



*Dedicated to the memory of
Dr. Henry V. Kehiaian (1929–2009)*

LIQUID-LIQUID PHASE EQUILIBRIA
OF (1-PROPANOL + WATER + n-ALCOHOL) TERNARY SYSTEMS
AT 294.15 K. II.¹ 1-PROPANOL + WATER + 1-HEPTANOL
OR 1-OCTANOL OR 1-NONANOL OR 1-DECANOL

Cristina STOICESCU,^{a*} Olga IULIAN^b and Raluca ISOPESCU^b

^a“Ilie Murgulescu” Institute of Physical Chemistry, Thermodynamic Department, Roumanian Academy, 202 Spl. Independentei, 060021, Bucharest, Roumania

^b University “Politehnica” of Bucharest, Faculty of Applied Chemistry and Material Science, 1 Polizu str., 011061, Bucharest, Roumania

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Liquid-liquid equilibrium (LLE) data for the ternary systems: 1-propanol + water + n-alcohols (1-heptanol, 1-octanol, 1-nonanol or 1-decanol) were determined at 294.15 K and normal pressure. There were studied the ternary systems which include n-alcohols with up to 10 carbon atoms, which can be used as extraction solvents for the separation of 1-propanol from aqueous solutions. The miscibility curves, the conode lines and the plait points were obtained. The phase diagrams for all these systems are of type I in according to Trayball classification. The Othmer-Tobias and Hand equations, used to verify the quality of the experimental data, give similar and generally good results for all the systems. The experimental ternary liquid-liquid equilibrium data were correlated with the UNIQUAC model which represents well the obtained experimental data and gives the original UNIQUAC parameters for the ternary systems. Distribution coefficients (D_i), separation factors (S) and selectivity values were calculated from tie-line data to evaluate the extracting capability of the solvents. The extracting capability of studied n-alcohols increases with increasing alcohol chain length.

INTRODUCTION

This paper is a continuation of our work on liquid-liquid equilibria (LLE) in aqueous ternary systems with n-alcohols. The liquid-liquid equilibria (LLE) for the system of 1-propanol + water with one of three alcohols: 1-butanol, 1-pentanol and 1-hexanol at 294.15 K and atmospheric pressure were reported in our previous paper (Part I).¹

The phase equilibrium data of ternary systems with normal alcohols have been the subject of interest in the recent years in literature.²⁻⁵ Some organic solvents have been investigated and reported in the literature as extractants for 1-propanol from water.⁶

The aim of this study is to present the experimental data on the phase equilibria of water + 1-propanol with four alcohols as potential solvents: 1-heptanol, 1-octanol, 1-nonanol and 1-decanol at 294.15 K and normal pressure. No data on these ternary systems were found in literature.

The liquid-liquid equilibria were studied by the cloud-point method and Newsham and Ng technique.^{7, 8} The experimental tie line data were correlated to test consistency with the Othmer-Tobias⁹ and Hand¹⁰ equations. The LLE data were correlated with the UNIQUAC solution model,¹¹ and the values of the interaction parameters were obtained. For each ternary system, the plait point compositions using Coolidge methods⁸ have been determined.

* Corresponding author: cristina.silvia.stoicescu@gmail.com

The capability of n-alcohols for separating 1-propanol from water was investigated in terms of phase diagrams, distribution coefficients and separation factors.

EXPERIMENTAL

Chemicals. All chemicals used in this work (mass fraction purity > 0.995) were supplied by Merck and were used without further purification. The purity of these materials was verified by gas chromatography and by refractive indices measurements. Bi-distilled water was used throughout all the experiments.

The refractive indices of pure components were measured at 293.15 K and atmospheric pressure and compared to literature data. The refractive indices were measured using an Anton Paar (Abbemat RXA 170) refractometer, the refractive index being measured with an accuracy of $\pm 2 \times 10^{-5}$ and the temperature with an accuracy of 0.03 °C. The measured physical properties are presented together with literature data in Table 1.

Apparatus and procedure. Liquid-liquid equilibria were investigated using two separate techniques for solubility curves and liquid-liquid tie-lines determination, respectively. The LLE apparatus were previously described in detail^{13, 14} and the experimental procedures to obtaining the solubility data and the tie-lines for the ternary systems are similar to that presented in Part I of this paper.¹

Solubility data for the ternary systems were determined by the cloud-point method. The data measurements were made in an installation containing of an equilibrium cell equipped with

isothermal fluid jacketed vessel to keep the temperature constant, a thermostatically controlled bath which maintains the temperature of mixtures with an accuracy of ± 0.1 K, a magnetic stirrer and a microburette. The inner temperature of the cell was measured by a precision thermometer with an accuracy of ± 0.1 K. The binary mixtures were prepared by weighing. An electronic balance accurate to ± 0.01 mg was used. The third component was progressively added by means of a microburette with an accuracy of ± 0.05 cm³ that means around 0.014 g alcohol. The estimated uncertainties in the molar fraction were about ± 0.005 . The transition point between the heterogeneous and homogeneous was determined visually. All visual experiments were repeated to acquire high reproducibility. The data for the solubility curves were therefore obtained by titrating until turbidity disappeared.

