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Separation of Alcohols from *n*-Tetradecane Using 1-Ethyl-3-methylimidazolium Hydrogensulfate

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Abstract: Extraction of alcohols from *n*-tetradecane using various extraction solvents has been investigated at a range of temperatures from 295 to 393 K under ambient pressure. On the basis of the experimental liquid–liquid equilibrium data, the distribution ratio and selectivity were calculated for the extraction of 1-octanol, 1-decanol, and 1-dodecanol (C_8–C_{12}) in 1-ethyl-3-methylimidazolium hydrogensulfate [C_2mim][HSO_4] and sulfolane. Results showed that moderate selectivities were obtained in sulfolane with very low distribution coefficients. In contrast, [C_2mim][HSO_4] showed similar selectivity values with higher distribution coefficients. A study of a number of different 1-alcohols (C_4–C_{12}) showed that the decrease in hydrogen bonding compared to the increased van der Waals interactions between *n*-tetradecane and the higher-chain alcohols decreased the extraction selectivity in [C_2mim][HSO_4]. Increasing the temperature of the ionic liquid extraction medium resulted in increased chemical extraction for 1-butanol and 1-hexanol due to the formation of the corresponding alkylsulfate ionic liquid. In contrast, the selectivity decreased for 1-octanol, 1-decanol and 1-dodecanol due to the partial dissolution of the corresponding alkylsulfate ionic liquid into the *n*-tetradecane phase.

Keywords: ionic liquids; extraction; liquid–liquid equilibrium; *n*-tetradecane; alcohols

1. Introduction

Detergent alcohols with carbon numbers ranging between 8 and 12 are synthetically produced via the Oxo or the Ziegler processes [1,2]. Within this process, a feedstock containing an olefin/paraffin mixture undergoes hydroformylation, producing a mixture of paraffins and the corresponding product alcohols with one more carbon. For detergent-range alcohols, the product stream typically contains a mixture of C_{11}–C_{14} paraffins and the C_{12}–C_{15} analogous alcohol products. Therein, the two compounds most difficult to separate are *n*-tetradecane and 1-dodecanol as their boiling points differ by only 10 K [3]. Azeotropic distillation provides satisfactory separation of these compounds; however, extreme operating conditions using low vacuum pressure and high temperatures, as well as specific entrainers are required [4].

As an alternative, liquid–liquid extraction takes place at lower temperatures and ambient pressure and therefore some economic issues related to the energy consumption are negated. The conventional extraction solvents used in industry for olefin/paraffin separation [5] are solvents such as sulfolane [6] which, due to their generally volatility, toxicity and/or flammable nature, require further capital investment and energy for their recovery. More recently, γ-valerolactone has also been reported as a potential extractant

of polar oxygenated solutes (i.e., light alcohols and carboxylic acids) from their mixture with *n*-tetradecane [7]. However, to date, under ambient conditions, no solvent has been implemented for the separation of detergent alcohols from alkanes. Supercritical solvents have been suggested as an alternative technology, with differences in phase equilibria existing for detergent alcohols and their analogous alkane counterparts in both supercritical carbon dioxide and supercritical alkanes [8–12].

Ionic liquids have also emerged as an alternative technology for liquid–liquid separation, as their use under ambient pressure and moderate temperatures and potential recyclability could result in less energy intensive processes [13,14]. Ionic liquids have already demonstrated their high separation efficiencies in similar fields. For example, ethanol separation from *n*-hexane and *n*-heptane has been conducted using a range of alkylammonium-ionic liquids [15,16] and alkylimidazolium-ionic liquids [17]. In addition, methanol separation from alkanes has also been studied by Marciniak et al. [18] using cyclic alkylammonium bis(trifluoromethylsulfonyl)amide ionic liquids and using dialkylphosphate-based ionic liquids [19,20]. Aliphatic/aromatic separation using tetrafluoroborate-based ionic liquids has also been studied [21]. In all cases, regardless of the ionic liquid used, excellent selectivities along with good distribution ratios were achieved.

