



*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. I. 1-PROPANOL + WATER + 1-BUTANOL OR 1-PENTANOL OR 1-HEXANOL

Cristina STOICESCU,<sup>a\*</sup> Olga IULIAN<sup>b</sup> and Raluca ISOPESCU<sup>b</sup>

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

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

*Received March 29, 2010*

Liquid-liquid equilibrium (LLE) data for the ternary systems: (1-propanol + water + 1-butanol), (1-propanol + water + 1-pentanol), (1-propanol + water + 1-hexanol) at 294.15 K and atmospheric pressure are reported. The studied n-alcohols are possible extraction solvents for the separation of 1-propanol from aqueous solutions. The phase equilibrium diagrams for all studied systems: miscibility curves, tie-lines and plait points are presented. The ternary systems exhibit the type-1 behaviour of LLE. The Othmer-Tobias and Hand equations used to verify the quality of the experimental data, gave similar results. The experimental ternary liquid-liquid equilibrium data were correlated with the UNIQUAC model. The correlation of the liquid-liquid equilibrium data evidenced that the UNIQUAC model represents well the experimental data and gives the original UNIQUAC parameters for the ternary systems. The values of distribution coefficients ( $D_i$ ), separation factors ( $S$ ) and selectivity for solvent separation efficiency, derived from the tie-line data, were used to decide if these n-alcohols can serve as potential solvents for the separation of 1-propanol from aqueous solutions. A comparison of the extracting capabilities of the solvents with respect to distribution coefficients, separation factors, and solvent-free selectivity bases was made.

### INTRODUCTION

Phase equilibrium data are important in practice for simulation, design and optimization of the separation processes and in scientific research for the understanding of the properties of the multi-component systems. The liquid-liquid investigations of ternary systems with water + n-alcohols have been the subject of much interest in the recent years in literature.<sup>1-3</sup> Some researches have described the use of liquid-liquid extraction to selectively remove 1-propanol from water.<sup>3</sup> We have recently reported LLE data for the ternary mixture of 1-propanol + water + n-alcohols, where

n-alcohols were shown to be a feasible organic solvent for the extraction of this alcohol from aqueous mixtures.<sup>4-7</sup>

1-Propanol is a liquid that is soluble in water and miscible with organic solvents. It has better dissolution properties than ethanol for fats and oils, and dissolves polar resins. The mixture of 1-propanol and water forms an azeotrope at 360.15 K and  $x_{propanol}^{azeotrope} = 0.435$  (mole fraction), the separation of 1-propanol from the aqueous solutions is economically infeasible by using traditional distillation method. In this case, heterogeneous extractive distillation is a possible alternative method to separate such azeotropic mixtures.

\* Corresponding author: [cristina.silvia.stoicescu@gmail.com](mailto:cristina.silvia.stoicescu@gmail.com)

The focus of this study is to report the experimental data on the phase equilibria of water + 1-propanol with one of three potential solvents: 1-butanol, 1-pentanol and 1-hexanol at 294.15 K and normal pressure.

No data on 1-propanol + water + 1-hexanol system and some for systems with 1-butanol and 1-pentanol at 298.15 K have been found in literature.<sup>8,9</sup>

The liquid-liquid equilibria were studied by the cloud-point method and Newsham and Ng technique.<sup>8,10</sup> The experimental tie-line data were correlated with the Othmer–Tobias<sup>11</sup> and Hand<sup>12</sup> equations to test their consistency. The LLE data were correlated with the UNIQUAC solution model<sup>13</sup> and the values of the interaction parameters were obtained. For the each ternary system, the plait point compositions using Coolidge methods<sup>10</sup> have been determined.

