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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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ABSTRACT

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

1. Introduction

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

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

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

Liquid–liquid extraction requires reliable multicomponent phase equilibrium data to design and optimise the separation process. In this sense, the aim of the research was to determine the viability of using 1-undecanol as a solvent in the extraction of 2-propanol from water at different temperatures. For that reason, the primary purpose of this work is to determine the liquid-liquid-solid (L + L + S) phase equilibrium of the water + 2-propanol +1-undecanol ternary system. In the narrow temperature range studied, from 275.15 to 288.15 K, the water + 2-propanol + 1-undecanol

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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.

Table 2
Experimental (Liquid – Liquid) Equilibrium Data for the water (1) + 2-propanol (2) + 1-undecanol (3) system for mass fractions x at 101.3 kPa and temperature T = 288.15 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

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

mixtures form different phases, included the solid one, since the melting point of the undecanol (292 K) is relatively high. This particularity can be useful for designing separation sequences.

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

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 3
Experimental (Liquid - Liquid) Equilibrium Data for the water (1) + 2-propanol (2) + 1-undecanol (3) system for mass fractions x at 101.3 kPa and temperature T = 281.15 K.[a]

Aqueous phase			Organic phase		
x_1	x_2	x_3	x_1	x_2	x_3
One liquid phase + one solid phase (1-undecanol)					
1.000	0.000	0.000			
0.963	0.037	0.000			
0.933	0.067	0.000			
Two liquid phases + one liquid phase (1-undecanol)					
0.884	0.116	0.000	0.050	0.090	0.859
Two liquid phases					
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

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

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

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

Aqueous phase			Organic phase		
x_1	x_2	x_3	x_1	x_2	x_3
One liquid phase + one solid phase (1-undecanol)					
0.921	0.079	0.000			
Two liquid phases + one liquid phase (1-undecanol)					
0.818	0.182	0.000	0.092	0.273	0.635
Two liquid phases					
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

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

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