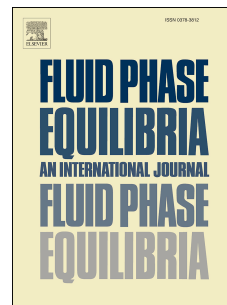


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Study of the Phase Equilibrium of the Water + 2-Propanol + 1-Undecanol Ternary System between 275.15 K and 288.15 K. Comparison with the Water + Ethanol + 1-Undecanol System

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1 Study of the Phase Equilibrium of the Water + 2-Propanol + 1-
2 Undecanol Ternary System between 275.15 K and 288.15 K.
3 Comparison with the Water + Ethanol + 1-Undecanol System

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6

7 **Abstract**

8 This paper reports the measurements of liquid+liquid, solid+liquid and
9 solid+liquid+liquid equilibrium data of the water + 2-propanol + 1-undecanol ternary system at
10 temperatures from 275.15 to 288.15 K. The three isothermal phase diagrams show different
11 regions depending on temperature. At 288.15 K a liquid+liquid region is observed, however,
12 below this temperature, solid phases appear. The experimental data have been compared with
13 the ternary water + ethanol + 1-undecanol system at the same temperatures; some differences
14 arise in the shapes of the different regions. Finally, by means of the distribution and selectivity
15 coefficients, the capability of the 1-undecanol as an extractant agent in alcohol dewatering has
16 been analyzed.

17

18 **Keywords:** Liquid–liquid equilibrium; extraction; 2-propanol; water; 1-undecanol.

19

20 **1. Introduction**

21 2-Propanol or isopropanol is a colourless, flammable liquid which is soluble in water
22 and miscible with other organic solvents. It is widely used in industry as a solvent or chemical
23 intermediate, as well as in consumer applications, typically in everyday products such as
24 cleaning products. In particular, it is commonly used in pharmaceutical and personal care
25 applications due to the low toxicity. During the manufacturing of 2-propanol via direct
26 hydration, it is formed in an aqueous solution that needs to be recovered. This is typically done
27 by distillation, however this is limited due to the formation of an azeotrope at 353.51 K with an
28 overhead vapour stream containing only 68% (mole basis) of 2-propanol [1]. For this reason,
29 different separation techniques are used for the alcohol dehydration such as azeotropic and

1 extractive distillation. Examples of effective agents are vinyl n-butyl ether for azeotropic
2 distillation and polyethylene glycol for extractive distillation [2].

3 In many cases liquid-liquid extraction is used after distillation when further extraction is
4 required. With this aim in mind, some authors have analyzed the behaviour of different
5 compounds such as oleic acid, different salts and ionic liquids [3, 4]. In particular, Sayar (1991)
6 [5] analyzed the behaviour of different solvents, mainly hydrocarbons and heavy alcohols, as
7 extractant agents for the 2-propanol dehydration process. This author points out that high-
8 boiling solvents showing low solubility in water are considered adequate separating agents.
9 Stoicescu et al. [6] did a similar analysis for the dehydration of 1-propanol trying different
10 heavy alcohols and found that 1-decanol and 1-dodecanol could serve as separating agents for
11 1-propanol at 298.15K.

12 Taking this into account, the main purpose of this research is to analyse the potential of
13 1-undecanol as an extractant agent in alcohol separation. 1-Undecanol is a fatty alcohol used as
14 a flavouring ingredient in food [7]. It is a high-boiling compound, water immiscible and solid
15 below 292 K. In addition, it presents low toxicity and for this reason, its application in the food
16 and the pharmaceutical industry could be interesting.

17 Liquid-liquid extraction requires reliable multicomponent phase equilibrium data to
18 design and optimise the separation process. In this sense, the aim of the research was to
19 determine the viability of using 1-undecanol as a solvent in the extraction of 2-propanol from
20 water at different temperatures. For that reason, the primary purpose of this work is to
21 determine the liquid-liquid-solid (L+L+S) phase equilibrium of the water + 2-propanol +1-
22 undecanol ternary system. In the narrow temperature range studied, from 275.15 to 288.15 K,
23 the water + 2-propanol + 1-undecanol mixtures form different phases, included the solid one,
24 since the melting point of the undecanol (292 K) is relatively high. This particularity can be
25 useful for designing separation sequences.

