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Separating 2-Propanol and Water: A Comparative Study of Extractive Distillation, Salting-Out, and Extraction

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Abstract

Separating azeotropes is an important, difficult, and expensive task, in particular for the 2-propanol–water mixture. The literature on the problem is rich in modeling studies but often lacking even the simplest experimental confirmation. In this paper, extractive distillation, liquid–liquid equilibrium-based extraction, and salting-out were experimentally tested for the desired separation. Among the four tested extractive distillation entrainers, none was able—in the investigated experimental setup—to push the system over the azeotropic composition threshold. Four novel hydrophobic deep eutectic extraction media were tested for the desired separation, and those based on menthol or thymol with decanoic acid were found most promising. Among 16 tested salting-out agents, 5 of them produced two-liquid phases, and only 4 hydrophilic inorganic salts promoted 2-propanol separation, with sodium carbonate being the most promising candidate. The purity of the products was tested with FTIR and ^{1}H-NMR. The experimental findings were compared with COSMO-RS model predictions, with moderate success.

Keywords: 2-propanol–water azeotrope; extractive distillation; liquid extraction; salting-out; deep eutectic solvents; COSMO-RS

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1. Introduction

2-Propanol (isopropanol, IPA) is an essential component in the pharmaceutical and cosmetic industries, functioning as a solvent for diverse active pharmaceutical components in medicinal formulations, a carrier for topical treatments, and a common ingredient in cosmetics, personal care items, and fragrances. Due to its capacity to dissolve various compounds, IPA serves as an efficient cleaning solvent in industrial cleaning procedures and degreasing and the electronics sector for cleaning circuit boards and components [1]. IPA is produced commercially by direct and indirect hydration of propylene [2] and hydrogenation of acetone [3,4]. The product of the aforementioned processes is a mixture of IPA and water. The formation of an azeotrope with 87.8% IPA [5] prevents the separation of the mixture through simple distillation.

The commercial processes for separating IPA and water are azeotropic or extractive distillation. In azeotropic distillation, di-isopropyl ether or cyclohexane is used as an auxiliary component, while extractive distillation is reportedly carried out with ethylene glycol

(EG) as an entrainer [6]. Both processes are energetically unfavorable, which is why the development of alternative processes for separating IPA and water is of great importance.

Various methods for the separation of IPA and water have been investigated. The separation of IPA and water has been effectively achieved using processes utilizing mass separating agents, such as heterogeneous azeotropic [7,8] and extractive distillation [9,10], salting-out [11,12], liquid–liquid extraction [13,14], pervaporation [15,16], or evapomeation [17]. To enhance energy efficiency, pressure swing distillation with heat integration [18] and azeotropic distillation within a dividing wall column [19] were investigated. Tables 1–3 provide an overview of published articles that refer to the separation methods used in this manuscript.

Table 1. Separation of 2-propanol and water by liquid–liquid extraction—overview of the recent literature data.

Entrainer	Feasibility Evaluation	Literature
1-pentanol, 1-hexanol, 1-heptanol	LLE determined experimentally, predicted with UNIFAC and COSMO-UNIFAC, and correlated with NRTL and UNIQUAC 1-Heptanol was the best entrainer, based on separation factors and partition coefficients determined	[20]
CO_2-switchable DESs (molar ratio 1:1): (MEA:BuOH), (MEA:PrOH), (MEA:2-meth), (MEA:3-meth), (MEA:4-meth) hydrophobic DESs (molar ratio 1:1): (T:DA), (DDA:DA]	Liquid–liquid extraction The best entrainer selected based on the distribution coefficient of IPA CO_2 switchable (MEA)-based DESs were better than hydrophobic ones	[21]
(M:DDA) (2:1), (M:DA) (1:1), (DA:MA) (5:1), (DA:PA) (8:1), (DA:DDA) (3:1)	LLE experimentally determined and correlated with NRTL Selectivity of all DESs was high	[5]
HBD:10-undecenoic acid HBA:carvacrol, terpineol, thymol, fenchol, DL-menthol, L-menthol HBD:HBA (1:2; 1:1; 2:1)	Experimental SLE for HDESs Liquid–liquid extraction Efficiency explained by the hydrophobicity of HBA The best HDES was one with DL-menthol as HBA The best molar ratio (HBA:HBD) was (2:1)	[22]
Trioctyl ammonium chloride: 1-hexanol Trioctyl ammonium chloride: 1-decanol	LLE experimentally determined and correlated with NRTL trioctyl ammonium chloride:1-decanol was found better, based on determined distribution ratio and separation factor	[23]
Ethyl butyrate *n*-pentyl acetate	LLE was experimentally determined and correlated with modified and extended UNIQUAC Distribution ratio and separation factor were determined	[13]