The tie-lines were obtained by using the same equilibrium apparatus. Equilibrium data were obtained by preparing mixtures of known overall composition (about 40 cm³) within the heterogeneous gap for the three ternary studied systems. Each of these mixtures was filled into the equilibrium cell and intense stirred (usually about 1 hour) under isothermal conditions and set for at least 1.5 hour at constant temperature until the each layer appeared perfectly clear. At the end of the setting period, samples were taken from both phases and analyzed. The techniques for the determination of phase compositions at equilibrium are the cloud-point method and the procedure of Newsham and Ng⁹ completed with an our own graphics program. The estimated precision of the mixture compositions of the tie-lines and the binodal curves was within $\pm (1-2)$ wt%.

The LLE measurements were made at temperatures of 294.15 K under atmospheric pressure.

Table 1

Pure component physical properties at 293.15 K and atmospheric pressure

Materials	Molecular weight [g·mol ⁻¹]	Refractive index n^{20}	
		This work	Literature data ¹²
water	18.02	1.33297	1.3325
1-propanol	60.10	1.38509	1.3850
1-heptanol	116.20	1.42416	1.4249
1-octanol	130.23	1.42897	1.4295
1-nonanol	144.26	1.43277	1.4333
1-decanol	158.28	1.43638	1.4372

RESULTS AND DISCUSSION

Experimental LLE data

The paper presents experimental liquid-liquid equilibrium data for (1-propanol + water + 1-heptanol), (1-propanol + water + 1-octanol), (1-propanol + water + 1-nonanol) and (1-propanol + water + 1-decanol) ternary systems at 294.15 K and normal pressure: miscibility curves, tie-lines and plait points. The current data for ternary systems containing 1-octanol and 1-decanol completes previously published data.¹⁴

Table 2 presents the experimental measurements for the binodal curves for the ternary systems (1-propanol + water + n-alcohols), x_i being the mole fraction of the i^{th} component. The experimental and calculated tie-line data of (1-propanol + water + n-alcohols) at 294.15 K were reported in Table 4, in which x_i^I and x_i^{II} refer to mole fraction of the i^{th} component in the aqueous and solvent phase, respectively. The liquid-liquid phase diagrams (the experimental binodal curves and tie lines data) for all studied ternary systems at 294.15 K are plotted and are shown in Figs. 1-4.

Table 2

The binodal curves (molar fractions)
for the 1-propanol (1) + water (2) + 1-heptanol (3) or 1-octanol, or 1-nonanol or 1-decanol ternary system at 294.15 K