However, surprisingly no feasible ionic liquid processes are available for the extraction of detergent alcohols from paraffin mixtures, to date. Consequently, the aim of this communication is to explore the influence of an ionic liquid on the selectivity and distribution ratio for the aliphatic alcohols from *n*-tetradecane.

2. Materials and Methods

2.1. Chemicals

n-Tetradecane ($\geq$99%), C_4–C_{12} alcohols ($\geq$98%) and sulfolane (99%) were purchased from Sigma-Aldrich and were dried over 3 Å molecular sieves. Materials for the synthesis of the IL (N-methylimidazole (99%) and dimethyl sulfate (99%) were used as received. Toluene (analytical grade) was supplied by Riedel de Hann. The ionic liquid 1-ethyl-3- methylimidazolium hydrogensulfate [C_2mim][HSO_4] ($\geq$97.0 wt.%) was obtained via synthesis from N-methylimidazole, see Section 2.2. The same IL was also purchased from BASF and both samples were dried under high vacuum (2.3×10^{-3} mbar) at 363 K for 2 days. This commercial IL was solely used therein to verify the purity of the homologue in-house made IL.

2.2. Synthesis of 1-Ethyl-3-methylimidazolium Hydrogensulfate

Diethylsulfate (0.2 mol) dissolved in anhydrous toluene (50 mL) was added slowly dropwise over a period of 1 h to a pre-cooled solution of N-methylimidazole (0.2 mol) in anhydrous toluene (150 mL). The mixture was continually cooled in an ice-bath under nitrogen taking care to maintain the reaction temperature below 298 K. After complete addition of diethylsulfate, the reaction mixture was then stirred at room temperature for 4 h. The upper organic phase of the resulting mixture was decanted, and the lower ionic liquid phase was washed with ethyl acetate (3 × 20 mL). After washing, the remaining solvents were removed by heating under reduced pressure. The IL was obtained with more than 98% of purity. Its structure was confirmed by comparison of ^{1}H NMR available in the literature [22].

The ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate, [C_2mim][$EtSO_4$], was then hydrolyzed to the corresponding hydrogensulfate analogue via the following procedure. The ionic liquid (0.15 mol) was placed in flask along with 30 mL of deionized water (18.2 MΩ). The mixture was then heated at 353 K under ambient pressure for 24 h. After hydrolysis had occurred the majority water was removed by rotary evaporation. The ionic liquid was then further dried under high vacuum (2.3×10^{-3} mbar) at 363 K for 2 days. The water content of the ionic liquid was deemed to be <300 ppm by Karl Fischer titration. Its structure was confirmed by comparison of ^{1}H and ^{13}C NMR spectra (see Figures S1 and S2 of the Supplementary Materials) with the commercially available IL [23,24].

$[C_2mim][EtSO_4]$: ^{1}H NMR (300 MHz, DMSO, ppm): 8.78 [s, 1 H, H-2], 7.56 [s, 1 H, H-4], 7.47 [s, 1 H, H-5], 4.28 [q, J = 7.37 Hz, 2 H, NCH_2CH_3], 4.19 [q, J = 7.12 Hz, 2 H, OCH_2CH_3], 3.93 [s, 3 H, NCH_3], 1.56 [t, J = 7.34 Hz, 3 H, NCH_2CH_3], 1.39 [t, J = 7.12 Hz, 3 H, OCH_2CH_3].
$[C_2mim][HSO_4]$: ^{1}H NMR (300 MHz, DMSO, ppm): 9.14 [s, 1 H, H-2], 7.79 [s, 1 H, H-4], 7.70 [s, 1 H, H-5], 4.18 [q, J = 7.32 Hz, 2 H, NCH_2CH_3], 3.84 [s, 3 H, NCH_3], 1.41 [t, J = 7.28 Hz, 3 H, NCH_2CH_3]. ^{13}C NMR (75 MHz, DMSO, ppm): 136.35 [s, C-2], 123.59 [s, C-4], 122.00 [s, C-5], 44.12 [s, NCH_2CH_3], 35.70 [s, NCH_3], 15.16 [s, NCH_2CH_3].