The extracting capability of n-alcohols as possible solvents for the separation of (water + 1-propanol) mixtures was analysed by 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 293.15K and atmospheric pressure. They were measured using an Anton Paar (Abbat RXA 170) refractometer, with an accuracy of  $\pm 2 \times 10^{-5}$ . The temperature was fixed with an

accuracy of 0.03 °C. The measured values together with those from literature are presented 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 and experimental procedure were previously described in detail.<sup>4</sup>

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  $\pm 0.1$  K, a magnetic stirrer and a microburette. The inner temperature of the cell was measured by a precision thermometer with an accuracy of  $\pm 0.1$  K. The binary mixtures were prepared by weighing. An electronic balance accurate to  $\pm 0.01$  mg was used. The third component was progressively added by means of a microburette with an accuracy of  $\pm 0.05$  cm<sup>3</sup> that means around 0.014g alcohol. The estimated uncertainties in the molar fraction were about  $\pm 0.005$ . The transitions point between the heterogeneous and homogeneous was determined visually. All visuals 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 cm<sup>3</sup>) 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 Ng<sup>9</sup> 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 <sup>-1</sup> ]	Refractive index n <sup>20</sup>	
		This work	Literature data <sup>14</sup>
water	18.02	1.33297	1.3325
1-propanol	60.10	1.38509	1.3850
1-butanol	74.12	1.39850	1.3993
1-pentanol	88.15	1.40917	1.4101
1-hexanol	102.18	1.41778	1.4178

## RESULTS AND DISCUSSION

### Experimental LLE data

The paper presents experimental liquid-liquid equilibrium data for (1-propanol + water +

1-butanol), (1-propanol + water + 1-pentanol), (1-propanol + water + 1-hexanol) ternary systems at 294.15 K and atmospheric pressure: miscibility curves, tie-lines and plait points. This paper completes the data for (1-propanol + water +

1-butanol) ternary systems at 294.15 K, that were partially published in our previous paper.<sup>6</sup>

Table 2 lists the experimental data of the binodal curves for the ternary systems (1-propanol + water + n-alcohols), where  $x_i$  is the mole fraction of the  $i^{\text{th}}$  components. The experimental and

calculated tie-line data of (1-propanol + water + n-alcohols) at 294.15 K were reported in Table 4. 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. 1-3.