Exp. No.	(x_1)	(x_2)	(x_3)	Exp. No.	(x_1)	(x_2)	(x_3)
1-propanol (x_1) + water (x_2) + 1-heptanol (x_3)							
1.	0.0000 ³	0.9997 ³	0.0003 ³	20.	0.2906	0.6526	0.0568
2.	0.0661	0.9328	0.0011	21.	0.2954	0.6447	0.0599
3.	0.0775	0.9203	0.0021	22.	0.0000 ³	0.2600 ³	0.7400 ³
4.	0.0859	0.9109	0.0032	23.	0.1952	0.2057	0.5990
5.	0.0941	0.9017	0.0042	24.	0.2411	0.3090	0.4499
6.	0.1015	0.8933	0.0052	25.	0.2864	0.3621	0.3515
7.	0.1319	0.8581	0.0100	26.	0.3187	0.3943	0.2870
8.	0.1541	0.8314	0.0145	27.	0.3347	0.4204	0.2448
9.	0.1751	0.8062	0.0187	28.	0.3459	0.4404	0.2137
10.	0.1942	0.7830	0.0227	29.	0.3491	0.4597	0.1912
11.	0.2106	0.7628	0.0266	30.	0.3486	0.4776	0.1738
12.	0.2247	0.7450	0.0303	31.	0.3504	0.4908	0.1588
13.	0.2372	0.7289	0.0338	32.	0.3493	0.5039	0.1467
14.	0.2481	0.7146	0.0373	33.	0.3476	0.5221	0.1303
15.	0.2580	0.7013	0.0407	34.	0.3435	0.5388	0.1177
16.	0.2664	0.6896	0.0440	35.	0.3399	0.5528	0.1073
17.	0.2733	0.6794	0.0473	36.	0.3364	0.5649	0.0987
18.	0.2797	0.6698	0.0505	37.	0.3310	0.5773	0.0917
19.	0.2853	0.6610	0.0537	38.	0.3266	0.5878	0.0856
				39.	0.3227	0.5971	0.0802
1-propanol (x_1) + water (x_2) + 1-octanol (x_3)							
1.	0.0000 ³	0.9999 ³	0.0001 ³	20.	0.3094	0.6407	0.0499
2.	0.0715	0.9276	0.0009	21.	0.3184	0.6266	0.0549
3.	0.0834	0.9148	0.0018	22.	0.0000 ³	0.2590 ³	0.7410 ³
4.	0.0912	0.9061	0.0026	23.	0.2211	0.2165	0.5624
5.	0.0986	0.8979	0.0035	24.	0.2974	0.3056	0.3970
6.	0.1056	0.8900	0.0043	25.	0.3365	0.3556	0.3080
7.	0.1237	0.8695	0.0068	26.	0.3532	0.3921	0.2547
8.	0.1390	0.8519	0.0091	27.	0.3662	0.4170	0.2167
9.	0.1531	0.8355	0.0114	28.	0.3770	0.4347	0.1883
10.	0.1666	0.8199	0.0136	29.	0.3789	0.4530	0.1681
11.	0.1792	0.8051	0.0157	30.	0.3742	0.4724	0.1534
12.	0.1977	0.7833	0.0191	31.	0.3703	0.4886	0.1411
13.	0.2157	0.7620	0.0223	32.	0.3677	0.5085	0.1239
14.	0.2304	0.7443	0.0254	33.	0.3658	0.5238	0.1104
15.	0.2436	0.7281	0.0284	34.	0.3594	0.5403	0.1003
16.	0.2550	0.7137	0.0313	35.	0.3570	0.5515	0.0915
17.	0.2647	0.7011	0.0341	36.	0.3543	0.5539	0.0919
18.	0.2829	0.6775	0.0396	37.	0.3452	0.5760	0.0788
19.	0.2971	0.6580	0.0449	38.	0.3330	0.5974	0.0695
				39.	0.3228	0.6150	0.0623
1-propanol (x_1) + water (x_2) + 1-nonanol (x_3)							
1.	0.0000 ³	1.0000 ³	0.0000 ³	22.	0.0000 ³	0.2510 ³	0.7490 ³
2.	0.0806	0.9185	0.0009	23.	0.3319	0.1810	0.4871
3.	0.0933	0.9050	0.0017	24.	0.3736	0.2670	0.3593
4.	0.1039	0.8936	0.0025	25.	0.4286	0.3416	0.2299
5.	0.1090	0.8876	0.0033	26.	0.4375	0.3656	0.1968
6.	0.1192	0.8767	0.0041	27.	0.4373	0.3884	0.1742
7.	0.1292	0.8660	0.0049	28.	0.4340	0.4088	0.1572
8.	0.1387	0.8548	0.0064	29.	0.4312	0.4256	0.1432
9.	0.1497	0.8424	0.0079	30.	0.4262	0.4417	0.1321
10.	0.1648	0.8258	0.0093	31.	0.4245	0.4535	0.1221
11.	0.1721	0.8172	0.0108	32.	0.4159	0.4693	0.1148
12.	0.1820	0.8058	0.0121	33.	0.4079	0.4906	0.1016
13.	0.2012	0.7840	0.0148	34.	0.3996	0.5091	0.0913
14.	0.2218	0.7603	0.0179	35.	0.3928	0.5242	0.0830
15.	0.2387	0.7404	0.0209	36.	0.3855	0.5383	0.0763
16.	0.2548	0.7215	0.0238	37.	0.3777	0.5516	0.0707
17.	0.2644	0.7090	0.0267	38.	0.3665	0.5719	0.0616
18.	0.2747	0.6958	0.0295	39.	0.3515	0.5934	0.0551
19.	0.2847	0.6832	0.0321	40.	0.3394	0.6108	0.0498
20.	0.2954	0.6700	0.0347	41.	0.3239	0.6303	0.0459
21.	0.3026	0.6601	0.0373	42.	0.3148	0.6430	0.0422

1-propanol (x_1) + water (x_2) + 1-decanol (x_3)							
1.	0.0000 ³	1.0000 ³	0.0000 ³	24.	0.3033	0.6569	0.0398
2.	0.0819	0.9173	0.0007	25.	0.0000 ³	0.2470 ³	0.7530 ³
3.	0.0933	0.9052	0.0015	26.	0.3418	0.2114	0.4468
4.	0.1006	0.8972	0.0022	27.	0.3897	0.3581	0.2522
5.	0.1075	0.8896	0.0029	28.	0.3963	0.3950	0.2087
6.	0.1159	0.8806	0.0036	29.	0.3956	0.4248	0.1795
7.	0.1229	0.8728	0.0042	30.	0.3977	0.4455	0.1569
8.	0.1315	0.8629	0.0056	31.	0.3915	0.4674	0.1411
9.	0.1418	0.8513	0.0069	32.	0.3891	0.4832	0.1276
10.	0.1498	0.8420	0.0082	33.	0.3866	0.4967	0.1166
11.	0.1595	0.8310	0.0094	34.	0.3833	0.5091	0.1076
12.	0.1676	0.8218	0.0106	35.	0.3761	0.5282	0.0957
13.	0.1832	0.8038	0.0130	36.	0.3727	0.5415	0.0858
14.	0.2004	0.7837	0.0158	37.	0.3642	0.5573	0.0785
15.	0.2173	0.7642	0.0185	38.	0.3557	0.5718	0.0725
16.	0.2298	0.7490	0.0212	39.	0.3505	0.5824	0.0671
17.	0.2424	0.7338	0.0237	40.	0.3440	0.5933	0.0627
18.	0.2536	0.7201	0.0262	41.	0.3342	0.6105	0.0553
19.	0.2651	0.7063	0.0286	42.	0.3231	0.6272	0.0497
20.	0.2719	0.6971	0.0310	43.	0.3131	0.6417	0.0452
21.	0.2796	0.6871	0.0333	44.	0.3044	0.6541	0.0415
22.	0.2869	0.6774	0.0356	45.	0.2963	0.6654	0.0383
23.	0.2934	0.6687	0.0379				