2.3. Experimental Procedure

The LLE runs were carried out in 15 cm^3 vials with screw caps providing hermetic sealing. 1-Alcohol/*n*-tetradecane feeds with a 1:1 molar composition was transferred to the vials. After reweighing the vials, the extracting solvent 1.5 cm^3 (sulfolane or ionic liquid) was added to the feed. The vials were then rapidly stirred at 1000 rpm between 298–373 K overnight to reach thermodynamic equilibrium. The set temperature ($\pm$0.5 K) was controlled using a standard Pt 100 Ω resistance thermometer with a precision of $\pm$0.1 K and an accuracy of $\pm$0.5 K. Finally, they were left to cool to ambient temperature if required and centrifuged using an Eppendorf 5702 at 2000 rpm for 10 min. Samples from the lower extractant phase and upper *n*-tetradecane phases were analyzed by a Bruker Avance 300 MHz NMR Spectrometer. Samples of each phase were taken and analyzed neat within the NMR tubes using a d$_6$-DMSO filled capillary within a repeatability of $\pm$0.001 in mole fraction units while the maximum error was found to be $\pm$0.005 in mole fraction units.

Binary mixtures were conducted in a similar fashion, with 1 cm^3 of ionic liquid or sulfolane and 1cm^3 of each alcohol were contacted and left to reach equilibrium overnight. Due to the possible solidification of sulfolane the LLE binary mixture experiments were conducted at 308 K ($\pm$0.5 K). In these experiments, the upper and lower phases were analyzed by ^{1}H-NMR using CDCl$_3$ and d$_6$-DMSO, respectively. Representative NMR data from LLE experiments using 1-butanol and 1-decanol are shown in the Supplementary Materials, Figures S3–S6.

3. Results

The hydrophilic ionic liquid 1-ethyl-3-methylimidazolium hydrogensulfate $[C_2mim][HSO_4]$ was selected on the basis of price, commercial availability and its lower toxicity than other aprotic ionic liquids [25–28]. The alcohols ranging from C$_4$–C$_{12}$ are completely miscible with *n*-tetradecane under the experimental conditions employed. In addition $[C_2mim][HSO_4]$ and sulfolane (TMS) are almost completely immiscible with *n*-tetradecane under the experimental conditions as analyzed by ^{1}H NMR. Therein, the mole fraction, (x_{IL} or x_{TMS}) was <0.005 in the tetradecane phase. The binary experimental LLE data for the maximum solubility of alcohol in ionic liquid and sulfolane at 303 K is shown in Table 1. A temperature of 303 K was chosen to be slightly above the melting point (300 K) of sulfolane.

Unsurprisingly, the hydrophilic alcohol, 1-butanol is widely soluble in both the ionic liquid and mutually soluble in sulfolane as both these solvents are considered polar. As the carbon chain increases to C$_6$ and above these alcohols become increasingly hydrophobic resulting in significant changes in solubility. While significant amounts of sulfolane are solubilized in the alcohol phase, no IL was detectable by ^{1}H-NMR in any of the alcohol phases regardless of the alcohol chain length.

The experimental LLE data for the ternary system containing *n*-tetradecane (1), 1-alcohol (2) and extracting solvent (4) at 295 K are given in Table 2. A temperature of 295 K could be adopted as the binary experiments showed that solidification would not be problematic due to the alcohol solubility in the sulfolane phase.

Table 1. Mutual miscibility expressed in mole fraction units of selected 1-alcohols (Alc.) with 1-ethyl-3-methylimidazolium hydrogensulfate [C_2mim][HSO_4] or with sulfolane (TMS) at 303 K and at 101 kPa [a].

