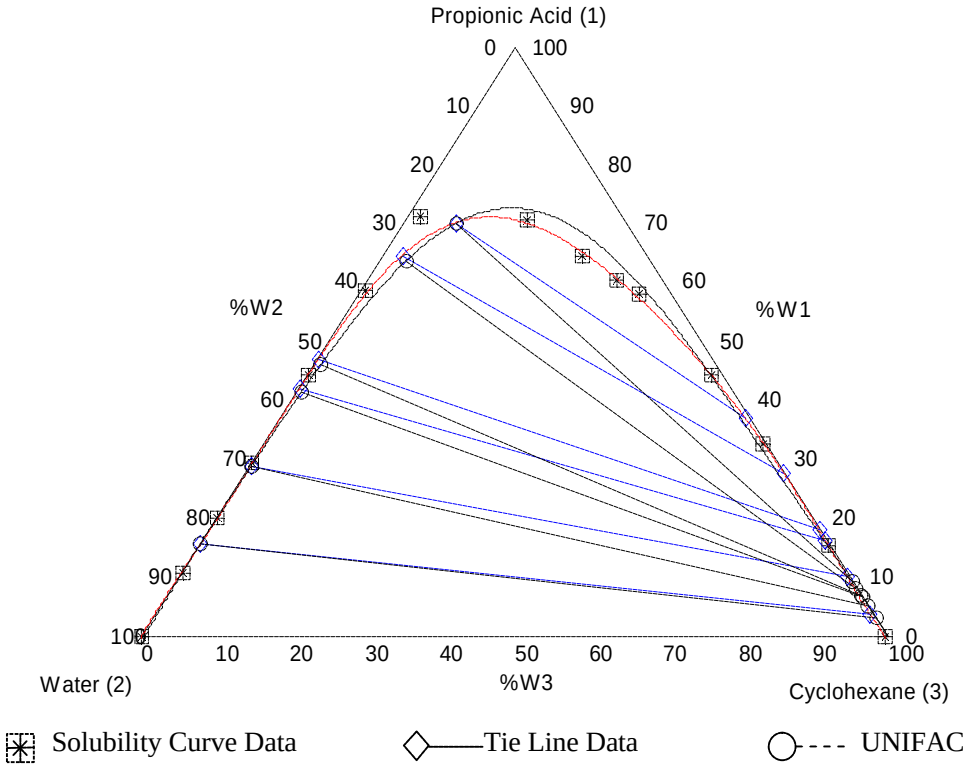

Figure 4: Experimental and Predicted Ternary Diagram for the Propionic Acid (1)-Water (2) - Cyclohexane (3) System at 298.15 K

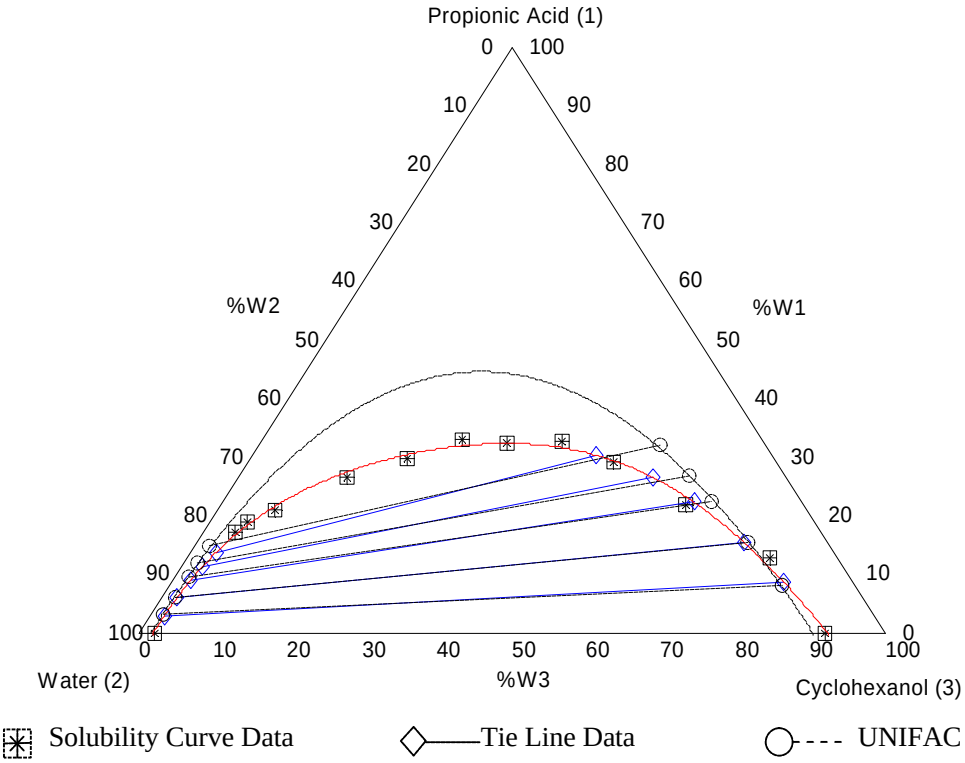

Figure 5: Experimental and Predicted Ternary Diagram for the Propionic Acid (1)-Water (2) - Cyclohexanol (3) System at 298.15 K