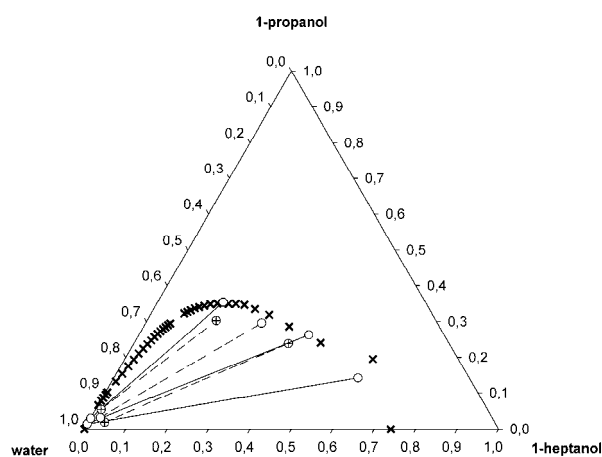


Fig. 1 – LLE data (molar fractions) for 1-propanol (1) + water (2) + 1-heptanol (3) system at 294.15 K: (x) solubility data, (○) experimental tie-lines data, (○+) UNIQAC tie-lines data.

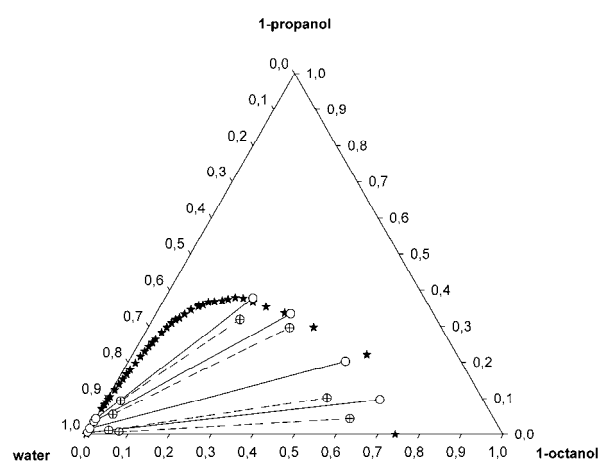


Fig. 2 – LLE data (molar fractions) for 1-propanol (1) + water (2) + 1-octanol (3) system at 294.15 K: (*) solubility data, (○) experimental tie-lines data, (○+) UNIQAC tie-lines data.

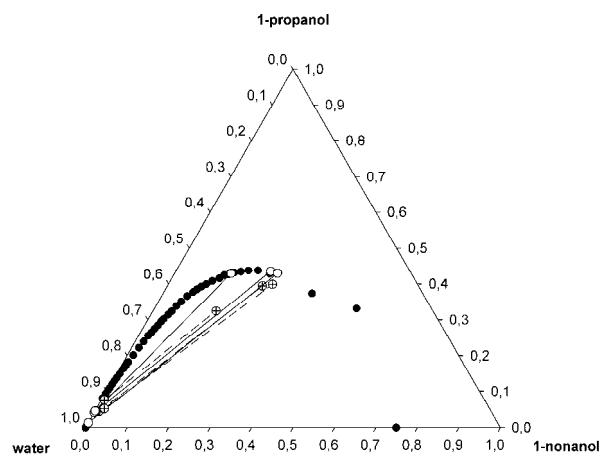


Fig. 3 – LLE data (molar fractions) for 1-propanol (1) + water (2) + 1-nonanol (3) system at 294.15 K: (●) solubility data, (○) experimental tie-lines data, (○+) UNIQAC tie-lines data.