26 On the other hand, this study is a continuation of previous works done on L+L+S
27 equilibrium in ternary systems with heavy alcohols [8, 9], which includes experimental results
28 for the water + ethanol + 1-undecanol ternary system [10], which will be compared with those
29 of the system with 2-propanol. These data can be used to do a preliminary review of the
30 viability of using 1-undecanol to extract alcohols from water.

31

2. Experimental Section

2.1. Chemicals

All chemicals used in the experiments are listed in Table 1 and they were used as supplied by the provider without further treatment after the chromatographic analysis failed to show significant impurities. The Karl-Fischer titration method was used to determine the water content of the chemicals. Ethanol was added as the internal standard for the chromatographic analysis to prevent phase split during the analysis. De-ionized water from a Nanopure Barnstead ultrapure system was used.

Table 1. Specifications of chemical compounds.

Chemical	Provider	Initial purity (mass %)	Water content (mass %)	Purification method	Analysis method
1-Undecanol	Merck	> 98.0	0.10	none	GC ^a
2-Propanol	Merck	> 99.9	0.05	none	GC ^a
Ethanol	Merck	> 99.9	0.10	none	GC ^a

^a GC = Gas chromatography

2.2. Experimental procedure

The equipment used and the procedure for the determination of liquid-liquid data has been described in a previous paper [10]. First of all, the mass of 1-undecanol was measured into each of the test tubes and this was stored in the fridge. Once this was frozen, a known mixture of water and propanol was added into the tubes. As shown in the previous paper, this procedure has been developed to prevent the formation of a gel that cannot be easily separated. The mixtures were placed in a thermostatic bath (TECTRON 200 from SELECTA) and allowed to settle until separation is reached. The accuracy of the temperature measurements was ± 0.1 K (measured with a calibrated thermometer). Once the equilibrium was reached, samples were taken from both phases and analyzed by gas chromatography using ethanol as the internal standard. The water and 2-propanol content was analyzed in a Shimadzu GC-14A, equipped with a thermal conductivity detector (TCD). In addition, the water concentration of the organic phase was checked by Karl Fischer titration (Metrohm 737 KF Coulometer). In the organic phase, 1-undecanol (majority component) was inferred by difference. However, 1-undecanol in the aqueous phase was analyzed with a flame ionization detector (FID) in a Thermo Trace Fischer gas chromatograph.

The relative uncertainty of the mass fraction measurements was estimated at 2% for all components. A data reconciliation method [11] was used to check and fit experimental liquid-

1 liquid equilibrium data. To satisfy the material balances between the organic phase, the
 2 aqueous phase and the weighed mixture, the reconciliation method slightly changes the
 3 analytical concentrations within the interval given by the uncertainties.

4 3. Results and Discussion

5 3.1. Experimental data

6 Tables 2-4 display the experimental mass fraction compositions of aqueous and organic
 7 phases at different temperatures. The resulting phase diagrams for temperatures of 288.15,
 8 281.15, and 275.15 K are displayed in Figure 1, Figure 2, and Figure 3, respectively. The
 9 phases observed in the different regions are represented by L for liquid and S for solid. The
 10 initial compositions, or global mixture, are shown on the tie lines for reference. In the same
 11 Figures, the equilibrium diagrams for the water + ethanol + 1-undecanol system are presented
 12 for comparison.

13 3.1.1. Phase equilibrium at 288.15 K

14 At this temperature, two liquid phases were observed in the heterogeneous region. The
 15 L+L equilibrium phase diagram shows two completely miscible liquid pairs and one partially
 16 miscible liquid pair (water + 1-undecanol). Consequently, the ternary system studied exhibits
 17 type-1 of the L+L equilibrium behaviour [12]. It can be seen that the plait-point position is
 18 asymmetrical. Moreover, only when there is more than 30 wt % of isopropanol in the aqueous
 19 phase does the undecanol content in that phase increase significantly.