Table 2

The binodal curves (molar fractions)  
for the 1-propanol (1) + water (2) + 1-butanol (3) or 1-pentanol or 1-hexanol ternary systems 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-butanol ( $x_3$ )							
1.	0.0000 <sup>2</sup>	0.9801 <sup>2</sup>	0.0199 <sup>2</sup>	9.	0.0000 <sup>2</sup>	0.5115 <sup>2</sup>	0.4885 <sup>2</sup>
2.	0.0358	0.9477	0.0165	10.	0.0521	0.5995	0.3485
3.	0.0684	0.9002	0.0314	11.	0.1154	0.6375	0.2471
4.	0.0906	0.8642	0.0452	12.	0.1416	0.6651	0.1933
5.	0.1050	0.8366	0.0584	13.	0.1526	0.6875	0.1599
6.	0.1204	0.8091	0.0705	14.	0.1551	0.7077	0.1371
7.	0.1341	0.7839	0.0820	15.	0.1517	0.7275	0.1208
8.	0.1437	0.7631	0.0932	16.	0.1458	0.7458	0.1084
1-propanol ( $x_1$ ) + water ( $x_2$ ) + 1-pentanol ( $x_3$ )							
1.	0.0000 <sup>2</sup>	0.9953 <sup>2</sup>	0.0047 <sup>2</sup>	17.	0.2457	0.6609	0.0934
2.	0.0153	0.9820	0.0028	18.	0.2538	0.6458	0.1004
3.	0.0586	0.9361	0.0053	19.	0.2566	0.6356	0.1078
4.	0.0712	0.9210	0.0078	20.	0.0000 <sup>2</sup>	0.3530 <sup>2</sup>	0.6470 <sup>2</sup>
5.	0.0858	0.9040	0.0102	21.	0.0729	0.3297	0.5974
6.	0.0902	0.8971	0.0127	22.	0.1849	0.4276	0.3875
7.	0.1128	0.8676	0.0196	23.	0.2327	0.4783	0.2889
8.	0.1328	0.8411	0.0262	24.	0.2539	0.5134	0.2326
9.	0.1510	0.8167	0.0323	25.	0.2651	0.5394	0.1955
10.	0.1638	0.7979	0.0383	26.	0.2640	0.5652	0.1707
11.	0.1800	0.7762	0.0439	27.	0.2660	0.5831	0.1510
12.	0.1991	0.7480	0.0529	28.	0.2617	0.6019	0.1364
13.	0.2137	0.7248	0.0615	29.	0.2603	0.6157	0.1240
14.	0.2245	0.7057	0.0698	30.	0.2596	0.6268	0.1136
15.	0.2326	0.6894	0.0780	31.	0.2526	0.6469	0.1005
16.	0.2403	0.6739	0.0857	32.	0.2431	0.6663	0.0906
1-propanol ( $x_1$ ) + water ( $x_2$ ) + 1-hexanol ( $x_3$ )							
1.	0.0000 <sup>2</sup>	0.9989 <sup>2</sup>	0.0011 <sup>2</sup>	16.	0.2048	0.7652	0.0301
2.	0.0499	0.9488	0.0012	17.	0.2194	0.7464	0.0342
3.	0.0673	0.9302	0.0024	18.	0.2308	0.7309	0.0383
4.	0.0748	0.9216	0.0036	19.	0.2418	0.7160	0.0422
5.	0.0858	0.9095	0.0048	20.	0.2512	0.7027	0.0460
6.	0.0911	0.9030	0.0059	21.	0.0000 <sup>2</sup>	0.2950 <sup>2</sup>	0.7050 <sup>2</sup>
7.	0.0946	0.8984	0.0071	22.	0.2226	0.4036	0.3738
8.	0.1015	0.8903	0.0082	23.	0.3092	0.4722	0.2186
9.	0.1067	0.8841	0.0093	24.	0.3256	0.5153	0.1591
10.	0.1134	0.8763	0.0103	25.	0.3224	0.5502	0.1274
11.	0.1183	0.8703	0.0114	26.	0.3176	0.5758	0.1066
12.	0.1281	0.8590	0.0128	27.	0.3093	0.5983	0.0923
13.	0.1468	0.8367	0.0164	28.	0.3031	0.6155	0.0814
14.	0.1673	0.8114	0.0213	29.	0.2943	0.6325	0.0732
15.	0.1880	0.7863	0.0257	30.	0.2836	0.6496	0.0668

According to Treyball classification<sup>15</sup> all investigated ternary systems behave as type-1, *i.e.* they present only one binodal curve. This is because in case of any system only two of liquids, water and n-alcohol (1-butanol or 1-pentanol or

1-hexanol) are partially miscible, 1-propanol being miscible with both the other two.

Fig. 4 presents comparatively the measured solubility curves (in mass fractions for a better view) for studied systems at 294.15 K. The mutual

solubilities of water in n-alcohol and n-alcohol in water were taken from literature.<sup>2</sup> We note that, in homologous series, the miscibility of binaries water + n-alcohols decreases with the increase of

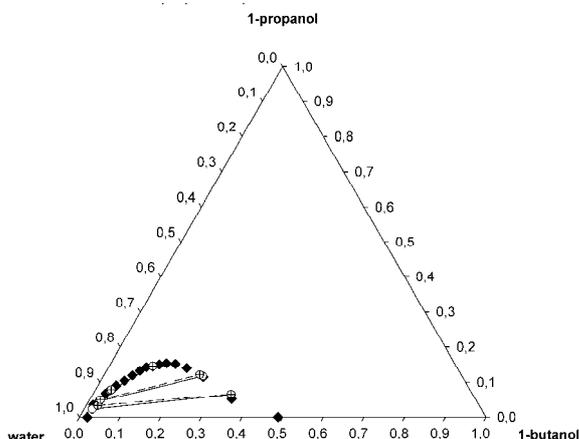


Fig. 1 – LLE data (molar fractions) for 1-propanol (1) + water (2) + 1-butanol (3) system at 294.15 K: (◆) solubility data, (—○) experimental tie-lines data, (—⊕—) UNIQUAC tie-lines data.

the carbon number of alcohols. For the ternary systems, the area of the two-phase region increases in the order 1-butanol < 1-pentanol < 1-hexanol.