Alcohol	IL System *		Sulfolane System			
	IL Phase		Sulfolane Phase		Alcohol Phase	
	x_{IL}	$x_{Alc.}$	x_{TMS}	$x_{Alc.}$	x_{TMS}	$x_{Alc.}$
1-butanol (C_4)	0.631	0.369	∞	∞	∞	∞
1-hexanol (C_6)	0.956	0.044	0.901	0.099	0.045	0.955
1-octanol (C_8)	0.968	0.032	0.926	0.074	0.203	0.797
1-decanol (C_{10})	0.977	0.023	0.943	0.057	0.242	0.758
1-dodecanol (C_{12})	0.987	0.013	0.980	0.020	0.174	0.826

* No IL was detectable by ^{1}H-NMR in the upper alcohol phase. [a] u(x_i) = 0.005; u(T) = 0.5 K; u(p) = 2 kPa.

Table 2. Solubility (mole fraction), selectivity (S) and distribution ratios (D) for detergent alcohol/n-tetradecane mixtures contacted with extraction solvents sulfolane and ionic liquid [C_2mim][HSO_4] at 295 K and at 101 kPa [a].

Extractant	Alcohols	Extractant Phase (Lower Layer)			n-Tetradecane Phase (Upper Layer)			Dist.	Select.
	C_nOH	x_1 II	x_2 II	x_3 II	x_1 I	x_2 I	x_3 I	D	S
Sulfolane	C_8	0.025	0.020	0.955	0.537	0.463	0	0.043	0.928
	C_{10}	0.006	0.013	0.981	0.508	0.492	0	0.026	2.237
	C_{12}	0.004	0.023	0.973	0.510	0.490	0	0.047	5.985
[C_2mim][HSO_4]	C_8	0.062	0.109	0.829	0.537	0.463	0	0.235	2.039
	C_{10}	0.051	0.099	0.850	0.523	0.477	0	0.207	2.120
	C_{12}	0.056	0.087	0.857	0.509	0.491	0	0.177	3.387

[a] u(x_i) = 0.005; u(T) = 0.5 K; u(p) = 2 kPa. I and II correspond to the upper and lower phases.

After the analysis of ^{1}H-NMR data, the distribution and selectivity of the alcohols in the extractant phase are determined.

For the distribution, the formula is:

$$D = \frac{x_2^{II}}{x_2^{I}} \tag{1}$$

Additionally, for the selectivity, the formula is:

$$S = \frac{x_2^{II} * x_1^{I}}{x_2^{I} * x_1^{II}} \tag{2}$$

where x is the molar fraction, superscripts *I* and *II* refer to the n-tetradecane-rich and ionic liquid-rich phases, and subscripts 1 and 2 refer to n-tetradecane and 1-alcohol, respectively.

Initially, we focused on the extraction of the C_8–C_{12} detergent alcohols from sulfolane and the ionic liquid.

Table 2 summarizes the effects of the solvent extraction on alcohol distribution ratio and selectivity. The results with the ionic liquid are compared with those of sulfolane which was used as a benchmark for this comparison. It is important to highlight that no degradation of the sulfolane nor the ionic liquid was observed during our measurements set at 295 K. As can be seen from Table 2, it was found that the upper layers (n-tetradecane-rich phase) are free of all extraction solvents and that the detergent alcohols have a much higher affinity for the n-tetradecane phase compared to the extractant phase. With the exception

of 1-octanol, the distribution coefficients for the detergent alcohols are all higher in the IL compared to sulfolane; however, their selectivities are lower.

To improve the distribution and selectivity values in the IL extraction procedure the analogous reactions were conducted at 393 K. In addition to the detergent alcohols, 1-butanol (C_4) and 1-hexanol (C_6) alcohols were also used to probe the mechanism of the extraction at the various temperatures. Hydrogensulfate-based ILs are known to undergo transesterification reactions (Equation (1)) in the presence of alcohols at elevated temperatures forming new alkylsulfate ionic liquids as highlighted in Equation (3) [23,24]:

$$IL\ HSO_4 + C_nOH + C_{14} \leftrightarrow\ IL\ C_nSO_4 + C_{14} + H_2O \qquad (3)$$

The impact of forming a new alkylsulfate based-ionic liquid could prove appealing; the ability to achieve a higher extraction selectivity if the alcohol is covalently tagged to the ionic liquid.