MEA—monoethanolamine; BuOH—1-butanol; PrOH—1-propanol; meth—methoxyphenol; T—thymol; DA—decanoic acid; DDA—dodecanoic acid; MA—myristic acid; PA—palmitic acid; M—menthol; HBA—hydrogen bond acceptor; HBD—hydrogen bond donor; LLE—liquid–liquid equilibria; SLE—solid–liquid equilibria; DES—deep eutectic solvent; IPA—2-propanol.

Recently, the possibility of using deep eutectic solvents (DESs) as entrainers for the separation of azeotropic mixtures was increasingly investigated due to their tunable properties. Haider et al. [5] prepared five sustainable, natural hydrophobic DESs from natural compounds to be used for IPA–water separation by liquid–liquid extraction. These DESs exhibited desirable properties, including low viscosity, high thermal stability, and significant density differences from water. Liquid–liquid equilibrium (LLE) studies confirmed their Treybal type I ternary phase diagrams with wide immiscibility ranges, indicating their potential for effective IPA extraction, with experimental data modeled using the non-random two-liquid (NRTL) thermodynamic model. Audeh et al. investigated novel hydrophobic deep eutectic solvents (HDESs) consisting of terpenes and 10-undecenoic acid for the liquid–liquid separation of alcoholic mixtures. The 2:1 molar ratio of these HDESs exhibited the best extraction efficiency, reaching up to 36.59% for IPA, with the hydrophobicity of the hydrogen bond acceptor being the main driving force. These results pointed to HDESs as promising environmentally friendly alternatives to improve alcohol–water separation processes [22]. Xu et al. [23] investigated the liquid–liquid extraction of the isopropanol–water azeotrope with two DESs prepared from methyltrioctylammonium chloride and 1-hexanol or 1-decanol. Experimental data at 298.15 K and 308.15 K confirmed the feasibility of the separation. The results were successfully fitted with the NRTL model and provided important parameters for the design and simulation of the separation process.

Lee et al. presented a novel CO_2-switchable DES (monoethanolamine–*n*-butanol) for the energy-efficient separation of IPA and water at room temperature. Its low viscosity and specific interactions enabled effective IPA separation, producing a valuable *n*-butanol–IPA mixture. This process offered a cost-effective, energy-saving, and environmentally friendly way to recycle IPA waste into potential alternative fuels [21].

Table 2. Separation of 2-propanol and water by extractive distillation—overview of the recent literature data.

Entrainer	Feasibility Evaluation	Literature
(ChCl:U:LiCl) (1:2:0.44) ($ChCl:SnCl_2$) (1:2) ($ChCl:ZnCl_2:SnCl_2$) (1:1:1) ($ChCl:U:CaCl_2$) (1:2:0.36) (U:NaI) (4:1) ($ChCl:Gly:CaCl_2$) (1:2:0.09) (ChCl:Gly:LiCl) (1:2:0.09)	Isobaric VLE was determined experimentally and correlated with NRTL Conceptual design involving partial heat integration and intermediate reboilers was developed in Aspen Plus Energy efficiency, environmental impact, and economic feasibility were evaluated ($ChCl:U:CaCl_2$) (1:2:0.36) was recommended	[24]
[EMIM][BF_4] (ChCl:Gly) (1:2) (ChCl:EG) (1:2) DMSO	Process modeling and simulation were performed in Aspen Plus VLE was calculated with NRTL A new design with a flash column for regeneration of the entrainer was developed High-purity IPA could be obtained (>99.9 mol %)	[25]
380 ILs Gly, EG, DEG, TEG, DMSO, DMF, NMP	Entrainers were selected based on the VLE and relative volatility evaluation for organic solvents Selectivity of ILs was evaluated by COSMO RS VLE was modeled with UNIFAC Process simulation with EG and [EMIM][DCA] was performed in Aspen Plus	[26]
U	Isobaric VLE was determined experimentally and correlated with NRTL 13 mol% of the entrainer was required for breaking the azeotrope	[10]
EG	Process simulation was performed in ASPEN Plus High-purity IPA could be obtained (99.974 mol %)	[9]
(ChCl:EG) (1:2; 1:4; 1:8) EG	Isobaric VLE was determined experimentally and correlated with NRTL ChCl influenced activity coefficients of H_2O and IPA DESs were found better than EG 15.7 wt% of DES was required for breaking the azeotrope	[27]