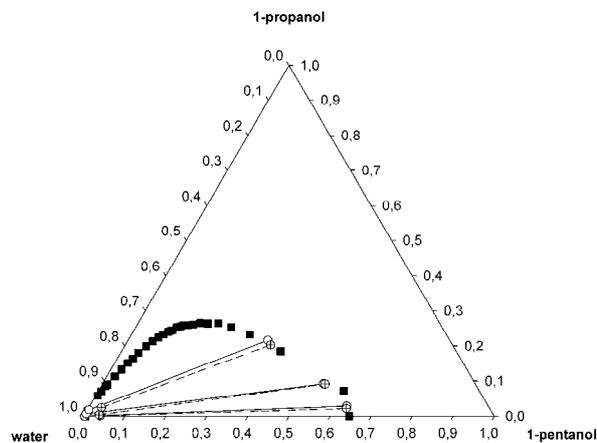


Fig. 2 – LLE data (molar fractions) for 1-propanol (1) + water (2) + 1-pentanol (3) system at 294.15 K: (■) solubility data, (—○) experimental tie-lines data, (—⊕—) UNIQUAC tie-lines data.

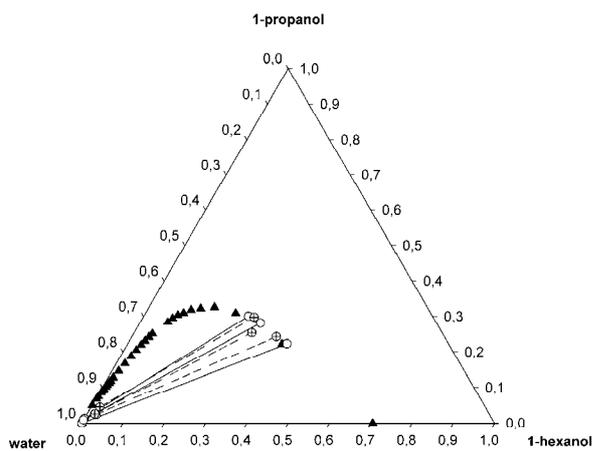


Fig. 3 – LLE data (molar fractions) for 1-propanol (1) + water (2) + 1-hexanol (3) system at 294.15 K: (▲) solubility data, (—○) experimental tie-lines data, (—⊕—) UNIQUAC tie-lines data.

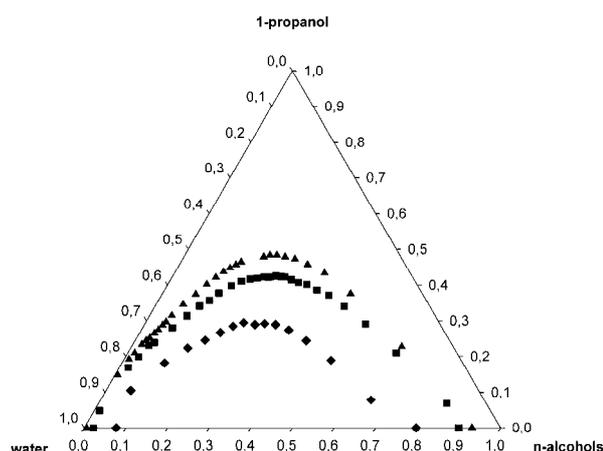


Fig. 4 – Binodal curves (mass fractions) data for 1-propanol + water + n-alcohols at 294.15 K: (◆) 1-butanol, (■) 1-pentanol, (▲) 1-hexanol system.