21 **Table 2.** Experimental (Liquid – Liquid) Equilibrium Data for the water (1) + 2-propanol (2) + 1-undecanol (3)
 22 system for mass fractions x at 101.3 kPa and the Temperature $T = 288.15 \text{ K}^a$.

Aqueous phase			Organic phase		
x_1	x_2	x_3	x_1	x_2	x_3
1.000	0.000	0.000	0.035	0.000	0.965
0.942	0.058	0.000	0.040	0.031	0.929
0.872	0.127	0.000	0.052	0.122	0.826
0.828	0.171	0.001	0.062	0.189	0.748
0.796	0.204	0.001	0.089	0.261	0.651
0.755	0.245	0.001	0.127	0.346	0.527
0.723	0.275	0.003	0.183	0.412	0.405
0.649	0.330	0.021	0.288	0.450	0.262
0.558	0.398	0.044	0.396	0.451	0.154

23 ^a Standard uncertainties u are $u(T) = 0.1 \text{ K}$, and relative uncertainty u_r is $u_r(x) = \frac{u(x)}{x} = 0.02$

1 3.1.2. Phase equilibrium at 281.15 K

2 At this temperature, solid phases are present in the ternary mixture. The equilibrium
3 diagram presents four heterogeneous regions: a large region with two liquid phases (L+L) and
4 three other small regions, the first one with three phases (liquid-liquid-solid, L+L+S) and the
5 others with two phases (L+S), similar to the water + ethanol + 1-undecanol ternary at the same
6 temperature.

7
8 **Table 3.** Experimental (Liquid - Liquid) Equilibrium Data for the water (1) + 2-propanol (2) + 1-undecanol (3)
9 system for mass fractions x at 101.3 kPa and the Temperature $T = 281.15 \text{ K}^a$.

Aqueous phase			Organic phase		
x_1	x_2	x_3	x_1	x_2	x_3
<i>One liquid phase + one solid phase (1-undecanol)</i>					
1.000	0.000	0.000			
0.963	0.037	0.000			
0.933	0.067	0.000			
<i>Two liquid phases + one liquid phase (1-undecanol)</i>					
0.884	0.116	0.000	0.050	0.090	0.859
<i>Two liquid phases</i>					
0.868	0.132	0.000	0.048	0.106	0.846
0.821	0.179	0.000	0.060	0.172	0.768
0.783	0.217	0.000	0.086	0.265	0.649
0.763	0.236	0.000	0.108	0.317	0.575
0.713	0.283	0.004	0.183	0.417	0.400
0.660	0.325	0.015	0.217	0.455	0.328
0.624	0.360	0.016	0.284	0.461	0.255

10 ^a Standard uncertainties u are $u(T) = 0.1 \text{ K}$, and relative uncertainty u_r is $u_r(x) = \frac{u(x)}{x} = 0.02$

11
12 3.1.3. Phase equilibrium at 275.15 K

13 As expected, as the temperature decreases, the coverage for solid undecanol phase
14 appearance increases. At this temperature, the L+S and the L+L+S regions become larger. In
15 contrast, the whole heterogeneous region (including, L+S, L+L+S and L+L regions) is not very
16 sensitive with temperature and therefore the top of the heterogeneous region does not vary very
17 much.