Table 2. *Cont.*

Entrainer	Feasibility Evaluation	Literature
(ChCl:Gly) (1:2) Gly	Isobaric VLE was determined experimentally and correlated with NRTL DES was found better than Gly 14.2 wt% of DES was required for breaking the azeotrope	[28]
[EMIM][OAc] [BMIM][OAc] [EMIM][Br]	Isobaric VLE was determined experimentally and correlated with NRTL All tested ILs enhanced relative volatility of IPA to H_2O [EMIM][OAc] was the best entrainer	[29]

IL—ionic liquid; U—urea; [EMIM]—1-ethyl-3-methylimidazolium; [BMIM]—1-butyl-3-methylimidazolium; [BF_4]—tetrafluoroborate; [DCA]—dicyandiamide; DEG—diethylene glycol; TEG—triethylene glycol; DMSO—dimethyl sulfoxide; DMF—dimethylformamide; NMP—*N*-methylpyrrolidone; [OAc]—acetate; [Br]—bromide; EG—ethylene glycol; Gly—glycerol; IPA—2-propanol; VLE—vapor–liquid equilibria.

In a study by Yin et al. [24], the separation of IPA/water was intensified by combining a salt-based DES entrainer for extractive distillation (choline chloride–urea–$CaCl_2$) (1:2:0.36) with a partial heat-integrated intermediate evaporator (PHI-IR) scheme. The PHI-IR process significantly reduced total annual costs (TAC) (70.25%), energy consumption (72.29%), and CO_2 emissions (74.47%) compared with conventional extractive distillation with glycerol (Gly). These results demonstrated the superior energy and economic and environmental performance of the PHI-IR process and highlighted its industrial potential for the separation of IPA–water mixtures.

Gomey et al. [25] investigated the extractive distillation of the IPA– water azeotrope using an ionic liquid (IL) 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]) and two DESs (choline chloride–Gly 1:2, choline chloride–EG 1:2) and compared their performance with that of conventional dimethyl sulfoxide solvent (DMSO). Process simulations in Aspen Plus showed that an IPA purity of over 99.9 mol% could be achieved, with the [EMIM][BF_4] IL entrainer requiring less energy than DMSO in conventional setups. In addition, an alternative process design was proposed using a flash drum to recover the entrainer, which significantly reduced the energy requirements for both IL and DES systems. In a study by Kang et al. [26], the extractive distillation of IPA–1-propanol–water mixtures was investigated, comparing the ionic liquid [EMIM] dicyanamide ([EMIM][DCA]) with EG as an entrainer. Process optimization showed that the use of [EMIM][DCA] reduced TAC by 44.6% and total gas emissions by 29.9% compared with EG. Molecular level analysis also explained the greater ability of [EMIM][DCA] to break the IPA–water azeotrope, demonstrating its potential for an efficient and environmentally friendly industrial separation.

In a study by Zhang et al., the mixed solvent of choline chloride (ChCl) and EG was investigated as an entrainer for the dehydration of IPA by extractive distillation. Isobaric vapor–liquid equilibrium (VLE) data were measured and successfully correlated with the NRTL equation, showing the ability of ChCl–EG (1:2) DES to effectively break the IPA–water azeotrope at a solvent mass fraction of 0.157. This DES represents a promising and potentially superior alternative to commonly used entrainers such as EG and potassium acetate for industrial 2-propanol dehydration [27]. A renewable ChCl–Gly 1:2 DES was investigated as an entrainer for the dehydration of IPA by extractive distillation [28]. Isobaric VLE data at 100 kPa showed that this DES effectively removed the IPA–water azeotrope at a low solvent mass fraction of 0.142, significantly less than Gly alone. The successful correlation with the NRTL equation indicated this DES as a potentially effective entrainer for the dehydration of IPA, also benefiting from its relatively low viscosity.