### Consistency of experimental tie-line data

For each system, the thermodynamic consistency of the experimental tie lines data was obtained by applying the Othmer-Tobias ((Eq. (1)) and Hand ((Eq. (2)) equations<sup>11, 12</sup> 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 reported in Table 3. The Othmer-Tobias and Hand equations show very good and good correlations

for the studied ternary systems. Furthermore, as seen from Figs. 5, 6 the linearity of the plot reveals that our measured LLE data in this study have high degree of consistency.

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-butanol (3)					
2.1417	1.5386	0.9709	1.9041	1.4992	0.9882
1-propanol (1) + water (2) + 1-pentanol (3)					
1.5667	0.8263	0.9367	0.3082	0.3500	0.8628
1-propanol (1) + water (2) + 1-hexanol (3)					
0.7477	0.2545	0.9779	0.1144	0.1050	0.9470

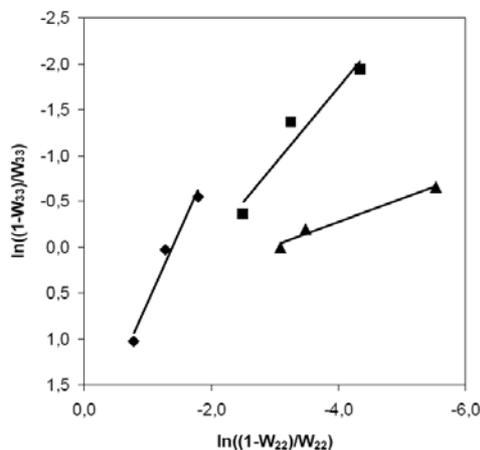


Fig. 5 – Othmer-Tobias equations for the 1-propanol (1) + water (2) + n-alcohols (3) systems at 294.15 K: (◆) 1-butanol, (■) 1-pentanol, (▲) 1-hexanol.

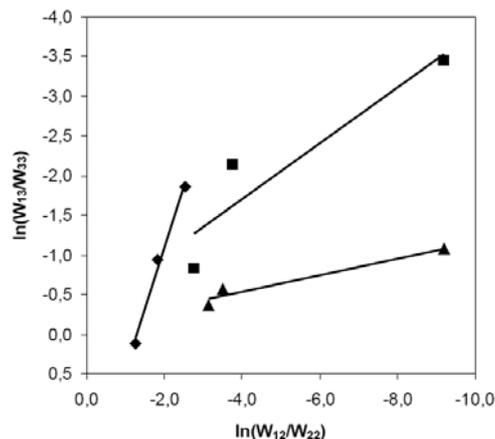


Fig. 6 – Hand equations for the 1-propanol (1) + water (2) + n-alcohols (3) systems at 294.15 K: (◆) 1-butanol, (■) 1-pentanol, (▲) 1-hexanol.

### LLE calculation

The experimental LLE data were correlated using the universal quasi-chemical model UNIQUAC.<sup>13</sup>

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.<sup>16</sup> For water the literature values were used.<sup>17</sup> The  $r$  and  $q$  values 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  $x_{ijk}^{\text{exp}}$  and  $x_{ijk}^{\text{calc}}$  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<sup>18, 19</sup> 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 are given in Table 4, in which  $x_i^I$  and  $x_i^{II}$  refer to mole fraction of the  $i^{\text{th}}$

component in the aqueous and solvent phase, respectively, and in Figs. 1-3 along with the experimental values at 294.15 K. The objective function values and UNIQUAC parameters obtained for the studied systems were listed in

Table 6. As it is seen, good agreements between the calculated results from the UNIQUAC model and experimental values have been obtained for this the investigated systems.