For the reactions conducted at temperature, i.e., where the new chemically bound alcohol is formed a new set of equations were adopted.

For the distribution, the formula is:

$$D\ =\ \frac{\left(x_2^{II} + x_3^{II}\right)}{\left(x_2^I + x_3^I\right)} \qquad (4)$$

Additionally, for the selectivity, the formula is:

$$S\ =\ \frac{\left(x_2^{II} + x_3^{II}\right)\ *\ x_1^I}{\left(x_2^I + x_2^I\right)\ *\ x_1^{II}} \qquad (5)$$

Therein, experiments were conducted using 1:1 molar feeds of alcohol/alkane mixtures at 393 K. The experimental LLE data for the system *n*-tetradecane (1), 1-alcohol (2), alcohol–ionic liquid adduct (3) and ionic liquid (4) at 295 and 393 K are given in Table 3.

Table 3. Selectivity and distribution ratios for 1-alcohol/*n*-tetradecane mixtures contacted with 1-ethyl-3-methylimidazolium hydrogensulfate at 323 and 393 K and at 101 kPa [a].

[C_2mim] [HSO_4] Solvent	IL Rich Phase (Lower Layer)				Tetradecane-Rich Phase (Upper Layer)			Distribution	Selectivity
T	x_1^{II}	x_2^{II}	x_3^{II}	x_4^{II}	x_1^I	x_2^I	x_3^I	D	S
				C_4OH					
323 K	0.014	0.262	0.185	0.539	0.899	0.101	0	0.388	7.674
393 K	0.051	0.308	0.228	0.413	0.854	0.146	0	2.110	35.325
				C_6OH					
323 K	0.071	0.291	0	0.638	0.533	0.467	0	0.301	3.130
393 K	0.066	0.373	0.295	0.266	0.728	0.272	0	1.371	15.126
				C_8OH					
323 K	0.108	0.175	0	0.717	0.524	0.476	0	0.642	7.001
393 K	0.420	0.319	0.090	0.171	0.488	0.373	0.139	0.855	0.994
				$C_{10}OH$					
323 K	0.087	0.194	0	0.719	0.522	0.478	0	0.890	5.556
393 K	0.153	0.249	0.075	0.523	0.567	0.362	0.071	0.688	2.549
				$C_{12}OH$					
323 K	0.036	0.273	0	0.691	0.529	0.471	0	0.568	8.182
393 K	0.130	0.442	0.185	0.243	0.611	0.325	0.064	1.360	6.915

[a] u(x_i) = 0.005; u(T) = 0.5 K; u(p) = 2 kPa. [I] and [II] correspond to the upper and lower phases.