Salting-out is another important method for separating IPA and water, as it effectively breaks up their azeotrope, which otherwise makes it difficult to obtain high-purity IPA by conventional distillation. By inducing phase splitting, this technique offers a potentially energy-efficient and environmentally friendly alternative for IPA dehydration compared with other complex azeotropic separation processes. Wang et al. investigated the feasibility of Na_2CO_3 and K_2CO_3 as salting-out agents for the separation of IPA and ethanol from their aqueous mixtures [30]. Based on the experimentally determined binodal data and the calculated effective excluded volume of potassium carbonate and sodium carbonate in a solvent with IPA–water component and the salting-out coefficient, they concluded that Na_2CO_3 had a higher salting-out ability. Li et al. investigated four highly soluble inorganic salts for the separation of isopropanol from water and identified $K_4P_2O_7$ as the most effective at 298.15 K [31]. This aqueous two-phase system (ATPS) $K_4P_2O_7$/IPA achieved 100% recovery and a concentration coefficient of 5.74 for 2,3-butanediol without the salt passing into the extract phase. The study demonstrated the high selectivity, energy efficiency, and potential of this system for the recovery of biofuels from fermentation broths. Gomis et al. experimentally determined the lower critical solution temperature and the limits of use for ATPSs with water, short-chain alcohols (methanol to tert-butanol), and common salts [32]. It was found that the ability to form ATPS decreased from tert-butanol to methanol, with certain ratios of water-to-alcohol and salt concentration defining the operational limits. These energy-efficient ATPSs were proposed for phase transition extraction (PTE) processes, although more experimental data are needed to refine the thermodynamic models for simulation. In their study, Tabata et al. investigated the salting-out of fourteen water-miscible polar solvents from aqueous solutions using sodium chloride and successfully achieved phase separation for solvents such as acetone, acetonitrile, 1,4-dioxane, tetrahydrofuran, 1-propanol, and 2-propanol [12]. Zhigang et al. investigated the separation of IPA and water using different inorganic salts and organic solvents for the IPA/water/solvent systems [11]. The best system was IPA/water/*n*-hexane with K_2CO_3 as the salting-out compound. They also found that increasing the K_2CO_3 concentration had a positive effect on the separation performance.

Table 3. Separation of 2-propanol and water by salting out—overview of the literature data.

Entrainer	Feasibility Evaluation	Literature
Na_2CO_3, K_2CO_3	Binodal data were experimentally obtained Effective volume of salts and salting-out coefficient was determined Na_2CO_3 was better entrainer	[30]
$K_4P_2O_7$, K_2HPO_4, K_3PO_4, K_2CO_3	Experimental LLE data were determined Recovery of IPA and dehydration ratio were calculated $K_4P_2O_7$ was the most effective salting-out entrainer IPA/$K_4P_2O_7$ aqueous system was effective in separating 2,3-butanediol from aqueous solution	[31]
Cations: Na^+, K^+, Ca^{2+}, NH_4^+ Anions: Cl^-, SO_4^{2-}, CO_3^{2-}, NO_3^-	Experimentally obtained LCST and minimum salt concentration for phase splitting UNIQUAC and NRTL models were used for equilibrium calculation and simulation in Aspen Plus	[32]
NaCl, KCl, $CaCl_2$, Na_2CO_3, K_2CO_3, potassium ethanolate	Aqueous salt solution: water:IPA:*n*-hexane (1:1:1) LLE was determined experimentally IPA distribution coefficient between hexane and aqueous solution was evaluated K_2CO_3 was the best entrainer Salting-out experiment was performed in RPC	[11]
NaCl	Salting-out ability of NaCl was experimentally determined	[12]

LLE—liquid–liquid equilibria, IPA—2-propanol; RPC—reciprocating plate column; LCST—lower critical solution temperature.

Most publications evaluate the separation performance based on experimentally determined VLE or LLE or on simulation and optimization results of the selected separation process. Although such results can be helpful in the initial selection of the separation process, it is necessary to validate the results obtained by performing a suitable experiment. Thus, the aim of this study was the separation of IPA–water mixtures using DESs for extractive distillation and liquid–liquid extraction as well as various solid compounds for salting-out. The emphasis was put on the initial experimental check of the suggested separation route. In particular, it was investigated how the amount of added entrainer, the number of stages, and the reusability of DESs influence the overall separation performance.