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-butanol ( $x_3$ )					
Experimental					
0.0224	0.9572	0.0204	0.0652	0.5938	0.3410
0.0453	0.9282	0.0264	0.1177	0.6381	0.2442
0.0767	0.8861	0.0372	0.1477	0.7452	0.1071
UNIQUAC					
0.033	0.938	0.029	0.066	0.594	0.340
0.050	0.923	0.027	0.122	0.643	0.235
0.079	0.882	0.039	0.147	0.746	0.107
RMSD = $0.6320 \times 10^{-2}$					
1-propanol ( $x_1$ ) + water ( $x_2$ ) + 1-pentanol ( $x_3$ )					
Experimental					
0.00003	0.9974	0.0026	0.0292	0.3446	0.6262
0.0070	0.9900	0.00305	0.0928	0.3694	0.5378
0.0185	0.9776	0.0039	0.2165	0.4429	0.3406
UNIQUAC					
0.001	0.959	0.04	0.022	0.349	0.629
0.004	0.960	0.036	0.092	0.366	0.542
0.025	0.944	0.031	0.203	0.443	0.354
RMSD = $2.003 \times 10^{-2}$					
1-propanol ( $x_1$ ) + water ( $x_2$ ) + 1-hexanol ( $x_3$ )					
Experimental					
0.00003	0.9993	0.0007	0.2234	0.3913	0.3853
0.0149	0.9845	0.0005	0.3008	0.4455	0.2536
0.0090	0.9910	0.00002	0.2815	0.4260	0.2924
UNIQUAC					
0.023	0.024	0.953	0.350	0.243	0.407
0.022	0.045	0.933	0.269	0.298	0.433
0.019	0.026	0.955	0.285	0.254	0.461
RMSD = $2.776 \times 10^{-2}$					

Table 5

The UNIQUAC structural parameters

Component	$r$	$q$
1-Propanol	3.2499	3.1280
Water	0.9200	1.4000
1-Butanol	3.9243	3.6680
1-Pentanol	4.5987	4.2080
1-Hexanol	5.2731	4.7480

Table 6

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

1-propanol (1) + water (2) + 1-butanol (3)			
$a_{21}$	329.534	$a_{32}$	-102.806
$a_{31}$	-318.645	$a_{13}$	1125.655
$a_{12}$	-94.400	$a_{23}$	476.752
F <sub>ob</sub> = $0.072 \times 10^{-2}$			

Table 6 (continued)

1-propanol (1) + water (2) + 1-pentanol (3)			
$a_{21}$	-65.893	$a_{32}$	516.687
$a_{31}$	-308.490	$a_{13}$	296.788
$a_{12}$	404.342	$a_{23}$	-77.120
$F_{ob} = 1.478 \times 10^{-2}$			
1-propanol (1) + water (2) + 1-hexanol (3)			
$a_{21}$	-146.876	$a_{32}$	545.259
$a_{31}$	-428.385	$a_{13}$	571.305
$a_{12}$	589.387	$a_{23}$	-64.468
$F_{ob} = 1.710 \times 10^{-2}$			

The plait point composition for studied systems has been determined using Coolidge method<sup>10</sup> and the values are listed in Table 7. The plait point positions are asymmetrically for all systems because the solubility of 1-propanol in the aqueous and solvent phase, respectively, is different.

The effectiveness of extraction of 1-propanol from aqueous solutions by n-alcohols as solvents is given by separation factor ( $S$ ), which was a measure of the solvents ability to separate the 1-propanol from water:

$$S = \frac{(D_1)}{(D_2)}, \quad D_1 = \frac{W_{13}}{W_{12}}, \quad D_2 = \frac{W_{23}}{W_{22}} \quad (5)$$

( $D_1$ ) and ( $D_2$ ) are the distribution coefficients of 1-propanol and water, respectively. 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. In order to indicate and compare the ability of the solvents: 1-butanol or 1-pentanol or 1-hexanol to separate the 1-propanol from aqueous solutions, distribution coefficients for 1-propanol, water and the separation factor,  $S$ , were calculated. 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. 7, 8.