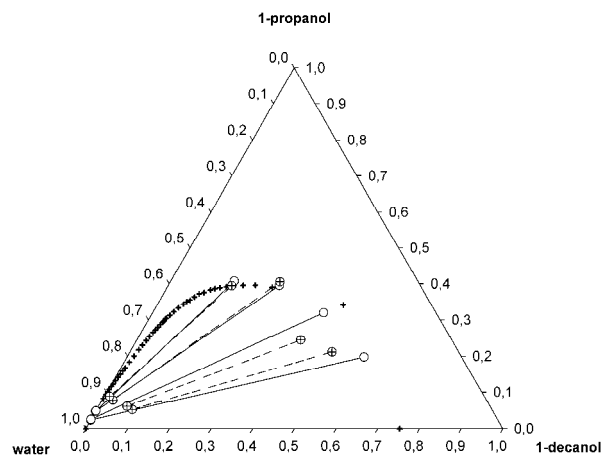


Fig. 4 – LLE data (molar fractions) for 1-propanol (1) + water (2) + 1-decanol (3) system at 294.15 K: (■) solubility data, (○) experimental tie-lines data, (○+) UNIQAC tie-lines data.

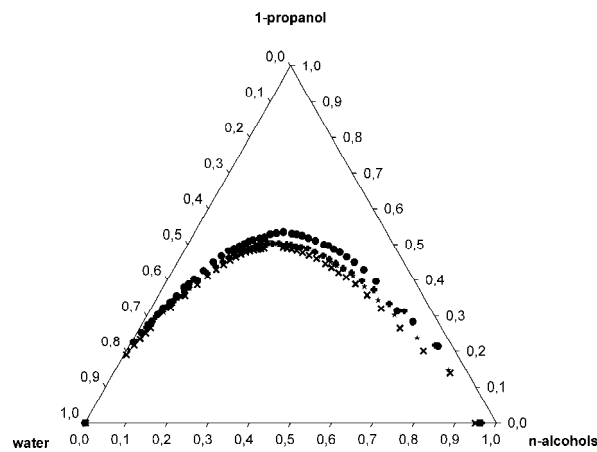


Fig. 5 – Binodal curves (mass fractions) data for 1-propanol + water + n-alcohols at 294.15 K: (x) 1-heptanol, (★) 1-octanol, (●) 1-nonanol, (■) 1-decanol system.

The LLE phase diagrams for (water + n-alcohols) mixtures show two liquid pairs (1-propanol + water) and (1-propanol + n-alcohol) that are completely miscible and one liquid pair that is partially miscible. As can be seen in these diagrams the heavy alcohols are practical insoluble in water, but miscible with 1-propanol. All investigated ternary systems behave as type-1 of LLE, after Treyball,¹⁵ the most frequent encountered situation of the measured ternary systems.

Fig. 5 presents comparatively the measured solubility curves in mass fractions (for better view) for the studied systems. The mutual solubilities for water + n-alcohol were taken from literature.³ The miscibility in homologous series of binaries water + n-alcohol decreases with the increase of the carbon number of alcohol. For the ternary systems, the area of the two-phase region increases in the order 1-heptanol < 1-octanol < 1-nonanol < 1-decanol.

Consistency of experimental tie-line data

The thermodynamic consistency of experimentally measured tie-lines data was obtained by applying the Othmer-Tobias and Hand equations^{9, 10} given as Eq. (1) and Eq. (2), which

are very sensitive to LLE data for aqueous-organic compound systems with very low solubility:

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

$$\ln\left(\frac{W_{13}}{W_{33}}\right) = a_2 + b_2 \ln\left(\frac{W_{12}}{W_{22}}\right) \quad (2)$$

a_1 , b_1 and a_2 , b_2 are the correlation coefficients of the Othmer-Tobias and Hand equations, respectively. W_{22} is the mass fraction of water in the water-rich phase, W_{33} – mass fraction of n-alcohol in organic-rich phase, W_{13} – mass fraction of 1-propanol in organic-rich phase, W_{12} – mass fraction of 1-propanol in the water-rich phase.

The constants (a, b) and correlation factors (r^2) determined by the least-squares method are given in Table 3. The plots of Othmer-Tobias correlation was made in Fig. 6 and the plots of Hand correlation was made in Fig. 7. The linearity of the plot indicates the degree of consistency of the related data, generally good, except for system with 1-nonanol.

Table 3

The Othmer-Tobias and Hand coefficients and correlation factors for the 1-propanol + water + n-alcohols systems at 294.15 K

Othmer-Tobias coefficients			Hand coefficients		
a_1	b_1	r^2	a_2	b_2	r^2
1-propanol (1) + water (2) + 1-heptanol (3)					
5.6370	2.2741	0.9143	5.7327	2.4304	0.8858

1-propanol (1) + water (2) + 1-octanol (3)					
1.7805	1.0454	0.9590	1.7394	1.1488	0.9697
1-propanol (1) + water (2) + 1-nonanol (3)					
0.9038	0.3407	0.4422	0.6041	0.3040	0.4443
1-propanol (1) + water (2) + 1-decanol (3)					
3.4088	1.9240	0.8471	3.2456	1.9554	0.8428