2. Materials and Methods

2.1. Chemicals

The list of chemicals used is shown in Tables 4 and 5. The components of hydrophilic DESs were previously dried in a vacuum oven. All other chemicals were used without prior treatment.

Table 4. List of chemicals used for the preparation of DESs and feed solutions.

Chemical	Manufacturer	CAS Number
Isopropyl alcohol, HPLC grade	Fisher Chemical	67-63-0
Ethanol absolute, p.a.	Alkaloid Skopje	64-17-5
Choline chloride, 99%	Acros Organics	67-48-1
Ethylene glycol, p.a.	Lach-Ner	107-21-1
Glycerol anhydrous	Lach-Ner	56-81-5
DL-menthol, >98%	Thermo Scientific	89-78-1
Potassium carbonate, p.a.	Lach-Ner	584-08-7
Decanoic acid, >98%	TCI	334-48-5
Dodecanoic acid, >98%	TCI	143-07-7
Thymol, >98.5%	Gram Mol	89-83-8
1-octanol, 99%	Thermo Scientific	111-87-5

Table 5. List of chemicals used for salting-out.

Chemical	Manufacturer	CAS Number
Caffeine	VWR	58-08-2
Glycine	VWR	56-40-6
Piperine	VWR	94-62-2
Pentaerythritol	Acros Organics	115-77-5
Potassium carbonate	Lach-Ner	584-08-7
Potassium chloride	Kemika d.d.	7447-40-7
Potassium iodide	VWR	7681-11-0
Potassium sulfate	Kemika d.d.	7778-80-5
Sodium carbonate	Lach-Ner	497-19-8
Sodium bicarbonate	Lach-Ner	144-55-8
Sodium chloride	Kemika d.d.	7647-14-5
Sodium sulfate	Kemika d.d.	7757-82-6
Sodium thiosulfate	VWR	7772-98-7
Sorbitol	VWR	50-70-4

2.2. Solubility Measurements

To determine the solubility of the salting-out chemicals in water and IPA at 25 °C, a gravimetric analysis was performed. A Kern ALJ 220-4 NM analytical balance (accuracy: ±0.0001 g) was used for precise mass measurements. The experimental procedure involved supersaturation of the solvents with the solid compounds listed in Table 5, followed by 4 h of mixing, as presented in [33], on a Biosan PSU-10i orbital shaker at 250 rpm. After mixing, a sample of the clear solution was taken, and the solubility was quantified by complete evaporation of the solvent. Each solubility measurement was performed in triplicate, and the values reported represent the average of these replicates.

2.3. Preparation of DESs

Hydrophilic DESs were prepared by mixing the components in a specific molar ratio at reduced pressure and elevated temperature in a rotary vacuum evaporator until a clear homogeneous liquid was obtained. Hydrophobic DESs were prepared by mixing the components at atmospheric pressure and room temperature. Table 6 lists the hydrophilic and hydrophobic DESs.

Table 6. List of the prepared DESs.

DES Type	Label	DES
Hydrophilic DESs	DES 1	ChCl–EG (1:2.5)
	DES 2	ChCl–Gly (1:2)
	DES 3	K_2CO_3–Gly (1:6)
	DES 4	K_2CO_3–EG (1:10)
Hydrophobic DESs	DES 5	M–DA (2:1)
	DES 6	T–DA (1:1)
	DES 7	DA–DDA (2:1)
	DES 8	M–O (1:1)

ChCl—choline chloride; EG—ethylene glycol; Gly—glycerol; M—menthol; DA—decanoic acid; DDA—dodecanoic acid; T—thymol, O—1-octanol.

2.4. COSMO-RS Prediction

All the equilibrium thermodynamic quantities were predicted by the COSMO-RS model [34], employing the idea of charge density screening in liquids and based on the modeling of thermodynamic interaction terms. The calculations were performed by the COSMOthermX software package, version 21.0, BioVia Dassault Systèmes, France, with the BP/defTZVP level of theory data. All the ionic components—including ChCl—were treated as separate ions. For all the components available in the built-in database, the multi-conformer option was selected. The components not available in the database were carbonate and thiosulfate dianions. Their geometries were optimized using the TURBOMOLE program package, version 7.4.1, TURBOMOLE, Germany, with the same level of theory as before. For those components, a single conformer was used. The calculations involved Activity Coefficient, VLE/LLE, and Multiple Solvents COSMOthermX routines.