Figure 1 shows a typical ^{1}H-NMR spectrum of the lower phase containing all components. Shown in the inset, as the region of interest, one set of methylene protons (CH$_2$) in the ionic liquid (IL) at 4.25 ppm, one set for 1-butanol at 3.4 ppm (Alc) and one set for the chemically bound 1-butanol at 3.7 ppm (IL-Alc) are highlighted.
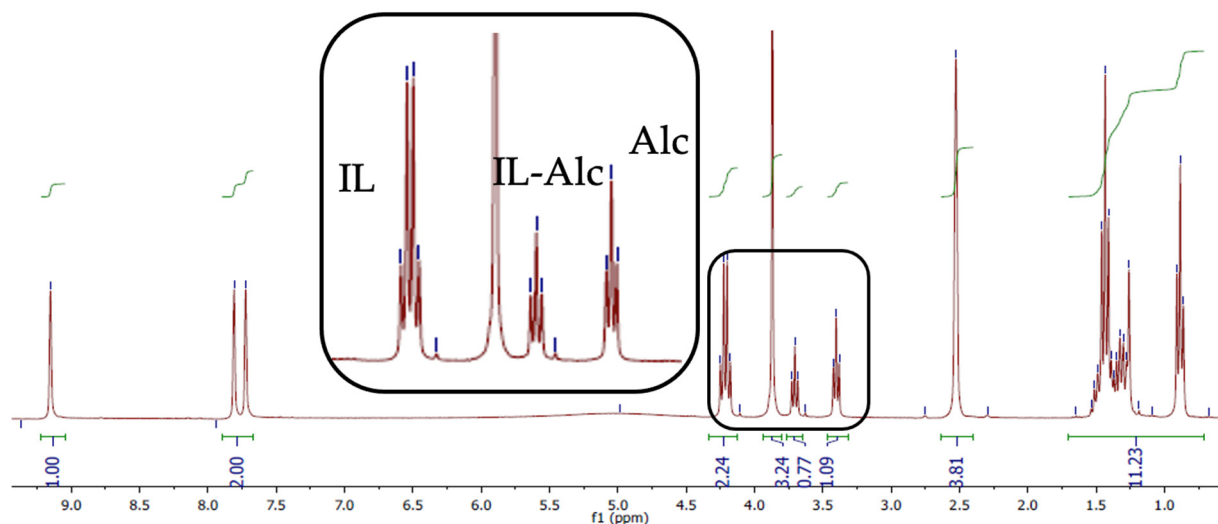

Figure 1. ^{1}H-NMR in d_6-DMSO of the lower phase after extraction of 1-butanol/*n*-tetradecane phase with ionic liquid at 393 K. Included is the expanded region of interest.

Table 3 summarizes the effects of the solvent extraction of alcohol chain length and temperature (323 and 393 K) on the distribution ratio and 1-alcohol/*n*-tetradecane selectivity.

In these experiments the reaction mixture was heated overnight and then left to cool to ambient temperature ~295 K. At 323 K, only 1-butanol reacted with the ionic liquid to form the corresponding alklysulfate-ionic liquid. However, at 393 K, all the alcohols underwent some degree of chemical reaction. With respect to the alcohol chain length, there was a crossover point in terms of both distribution and selectivity at the two temperatures studied. For example, both 1-butanol and 1-hexanol show markedly higher distribution and selectivity ratios as the temperature increased from 323 to 393 K. This was due to the increase in solubility of both the free alcohol (x_2^{II}) and the corresponding alkylsulfate-ionic liquid (x_3^{II}) in the ionic liquid phase. In addition, low/weak increase in the solubility of *n*-tetradecane (x_1^{II}) into the ionic liquid phase was recorded upon increasing the temperature coupled with the corresponding alkylsulfate-ionic liquid being below the detectable limit in the upper *n*-tetradecane phase (x_3^{I}); both factors which also helped to increase the distribution and selectivity profile.

However, for the detergent alcohols (e.g., 1-octanol, 1-decanol and 1-dodecanol), the distribution and selectivity coefficients increase upon increasing the temperature from 295 to 323 K, *c.f.* Tables 2 and 3. This is primarily due to the higher cohesive forces of the neat ionic liquid at 295 K compared to the higher temperatures. Interestingly, increasing the temperature from 323 to 393 K also results in a decrease in the selectivity. The significant increases in *n*-tetradecane (x_1^{II}) solubility in the ionic liquid phase along with the alkylsulfate-ionic liquid (x_3^{I}) also being distributed in the upper *n*-tetradecane phase seems to be responsible for this observation.

4. Discussion

The binary mixtures from Table 1 show that as the alcohol chain length increases significant decreases in solubility into the extractant phase are observed coupled with no detectable ionic liquid in any of the alcohol phases. This decrease in solubility has been previously observed for similar alcohols in a series of 1-butyl-3-methyl imidazolium ionic liquids [29], where the authors noted increases in the upper critical solution temperature