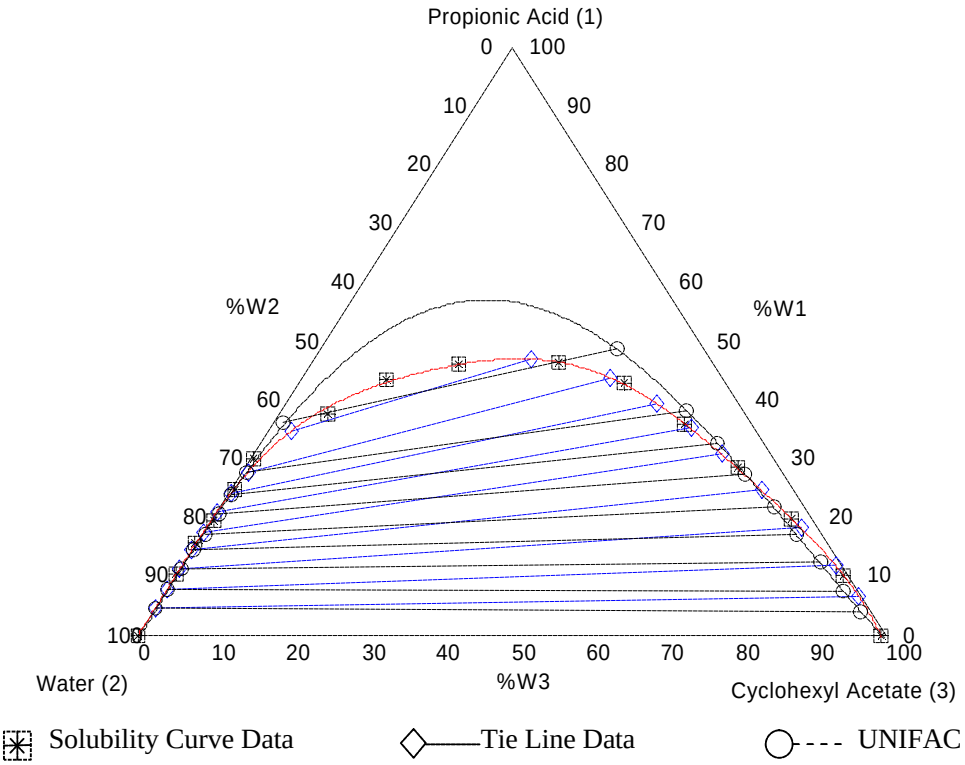

Figure 6: Experimental and Predicted Ternary Diagram for the Propionic Acid (1)-Water (2) - Cyclohexyl Acetate (3) System at 298.15 K

Table 9: Group-Volume (R_k) and Surface-Area (Q_k) Parameters*.

0,	Subgroup no.	Group or Subgroup	R_k	Q_k
1	1	CH3	0.9011	0.848
1	2	CH2	0.6744	0.540
1	3	CH	0.4469	0.228
5	15	OH	1.0000	1.200
7	17	H2O	0.9200	1.400
11	22	CH3COO	1.9031	1.728
20	43	COOH	1.3013	1.224

* Reid, R.C., Prausnitz, J.M., Poling, B.E., The Properties of Gases and Liquids, Fourth ed., McGraw-Hill Inc., ISBN 0-07-051799-1, Mexico, (1987).

Table 10: UNIFAC Group Interaction Parameters a_{mn}, in Kelvins *.

Main Group no.	1	5	7	11	20
1	0	986.5	1318	232.1	663.5
5	156.4	0	353.5	101.1	199
7	300	-229.1	0	72.87	-14.09
11	114.8	245.4	200.8	0	660.2
20	315.3	-151	-66.17	-256.3	0

* Reid, R.C., Prausnitz, J.M., Poling, B.E., The Properties of Gases and Liquids, Fourth ed., McGraw-Hill Inc., ISBN 0-07-051799-1, Mexico, (1987).

Table 11: The Root Mean Square Deviation Values for the UNIFAC-Predicted and Experimental Data.

	System	RMSD
1	Propionic Acid-Water-Cyclohexanol	2.65
2	Propionic Acid-Water-Cyclohexyl Acetate	5.02
3	Propionic Acid-Water-Cyclohexane	8.83
4	Propionic Acid-Water-n-Hexane	11.32

CONCLUSIONS

Considering the two-phase region, it can be said that n-hexane and cyclohexane are suitable extraction agent for aqueous propionic acid mixture, on the other hand distribution coefficient values show that cyclohexanol and cyclohexyl acetate are more suitable. When the all properties are taken into consideration it can be concluded that cyclohexyl acetate is the most suitable extractant studied in this research.

The slopes of experimental and UNIFAC-predicted data are similar for propionic acid-water-cyclohexanol and propionic acid-water-cyclohexyl acetate systems but different for propionic acid-water-n-hexane and propionic acid-water-cyclohexane systems. RMSD values show that UNIFAC gives the best fit for propionic acid-water-cyclohexanol system.

Both the Othmer-Tobias and the Hand equations show a good correlation and straight lines for each ternary.

ACKNOWLEDGEMENT

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NOMENCLATURE

a_1, b_1	Othmer-Tobias equation constant
a_2, b_2	Hand equation constant
b.p.	Boiling point [^{0}C]
d	Specific gravity [kg/L]
D_i	Distribution coefficient of the i^{th} component
M	Molecular mass [g/g-mol]
n_D	Refractive index
r^2	Othmer-Tobias and Hand correlation factor
S	Separation factor
W_i	Mass fraction of the i^{th} component
W_{i2}	Mass fraction of the i^{th} component in the aqueous phase
W_{i3}	Mass fraction of the i^{th} component in the solvent phase

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