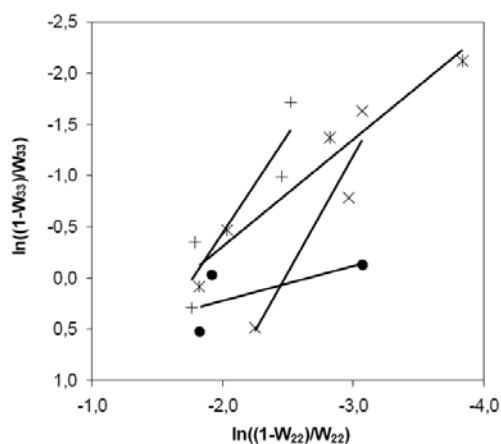


Fig. 6 – Othmer-Tobias equations for the 1-propanol (1) + water (2) + n-alcohols (3) systems at 294.15 K: (X) 1-heptanol, (*) 1-octanol, (●) 1-nonanol, (■) 1-decanol.

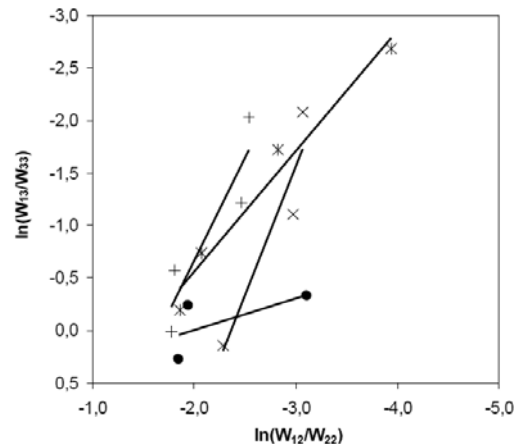


Fig. 7 – Hand equations for the 1-propanol (1) + water (2) + n-alcohols (3) systems at 294.15 K: (X) 1-heptanol, (*) 1-octanol, (●) 1-nonanol, (■) 1-decanol.

LLE calculation

The experimental LLE data were correlated using the universal quasi-chemical model UNIQUAC.¹¹ The UNIQUAC structural parameters r (the number of segments per molecule) and q (the relative surface area per molecule) were calculated from the Hansen's group contribution data.¹⁶ For water literature values were used.¹⁷ The values of r and q used in the UNIQUAC equation are presented in Table 5.

The isothermal thermal LLE were correlated by adjusting six model parameters simultaneously. The objective function (FO) of the parameter determination is defined as:

$$FO = \sum_k \sum_j \sum_i (x_{ijk}^{\text{exp}} - x_{ijk}^{\text{calc}})^2 \quad (3)$$

where x_{ijk}^{exp} and x_{ijk}^{calc} are the experimental and calculated compositions of component i in phase j along a tie line k , respectively. The random search method defined by Luus-Jaakola^{18, 19} was used for the minimization.

The quality of the correlation is measured by the root-mean squared deviation (RMSD) in the following equation:

$$RMSD = \left[\sum_{k=1}^N \left(\sum_{j=1}^{n_f} \sum_{i=1}^{n_c} \frac{(x_{ijk}^{\text{exp}} - x_{ijk}^{\text{calc}})^2}{n_c n_f N} \right) \right]^{1/2} \quad (4)$$

where N is the number of tie-lines, $k=1, 2, \dots, N$, n_f - is the number of the phases, n_c - is the number of the components.

The correlated results were plotted in Figs. 1-4 along with the experimental values at 294.15 K. As it is seen from Figs. 1-4 and Table 4, good and satisfactory agreements between the calculated results from the UNIQUAC model and experimental values have been obtained for all the investigated systems. The objective function values and UNIQUAC parameters obtained for the studied systems were summarized in Table 5.

The plait point composition for 1-propanol + water + n-alcohols systems has been determined using Coolidge method¹⁰ and the obtained values are listed in Table 7. The plait points positions are asymmetrically for all systems because the solubility of 1-propanol in the two phases are different.

The effectiveness of extraction of 1-propanol from aqueous solutions by superior n-alcohols is given by their separation factor (S), which was a measure of the solvents ability to separate the 1-propanol from water. The separation factor is defined as the ratio of distribution coefficient of the 1-propanol (D_1) to the distribution coefficient of the water (D_2): $S = (D_1)/(D_2)$.