The experimental results indicate that 1-hexanol has a higher separation factor thereby indicating the ability of 1-hexanol to extract 1-propanol from water. It is observed that the separation factor was found to be greater than 1, varying between 2.29 and 72.51 for the systems reported here, which means that the extraction of 1-propanol from water using n-alcohols is possible. Therefore, this solvents may be considered as a possible candidates for the recovery of 1-propanol from aqueous solution. The separation factor for 1-butanol is between 2.29 and 4.69, the superior alcohols, in this case 1-hexanol present the highest values, meaning that 1-butanol is not a preferable solvent for the extraction of 1-propanol from water.

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. 9 shows the dependence of mass fraction 1-propanol in alcoholic phase depending on the mass fraction of 1-propanol in the aqueous phase. It is observed that the extraction capacity of the studied alcohols depends on the compositions of the extractant mixture, in this case the selectivity performance of 1-hexanol is highest.

Table 7

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

Ternary systems	Plait points compositions (P)		
	$W_1$	$W_2$	$W_3$
1-propanol (1) + water (2) + 1-butanol (3)	0.25	0.58	0.17
1-propanol (1) + water (2) + 1-pentanol (3)	0.28	0.66	0.06
1-propanol (1) + water (2) + 1-hexanol (3)	0.34	0.60	0.06

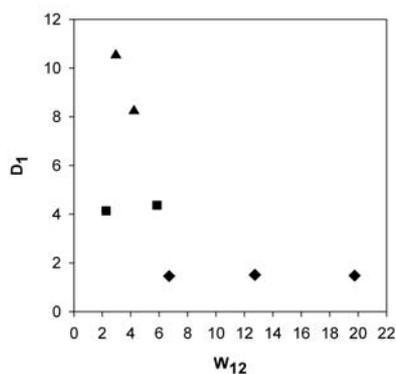


Fig. 7 – Plot of the distribution coefficient,  $D_1$ , of 1-propanol as a function of the mass fraction  $W_{12}$  of 1-propanol in water-rich phase, at 294.15 K: ( $\blacklozenge$ ) 1-butanol, ( $\blacksquare$ ) 1-pentanol, ( $\blacktriangle$ ) 1-hexanol.

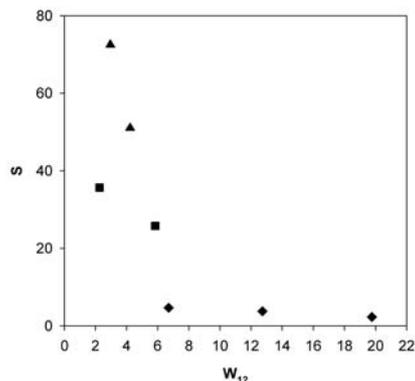


Fig. 8 – Separation factor,  $S$ , plotted against the mass fraction of 1-propanol in water-rich phase,  $W_{12}$  at 294.15 K: ( $\blacklozenge$ ) 1-butanol, ( $\blacksquare$ ) 1-pentanol, ( $\blacktriangle$ ) 1-hexanol.

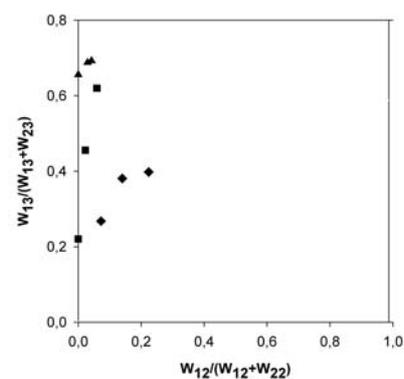


Fig. 9 – Comparative selectivity diagram (solvent-free basis) of (1-propanol + water + solvent) at 294.15 K: ( $\blacklozenge$ ) 1-butanol, ( $\blacksquare$ ) 1-pentanol, ( $\blacktriangle$ ) 1-hexanol.

## CONCLUSIONS

Liquid-liquid equilibria (LLE) data for 1-propanol + water + n-alcohol ternary systems were determined at atmospheric pressure and 294.15 K. All the investigated systems form type 1 phase diagrams of LLE. The area of the two-phase region increases in the order 1-butanol < 1-pentanol < 1-hexanol.