2.5. Extractive Distillation

The separation of a mixture of IPA and water with and without an entrainer was carried out at atmospheric pressure (1000 ± 20 hPa) by batch distillation in an apparatus described in detail in a previously published article [35]. In brief, the apparatus comprised a 2 dm^3 round-bottom flask, a heating jacket, a column head with a valve, an Erlenmeyer flask for distillate collection, and two thermometers to measure the temperatures of the top and bottom products, without the use of a distillation column. The results corresponded to batch distillation operating in total reflux mode (i.e., with no products withdrawn) and a minimum of two separation stages (round-bottom flask neck and condenser). The masses of 5%, 10%, 15%, and 20% of the selected solvents (DES 1, DES 2, EG, Gly) were added to the feed mixture containing 50 wt% IPA. DESs were selected on the basis of literature data. In the published reports [27,28], the authors emphasized that the DESs selected in this work allowed for the extraction of IPA with very high purity based on the VLE data. In addition, extractive distillation was carried out with glycerol and ethylene glycol, i.e., with the hydrogen bond donors (HBDs) of the DESs studied. After the temperatures of distillate and bottom product had stabilized, samples of the distillate were taken and their refractive index was measured. The efficiency of the entrainers was calculated using the following equation:

$$\varepsilon = \frac{w_D - w_{D,0}}{w_{D,0}} \cdot 100$$

where w_D and $w_{D,0}$ are the mass fraction of IPA in the distillate with and without an entrainer, respectively.

2.6. Extraction

The separation of a mixture of IPA and water was carried out by liquid–liquid extraction and salting-out. Table 6 lists the hydrophilic (DES 3 and DES 4) and hydrophobic DESs used in the liquid–liquid extraction. The influence of the type of solvent and the composition of the feed mixture (40 and 60 wt% IPA) on the extraction efficiency was investigated. The measurements were carried out in a jacketed flat-bottom flask posed on a magnetic stirrer at a DES-to-feed mass ratio of 1:1 kg/kg, at atmospheric pressure and room temperature (25 °C). When DESs were used as selective solvents, low extraction times were commonly reported due to their high solvation capacity and high mass transfer rates [36–38], so extraction time was set to 1 h. After 1 h, the phases were separated and the refractive index of the aqueous phase was measured. The solids used as entrainers in the salting-out extraction are listed in Table 5. The influence of the amount of entrainer on the extraction efficiency by salting-out was investigated for different feed compositions. The measurements were carried out on a magnetic stirrer at atmospheric pressure and room temperature (25 °C), until the entire added solid compound was dissolved. The refractive index of the IPA-rich phase was measured after phase separation. Heterogeneous systems resulting from the addition of DES were separated by centrifugation. The efficiency of the entrainers was calculated using

$$\varepsilon = \frac{w_F - w_R}{w_F} \cdot 100$$

for the liquid–liquid extraction, where w_F and w_R are the mass fraction of IPA in the feed and raffinate, respectively, and

$$\varepsilon = \frac{w_F - w_O}{w_F} \cdot 100$$

for the salting-out, where w_F and w_O are the mass fraction of water in the feed and the newly formed phase, respectively.

2.7. Characterization

The mass fraction of IPA in the distillate and raffinate phase was determined by measuring the refractive index, with the assumption that an entrainer was not present in the sample. For this purpose, a calibration curve was first measured in the range of mass fractions of IPA in water from 10% to 90%. The obtained dependence of the mass fraction of IPA in water on the refractive index was correlated by the following equation:

$$w(\mathrm{IPA}) = 13{,}637.816 \cdot n_{D,25}^3 - 54{,}918.614 \cdot n_{D,25}^2 + 73{,}730.736 \cdot n_{D,25} - 33{,}001.189$$

Fourier-transform infrared spectra (FTIR) and ^{1}H nuclear magnetic resonance spectra (^{1}H NMR) were recorded to determine the presence of the entrainer in the aqueous or organic phase. The solubility of the solid compounds used as entrainers in the raffinate phase was also determined gravimetrically by drying the sample in an infrared dryer at 105 °C.

3. Results

In the extractive distillation of the azeotropic IPA–water mixture, two hydrophilic DESs (DES 1 and DES 2; see Table 3) and two conventional solvents (glycerol and ethylene glycol) were used as entrainers. In addition, two hydrophilic and four hydrophobic DESs (Table 3) and various solid compounds (Table 2) were investigated as entrainers in liquid–liquid and solid–liquid extraction processes.