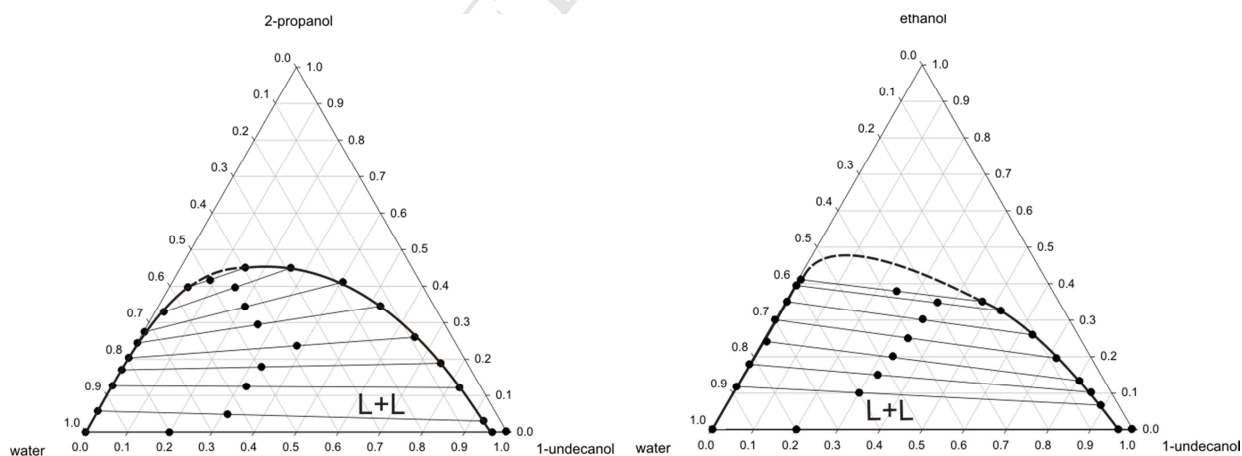
1 **Table 4.** Experimental Equilibrium Data for the water (1) + 2-propanol (2) + 1-undecanol (3) system for mass
 2 fractions x at 101.3 kPa and the Temperature $T = 275.15$ K^a.

Aqueous phase			Organic phase		
x_1	x_2	x_3	x_1	x_2	x_3
<i>One liquid phase + one solid phase (1-undecanol)</i>					
0.921	0.079	0.000			
<i>Two liquid phases + one liquid phase (1-undecanol)</i>					
0.818	0.182	0.000	0.092	0.273	0.635
<i>Two liquid phases</i>					
0.776	0.224	0.000	0.097	0.288	0.616
0.731	0.269	0.001	0.132	0.363	0.505
0.707	0.291	0.002	0.190	0.422	0.388
0.673	0.317	0.010	0.243	0.451	0.305
0.569	0.385	0.046	0.345	0.453	0.201

3 ^a Standard uncertainties u are $u(T) = 0.1$ K, and relative uncertainty u_r is $u_r(x) = \frac{u(x)}{x} = 0.02$

3.1.4. Comparison with the water + ethanol + 1-undecanol system

6 The system studied at 288.15 K closely resembles the water + ethanol + 1-undecanol
 7 system at this same temperature. These are shown side by side in Figure 1 for clarity.



10 **Figure 1.** Phase diagrams comparison at 288.15 K.

12 At this temperature the system is below the melting point of the undecanol but there is
 13 only a very small solid region in these systems. As can be seen, the slope of the tie lines is
 14 different in both systems. In fact, in the 2-propanol system the slopes of the tie lines change
 15 their orientation so it is a solutropic system.