as the alcohol chain length increases. Therein, up to 2 mol% of the ionic liquid could be dissolved in the alcohol phase although hydrogensulfate-based ionic liquids were not studied. The results from Table 2 show that the capacity for the ionic liquid to have a higher affinity for the detergent alcohols compared to sulfolane could be due to the higher hydrogen bonding ability of both the imidazolium cation [30] and hydrogensulfate anion [31,32] compared to sulfolane. Nevertheless, this increase in alcohol solubility appears to be at the expense of the selectivity as the ionic liquid phase also contains more dissolved *n*-tetradecane compared to sulfolane. This is most probably due to van der Waals interactions between the detergent alcohol and *n*-tetradecane [33]. Furthermore, as highlighted in Table 3, the influence of hydrogen bonding interactions coupled with the decrease in van der Waals interactions results in higher distribution and selectivity coefficients for the lower-chain alcohols, 1-butanol and 1-hexanol, compared to the detergent alcohols 1-octanol, 1-decanol and 1-dodecanol.

Upon increasing the temperature, the formation of the alkylsulfate ionic liquid could be potentially promising as a novel chemical tag, see Table 3. This strategy of reactive extraction appears to work for both 1-butanol and 1-hexanol, where the formation of the corresponding alkylsulfate ionic liquid also increases the dissolution of the free alcohol into the ionic liquid phase. In addition, the alkylsulfate-ionic liquid partitioning into the upper phase was below the detectable limit. In comparison, the formation of alkylsulfate ionic liquids with longer alkyl chains (*n*-octyl, *n*-decyl and *n*-dodecyl) show an increase in solubility into the upper *n*-tetradecane phase, again most probably due to increased van der Waals interactions. In this regard, the solubility of 1-butyl-3-methylimidazolium octylsulfate was observed to be significantly higher than the corresponding methylsulfate ionic liquid in alkanes ranging from *n*-pentane to *n*-decane [34]. Similarly, the same authors also noted that 1-methyl-3-methylimidazolium methylsulfate resulted in a binary mixture with 1-hexanol, 1-octanol and 1-decanol. In contrast, increasing the carbon chain on the ionic liquid by only one unit resulted in complete miscibility with these three alcohols and 1-ethyl-3-methylimidazolium methylsulfate.

As highlighted in Equation (3), the role of water formed during this equilibrium reaction at 393 K also cannot be ignored. Any water formed during this reaction will almost exclusively reside in the lower hydrophilic ionic liquid phase. The presence of this excess water could be responsible for large observed increases in distribution/selectivity profiles of the partially water miscible 1-butanol (as hydrogen bonding interactions increase) while forcing out the immiscible *n*-tetradecane as relative to the hydrogen bonding, van der Waals interactions decrease. As the chain length of the alcohol increases from 1-hexanol through to 1-dodecanol the hydrophobicity also increases. Therefore, any new alkylsulfate ionic liquid that is formed during the reactive extraction (Equation (3)) is also going to be more hydrophobic in character. This increase in hydrophobicity could potentially force the alkylsulfate ionic liquid out of the ionic liquid phase into the *n*-tetradecane phase impacting on both the selectivity and distribution coefficients, as per the results from Table 3 for 1-octanol, 1-decanol and 1-dodecanol.

5. Conclusions

In this work, the liquid–liquid extraction profiles of a series 1-alcohols from *n*-tetradecane using an ionic liquid as a function of temperature are reported. Obtained results were compared to those collected using sulfolane as a benchmark solvent. Promising results were reported, especially those obtained thanks to a reactive extraction approach led by a transesterification reaction between the 1-ethyl-3-methylimidazolium hydrogensulfate and selected alcohols. Reactive extraction results clearly show relatively high selectivity in the case of 1-butanol/*n*-tetradecane or 1-hexanol/*n*-tetradecane separation. However, this approach seems to be limited when the chain length of the alcohol increases from 1-hexanol through to 1-dodecanol as the hydrophobicity and van der Waals interactions of the formed 1-ethyl-3-methylimidazolium alkylsulfate also increase leading to a higher miscibility with

n-tetradecane. However, a further hydrolysis reaction of the rich-*n*-tetradecane phase could be then used to regenerate both the IL and the alcohol.

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