3.1. Extractive Distillation

3.1.1. COSMO-RS Predictions

The results related to extractive distillation were calculated by the activity coefficient routine and are presented in terms of the ratio of activity of IPA and water in the system with an entrainer, divided by the same ratio in the system without an entrainer (Figure 1). The temperature was set to 80 °C to comply with the experimentally investigated range.

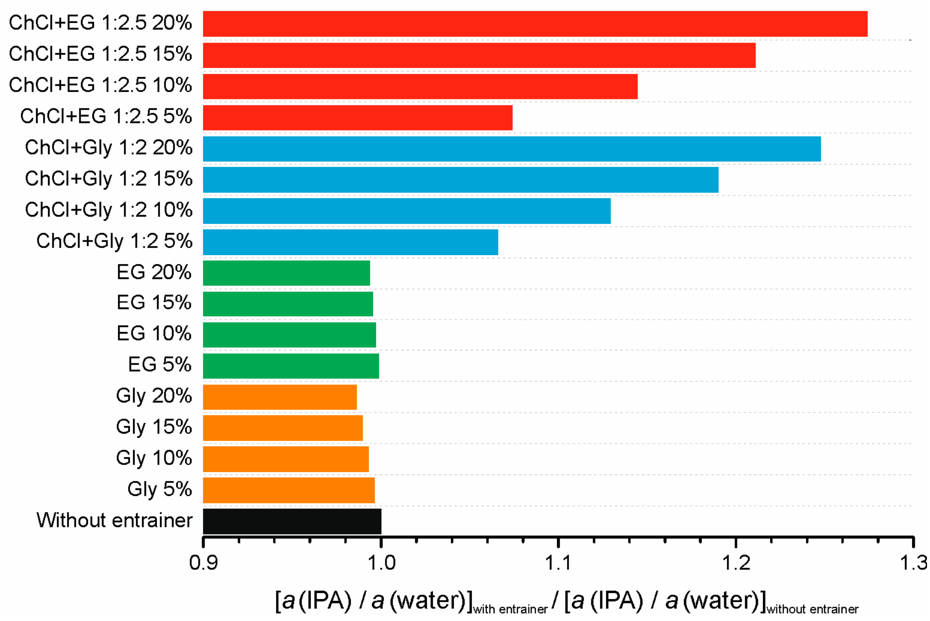

Figure 1. Ratio of activity of IPA and water in the system with an entrainer, divided by the same ratio in the system without an entrainer, as calculated by the COSMO-RS model at 80 °C. IPA—isopropanol; ChCl—choline chloride; EG—ethylene glycol; Gly—glycerol.

The activity ratio is crucial for the distillation separation of the components and may be brought into connection with the relative volatility. In ideal systems, activities are equal to component mole fractions. An activity larger than a mole fraction points to an increased tendency of a component to escape into the vapor phase. On the other hand, an activity smaller than a mole fraction points to an increased tendency of a component to retain in the liquid phase. Thus, the larger is the ratio of activities of IPA and water, the more effectively is IPA pushed towards the vapor phase. By dividing the ratio of activities of IPA to water with the same ratio in the non-entrained system, the efficiency of the entrainer is clearly deduced. The interpretation of the results is straightforward. First, adding a pure HBD component (Gly or EG) is practically ineffective in entraining the IPA–water mixture—in fact, the values are changed slightly in the undesired direction. Second, adding either of the DESs facilitates the distillation separation by keeping water in the liquid phase and driving IPA towards the vapor phase. The larger is the added DES amount, the stronger is the driving force for separation. By comparing the two DESs, the one with EG as a HBD component seems to be slightly more efficient.

3.1.2. Experimental Validation

Atmospheric distillation was carried out first to evaluate the efficiency of the entrainers in separating IPA from its aqueous solution. The distillate had an IPA mass fraction of 82.29%, below the azeotropic composition reported in the literature (87.58 wt% IPA). Extractive distillation experiments were then carried out at atmospheric pressure using different mass fractions of entrainers.