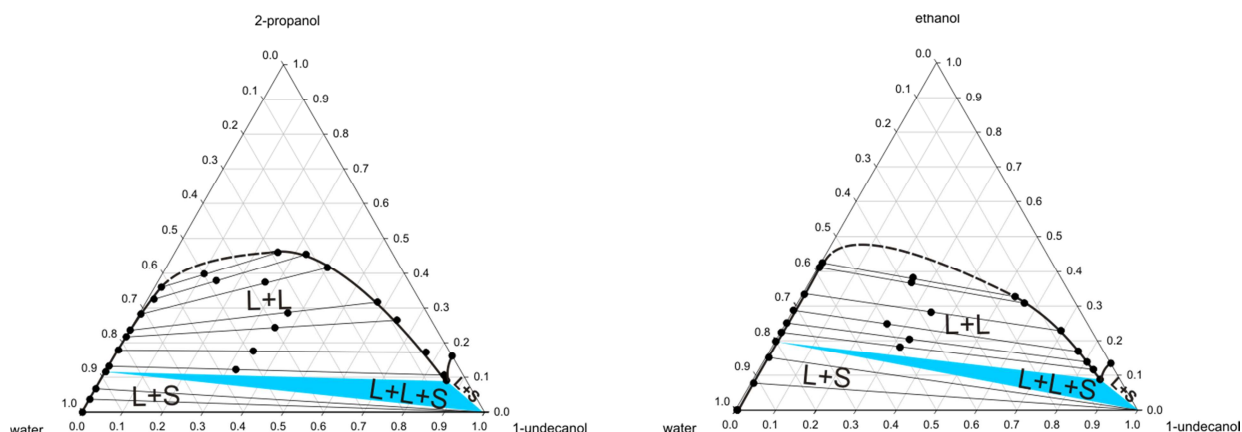


Figure 2. Phase diagrams comparison at 281.15 K.

At 281.15 K, as shown in Figure 2, the ethanol system has a larger L+S region at the same temperature when compared to the propanol results and moves the three-phase region upwards. As a consequence, the two-liquid region in the ternary water + ethanol + 1-undecanol system is smaller.

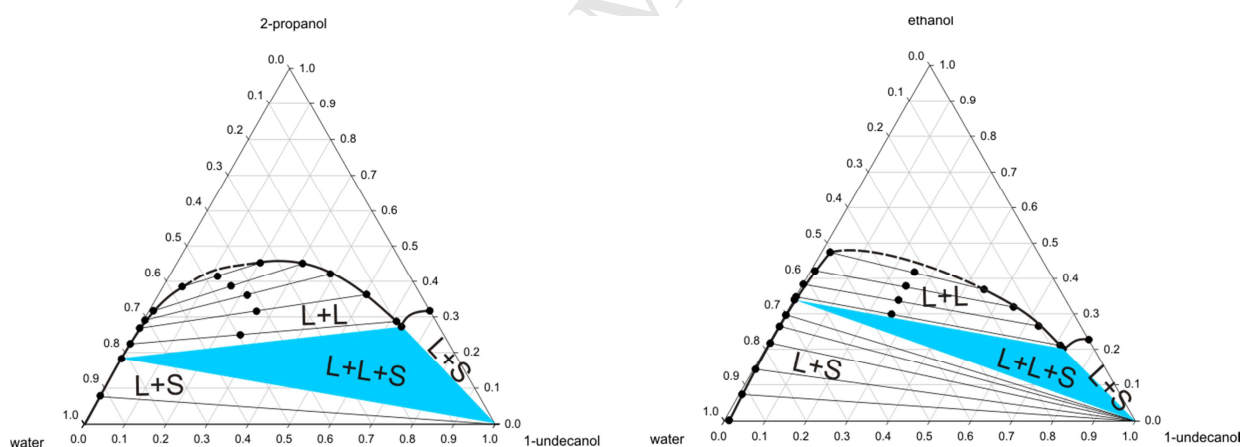


Figure 3. Phase diagrams comparison at 275.15 K.

Finally, the binodal curve is similar in shape for the two systems at this temperature but the plait-point is oriented towards an opposite direction as shown in Figure 3. The ternary water + ethanol + 1-undecanol system presents smaller L+L and L+L+S regions and, in contrast, a larger L+S region at the bottom.

3.2. Experimental data correlation at 288.15 K

These experimental data obtained at 288.15 K were correlated using the UNIQUAC thermodynamic model. The process simulator CHEMCAD 6 was used to perform the correlation, and the regression parameters sets obtained as well as the deviations are collected in Table 5. The composition mean deviations are the mean of the differences between the experimental composition of one component in one phase and the calculated data. Furthermore, plotted together in Figure 4 are the experimental binodal curve, those calculated using UNIQUAC and the curve predicted by UNIFAC LLE (with parameters from the CHEMCAD database). As can be seen, the UNIQUAC model reproduces reasonable well the binodal curve but the slope of the tie lines differs from the experimental ones. However, the UNIFAC models do not agree well with the obtained data.