The Othmer-Tobias and Hand equations used for consistency test show that the LLE data in this study have a high degree of consistency. The correlation of the obtained liquid-liquid equilibrium values evidenced that the UNIQUAC model represents very well the experimental data. The obtained plait points compositions with Coolidge method are asymmetrically in the water-rich phases for all systems because the solubility of 1-propanol in the aqueous and organic phase, respectively, is different.

The study of 1-butanol, 1-pentanol and 1-hexanol as solvents for separation of 1-propanol from its aqueous solution was made by liquid-liquid equilibrium data, distribution coefficient, separation factor, and selectivity diagram of ternary alcohols systems. All three solvents have relatively low solubility against water (less 1-butanol) and may serve as suitable solvents to extract 1-propanol from its aqueous solution. 1-hexanol is the most selective, having the highest distribution coefficient and separation factor.

**Acknowledgements:** The Anton Paar refractometer (Abbemat RXA 170) was purchased from POS-CCE, AXA 2, INFRANANOCHEM, contract nr. 19/01.03.2009. This paper was done within research programme Chemical Thermodynamics of the "Ilie Murgulescu" Institute of Physical Chemistry, financed by the Roumanian Academy.

## REFERENCES

- V. Gomis, F. Ruiz, M. Ramos and M. J. Fernández, *Fluid Phase Equilib.*, **1998**, 149, 139-145.
- M. Góral, B. W. Gocłowska and A. Mączynski, *J. Phys. Chem. Ref. Data*, **2006**, 35, 1391-1414.
- S. Çehrelı, D. Özmen and U. Dramur, *Fluid Phase Equilib.*, **2006**, 239, 156-160.
- C. Stoicescu, O. Iulian and F. Sirbu, *Rev. Roum. Chim.*, **2008**, 53, 363-367.
- C. Stoicescu, O. Iulian and F. Sirbu, *CHISA 18<sup>th</sup>*, August, 24-28, Prague, Czech Republic, **2008**, Summaries vol. 2, 582-583.
- C. Stoicescu, O. Iulian and F. Sirbu, *Rev. Roum. Chim.*, **2008**, 53, 1117-1123.
- C. Stoicescu, R. Isopescu and O. Iulian, *RICCCE 16<sup>th</sup>* September 9-12, Sinaia, Roumania, **2009**, 85-92.
- D. M. T. Newsham and S. B. Ng, *J. Chem. Eng. Data*, **1972**, 17, 205-207.
- J. F. McCants, J. H. Jones and W. H. Hopson, *Ind. Eng. Chem.*, **1952**, 45, 454-456.
- J. P. Novák, J. Matouš and J. Pick, "Liquid-liquid equilibria", Academia Prague, 1987, p. 276-279.
- T. F. Othmer and P. E. Tobias, *Ind. Eng. Chem.*, **1942**, 34, 693-696.
- D. B. Hand, *J. Phys. Chem.*, **1930**, 34, 1961-2000.
- D. S. Abrams and J. M. Prausnitz, *AIChE J.*, **1975**, 21, 116-128.
- D. R. Lide, "CRC Handbook of Chemistry and Physics", 73<sup>rd</sup> Edition, CRC Press, Boca Raton, FL, 1992-1993.
- D. E. Treyball "Liquid Extraction", McGraw-Hill, New York, 1963.
- H. K. Hansen, P. Rasmussen, A. Fredenslund, M. Schiller and J. Gmehling, *Ind. Eng. Chem. Res.*, **1991**, 30, 2352-2355.
- B. E. Poling, J. M. Prausnitz and J. P. O'Connell, "The Properties of Gases and Liquids", Fifth Edition, McGraw-Hill Companies, 2004, www.Digitalengineeringlibrary.com.
- R. Luus and Thi. Jaakola, *AIChE J.*, **1973**, 19, 760-766.
- R. Luus, *Hung. J. Ind. Chem.*, **1998**, 26, 281-286.