Table 4

Experimental and calculated (molar fractions)
of tie-line data for 1-propanol (x_1) + water (x_2) + n-alcohols (x_3) ternary systems at 294.15 K

Water-rich phase			n-Alcohol-rich phase		
x_1'	x_2'	x_3'	x_1''	x_2''	x_3''
1-propanol (x_1) + water (x_2) + 1-heptanol (x_3)					
Experimental					
0.0250	0.9740	0.0010	0.2200	0.3810	0.3990
0.0380	0.9600	0.0020	0.2910	0.4310	0.2780
0.0430	0.9550	0.0020	0.3240	0.5170	0.1590
UNIQUAC					
0.0190	0.9410	0.0400	0.2390	0.3880	0.3730
0.0320	0.9450	0.0230	0.2960	0.4240	0.2800
0.0540	0.9320	0.0140	0.3030	0.5300	0.1670
RMSD = 1.827×10^{-2}					
1-propanol (x_1) + water (x_2) + 1-octanol (x_3)					
Experimental					
0.0058	0.9939	0.0003	0.0973	0.2470	0.6557
0.0175	0.9824	0.0001	0.2026	0.2772	0.5202
0.0365	0.9630	0.0005	0.3342	0.3426	0.3232
0.0445	0.9546	0.0009	0.3777	0.4112	0.2111
UNIQUAC					
0.0078	0.9173	0.0749	0.0445	0.3451	0.6104
0.0118	0.9399	0.0483	0.1021	0.3712	0.5267
0.0566	0.9076	0.0358	0.2962	0.3641	0.3397
0.0942	0.8698	0.0360	0.3189	0.4715	0.2096
RMSD = 5.546×10^{-2}					
1-propanol (x_1) + water (x_2) + 1-nonanol (x_3)					
Experimental					
0.0361	0.9636	0.0003	0.4566	0.3220	0.2214
0.0131	0.9866	0.0003	0.4299	0.3221	0.2479
0.0449	0.9546	0.0005	0.4292	0.4345	0.1363
UNIQUAC					
0.0437	0.9451	0.0112	0.3946	0.3764	0.2290
0.0515	0.9289	0.0196	0.3992	0.3498	0.2510
0.0756	0.9170	0.0074	0.3251	0.5227	0.1522
RMSD = 4.199×10^{-2}					
1-propanol (x_1) + water (x_2) + 1-decanol (x_3)					
Experimental					
0.0191	0.9808	0.0001	0.1977	0.2338	0.5685
0.0249	0.9750	0.0001	0.3202	0.2694	0.4104
0.0426	0.9573	0.0001	0.3958	0.3376	0.2666
0.0482	0.9515	0.0003	0.4070	0.4403	0.1528
UNIQUAC					
0.0521	0.8624	0.0855	0.2116	0.3036	0.4848
0.0606	0.8709	0.0685	0.2443	0.3622	0.3935
0.0777	0.8962	0.0261	0.4054	0.3315	0.2631
0.0883	0.8985	0.0132	0.3947	0.4525	0.1528
RMSD = 5.573×10^{-2}					

Table 5

The UNIQUAC structural parameters

Component	r	q
1-Propanol	3.2499	3.1280
Water	0.9200	1.4000
1-Heptanol	5.9475	5.2880
1-Octanol	6.6219	5.8280
1-Nonanol	7.2963	6.3680
1-Decanol	7.9707	6.9080

Table 6

The UNIQUAC binary parameters a_{ij} and a_{ji} (K) for the 1-propanol + water + n-alcohols systems at 294.15 K

1-propanol (1) + water (2) + 1-heptanol (3)			
a_{21}	-2.269	a_{32}	524.178
a_{31}	323.476	a_{13}	-642.719
a_{12}	174.638	a_{23}	-272.321
$F_{ob}=0.935 \times 10^{-2}$			
1-propanol (1) + water (2) + 1-octanol (3)			
a_{21}	-141.004	a_{32}	691.369
a_{31}	-213.030	a_{13}	62.913
a_{12}	483.523	a_{23}	-120.286
$F_{ob}=8.729 \times 10^{-2}$			
1-propanol (1) + water (2) + 1-nonanol (3)			
a_{21}	-262.423	a_{32}	986.981
a_{31}	-316.058	a_{13}	-205.182
a_{12}	519.689	a_{23}	-252.763
$F_{ob}=3.290 \times 10^{-2}$			
1-propanol (1) + water (2) + 1-decanol (3)			
a_{21}	-158.077	a_{32}	677.515
a_{31}	-379.963	a_{13}	459.495
a_{12}	969.715	a_{23}	-117.000
$F_{ob}=9.547 \times 10^{-2}$			

Table 7

Plait points compositions (mass fractions) for 1-propanol + water + n-alcohols systems at 294.15 K

Ternary systems	Plait points compositions (P)		
	W_1	W_2	W_3
1-propanol (1) + water (2) + 1-heptanol (3)	0.38	0.55	0.07
1-propanol (1) + water (2) + 1-octanol (3)	0.40	0.52	0.08
1-propanol (1) + water (2) + 1-nonanol (3)	0.42	0.49	0.09
1-propanol (1) + water (2) + 1-decanol (3)	0.42	0.50	0.08

In order to indicate and compare the ability of the solvents 1-heptanol or 1-octanol or 1-nonanol or 1-decanol to separate the 1-propanol from aqueous phase, distribution coefficient for 1-propanol $D_1 = W_{13}/W_{12}$, distribution coefficient for water $D_2 = W_{23}/W_{22}$ and the separation factor, S , were calculated. The W_{13} and W_{23} are the mass fractions of 1-propanol and water in the organic-rich phase, respectively. The W_{12} and W_{22} are the mass fractions of 1-propanol and water in the aqueous phase, respectively. The variation of the distribution coefficients and separation factor of 1-propanol as a function of the mass fraction of the 1-propanol in aqueous phase for the ternary systems is shown in Figs. 8, 9.