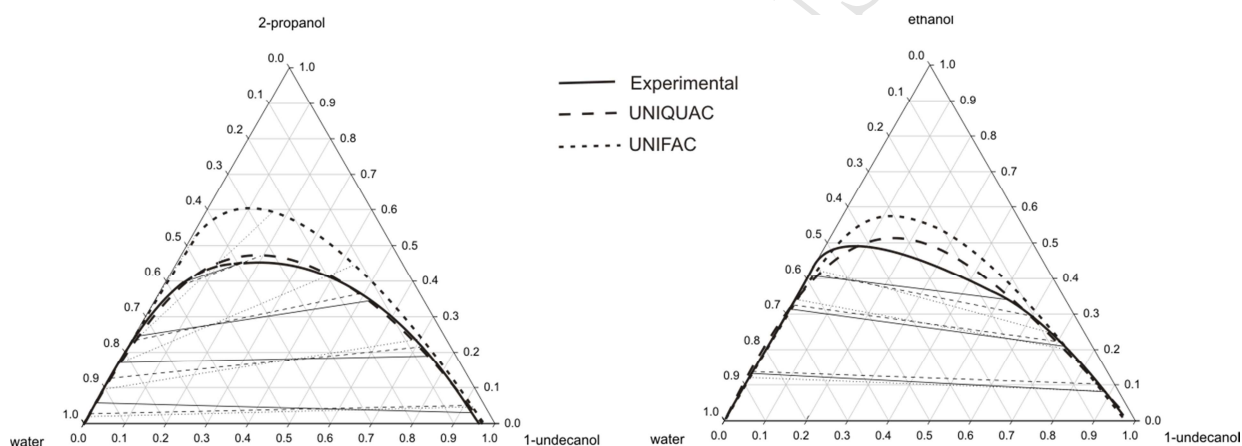


Figure 4. Comparison of the LLE correlations for mass fractions.

Table 5. Parameters and mean deviations of the LLE correlation. U_{ij} - U_{ii} binary interaction parameters for UNIQUAC (K). Mean deviations of mass fractions of water (1) and propanol/ethanol (2) in organic phase (1) and aqueous phase (2).

i	j	U_{ij} - U_{ii}	U_{ii} - U_{ii}
water	2-propanol	-49.57	-42.99
water	1-undecanol	138.81	274.54
2-propanol	1-undecanol	734.98	-474.01
$D_{-x_{11}}$	$D_{-x_{12}}$	$D_{-x_{21}}$	$D_{-x_{22}}$
0.0144	0.0131	0.021	0.0102
i	j	U_{ij} - U_{ii}	U_{ii} - U_{ii}
water	ethanol	-293.5930	-136.3002
water	1-undecanol	288.4441	195.6909
ethanol	1-undecanol	-243.6891	-146.9725
$D_{-x_{11}}$	$D_{-x_{12}}$	$D_{-x_{21}}$	$D_{-x_{22}}$
0.0716	0.0382	0.0732	0.0365

3.3. Study of the capability of 1-undecanol as a solvent at 288.15 K

A study was made of the capability of 1-undecanol as a solvent in the separation of the water + propanol system by liquid-liquid extraction. The size of the heterogeneous zone and its shape is adequate, so 1-undecanol can be considered as a relatively good solvent.

Industrial purposes usually require distribution coefficient values higher than 0.2 and separation factors higher than 10 [5]. Taking this into account, 1-undecanol may be a suitable entrainer for isopropanol dehydration, as seen in Table 6. In this Table the distribution coefficient and the selectivity have been calculated for the increasing amount of solvent (2-propanol and ethanol). To facilitate interpretation, these coefficients have been represented in Figure 5.

Table 6. Distribution (K_s) and selectivity (S) coefficients for the water (1) + 2-propanol (2) + 1-undecanol (3) system and water (1) + ethanol (2) + 1-undecanol (3) system calculated at 288.15 K. OP = organic phase, AP = aqueous phase

2-Propanol			Ethanol		
$x_{2,AP}$	K_s	S	$x_{2,AP}$	K_s	S
	$x_{2,OP}/x_{2,AP}$	$\frac{(x_2/x_1)_{OP}}{(x_2/x_1)_{AP}}$		$x_{2,OP}/x_{2,AP}$	$\frac{(x_2/x_1)_{OP}}{(x_2/x_1)_{AP}}$
0.942	0.53	12.56	0.117	0.56	11.91
0.872	0.96	16.25	0.179	0.56	9.30
0.828	1.11	14.73	0.241	0.55	6.91
0.796	1.28	11.48	0.300	0.65	5.61
0.755	1.41	8.39	0.350	0.74	4.44
0.723	1.50	5.90	0.395	0.82	3.18
0.649	1.36	3.08	0.411	0.85	2.85
0.558	1.13	1.60			

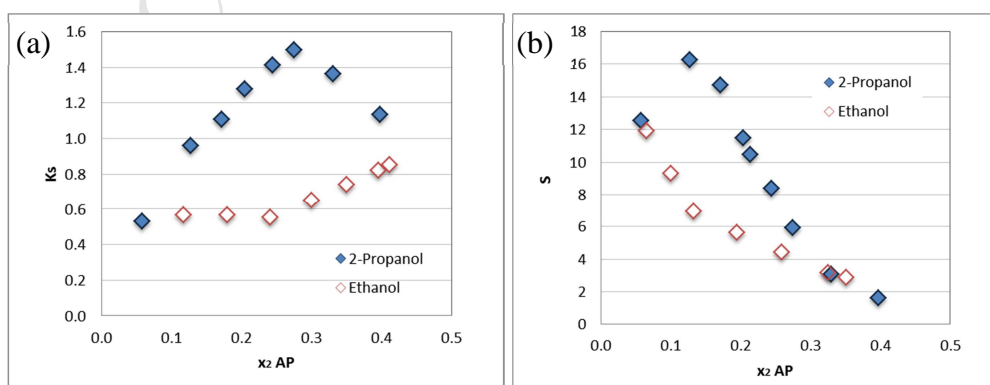


Figure 5. Distribution (a) and selectivity (b) coefficient for the water + 2-propanol + 1-undecanol system and water + ethanol + 1-undecanol system calculated at 288.15 K.

1 As can be seen, the distribution coefficient is higher than 0.2 and the selectivity is
2 higher than 10 for low concentrations of alcohol. Furthermore, these parameters are higher for
3 the 2-propanol system. Therefore, 1-undecanol can be a suitable extraction agent for both
4 solvents but it could be better, at first glance, for 2-propanol.

6 **4. Conclusions**

7 To analyse the ability to separate systems such as alcohols and water, it is necessary to
8 know the phase equilibrium behaviour of the ternary systems. Furthermore, to have reliable
9 experimental data is a critical step in future process design development.

10 In this research, the determination of the equilibrium phases for the water + propanol +
11 1-undecanol system was carried out at three different temperatures, 275.15, 281.15 and 288.15
12 K.

13 At 288.15 K, there were only two liquid phases observed in the heterogeneous region.
14 However, at 281.15 K, solid phases are present in the ternary system. A region of two liquids, a
15 region of one solid and a liquid and a small region of two liquids and one solid were observed.
16 The same regions appear at 275.15 K but the regions that have a solid were broader.

17 In comparison with the water + ethanol + 1-undecanol system previously determined,
18 it was observed that the phase diagrams are very closely similar to the system studied at the
19 same temperatures.

20 In order to study the viability of 1-undecanol for the water + 2-propanol liquid-liquid
21 extraction, the capability of 1-undecanol as a solvent was assessed through the distribution and
22 selectivity coefficients at 288.15 K. It can be concluded that 1-undecanol can be considered a
23 suitable solvent for the separation of the water + 2-propanol mixture.

25 **Acknowledgements**

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