The experimental results indicate that 1-nonanol and 1-decanol have a higher separation factors thereby indicating the capability of these superior alcohols to extract 1-propanol from water. It is observed that the separation factor was found

to be greater than 1, varying between 18.23 and 100.35 for the systems reported in this work, which means that the extraction of 1-propanol from water using superior n-alcohols is possible. Therefore, these n-alcohols can be used practically with better results than other solvents in the literature.²

The separation factor for all the alcohols present the highest values, meaning that the 1-heptanol, 1-octanol, 1-nonanol and 1-decanol are preferable solvents for the extraction of 1-propanol from water.

Also, the selectivity diagrams on a solvent-free basis are obtained by plotting $W_{13}/(W_{13} + W_{23})$ vs. $W_{12}/(W_{12} + W_{22})$ for each solvent. Fig. 10 shows the dependence of mass fraction 1-propanol in alcoholic phase depending on the mass fraction of 1-propanol in the aqueous phase. The selectivity performance of superior alcohols 1-nonanol and 1-decanol are higher than 1-heptanol and 1-octanol.¹

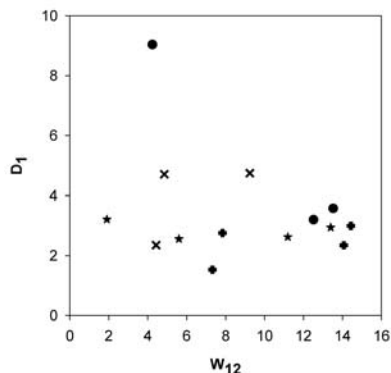


Fig. 8 – Plot of the distribution coefficient, D_1 of 1-propanol as a function of the mass fraction W_{12} of 1-propanol in water-rich phase, at 294.15 K: (X) 1-heptanol, (★) 1-octanol, (●) 1-nonanol, (⊕) 1-decanol.

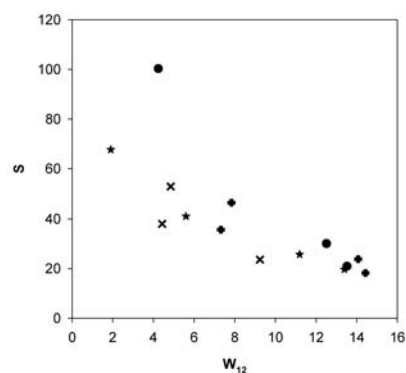


Fig. 9 – Separation factor, S , plotted against the mass fraction of 1-propanol in water-rich phase, W_{12} at 294.15 K: (X) 1-heptanol, (★) 1-octanol, (●) 1-nonanol, (⊕) 1-decanol.

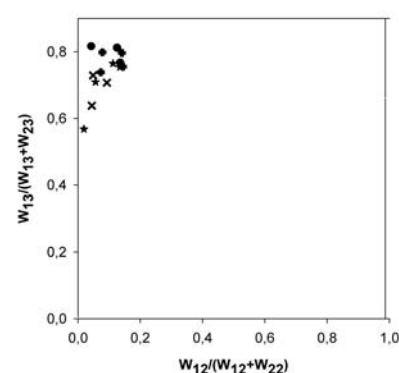


Fig. 10 – Comparative selectivity diagram (solvent-free basis) of (1-propanol + water + solvent) at 294.15 K: (X) 1-heptanol, (★) 1-octanol, (●) 1-nonanol, (⊕) 1-decanol.

CONCLUSIONS

Liquid-liquid equilibria (LLE) data for 1-propanol + water + n-alcohol (1-heptanol or 1-octanol or 1-nonanol or 1-decanol) ternary systems were determined at atmospheric pressure and 294.15 K. All the investigated systems form type-1 phase diagram of LLE. The two-phase region increases in the order 1-heptanol < 1-octanol < 1-nonanol < 1-decanol, without major difference between n-alcohols.

The Othmer-Tobias and Hand equations show that the LLE data in this study have a good degree of consistency. The UNIQUAC model represents well the experimental ternary liquid-liquid equilibrium data.

In all the cases the plait-points were determined by Coolidge method. In every case it is located asymmetrically on the binodal curve because the solubility of 1-propanol in aqueous and alcoholic phase is very different.

The separation capacity of 1-heptanol, 1-octanol, 1-nonanol, 1-decanol for aqueous solutions of 1-propanol was assessed by determining the distribution coefficients, separation and selectivity factors. All the four n-alcohols can serve as suitable solvents to extract 1-propanol from its aqueous solution; among these solvents 1-nonanol and 1-decanol are the most selective, having the highest distribution coefficients and separation factors.

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