The DESs examined in this paper were chosen largely for their hydrophilic properties and perfect miscibility with the feed mixture. As mentioned before, the choline chloride-based DESs were chosen to experimentally assess their potential as entrainers in the extractive distillation of isopropanol–water mixtures, as previous studies have examined them through experimentally established VLE [27,28] or simulation [25,39]. The DES composed of ethylene glycol and choline chloride was prepared with a small variation in the molar ratio of choline chloride to ethylene glycol with respect to other authors' choice, but in accordance with our previous investigations where both chosen DESs were examined as entrainers for the separation of *n*-hexane and ethanol [40] as well as acetonitrile and water [35].

None of the entrainers used were able to obtain a distillate with a mass fraction of IPA above the azeotropic composition (>87.58 wt%) (Table 7).

Table 7. The influence of the type and concentration of entrainer in the mixture on the mass fraction of 2-propanol (IPA) in distillate. Mass fraction of IPA in the feed was 50%.

Entrainer	n(DES)/n(Feed), mol/mol	w(Entrainer), %	w(IPA), %	Efficiency, %
-	-	-	82.29	-
Glycerol	0.016	5	82.03	−0.316
	0.033	10	83.47	1.434
	0.053	15	84.14	2.248
	0.075	20	82.29	0
Ethylene glycol	0.023	5	65.39	−20.537
	0.049	10	65.20	−20.768
	0.079	15	67.21	−18.325
	0.112	20	77.73	−5.541
DES 1	0.017	5	84.94	3.220
	0.037	10	86.40	4.995
	0.058	15	84.94	3.220
	0.082	20	82.42	0.158
DES 2	0.014	5	82.68	0.474
	0.029	10	85.35	3.719
	0.045	15	86.59	5.225
	0.064	20	85.93	4.423

The most striking observation is that the separation efficiencies for pure glycerol and pure ethylene glycol are significantly negative or close to zero. A negative separation efficiency means that these pure HBD compounds do not improve the separation of IPA and water, but rather hinder or even worsen it. In the context of extractive distillation, this could mean that they do not effectively increase the relative volatility of IPA to water or that they interact unfavorably with IPA, making IPA less volatile, in line with the COSMO-RS predictions. Although both glycerol and ethylene glycol are good hydrogen bond donors, when used alone, they lack the specific and complex ionic and hydrogen bonding network that a DES provides.

The results for DES 1 and DES 2 are positive though, indicating that EG and Gly can act successfully as entraining agents and improve separation only by forming DESs (with ChCl). However, their maximum efficiencies remain rather low. The presence of ChCl (the hydrogen bond acceptor, HBA) is crucial. It acts as an integral part of the DES structure and creates a robust and tightly packed hydrogen bond network with the polyol (ethylene glycol or glycerol). According to experimental findings, the DESs preferentially form strong hydrogen bonds with water molecules. This effectively reduces the evaporation tendency of water, which leads to a reduction in its partial pressure and volatility. As water becomes less volatile, the relative volatility of IPA increases, making it easier to separate.

For both DES 1 and DES 2, separation performance generally improves as the mass fraction of an entrainer is increased from 5% to an optimum point (10% for DES 1, 15% for DES 2). This is to be expected as more entrainer molecules provide more sites for favorable interactions with water, resulting in a greater change in VLE. DES 1 shows a strong peak at 10% and then a significant drop in efficiency at 15% and 20%. This suggests that, above a certain concentration, the benefits of adding more DES 1 are negated by other factors. This could be due to increased viscosity of the liquid phase, saturation of the active sites or non-ideal interactions (at very high concentrations, the DES could begin to interact unfavorably with IPA or form complexes that do not support or even hinder separation). The effect of viscosity is kinetic and not thermodynamic in nature, and as such, it cannot be predicted by the equilibrium model such as COSMO-RS. Thus, it might be advisable to always perform the experiments in a setup that would exclude viscosity effects. On the other hand, the effect of unfavorable interactions can, at least in principle, be predicted by COSMO-RS. The effect of complex formation (including saturation of the active sites as a special kind of complex formation) can be described by COSMO-RS, but the complexes have to be defined in advance, so this makes no true prediction, and as such, it is far beyond the scope of this article. Thus, one may conclude that COSMO-RS in the applied form may fail in describing the qualitative details observed in the systems.

DES 2 shows a more robust performance, peaking at 15% and dropping only slightly at 20%. This suggests that the glycerol-based DES maintains its efficacy better at higher concentrations. The results obtained emphasize the critical role of DES structure, particularly the number of hydroxyl groups in the hydrogen bonding donor, in the effective separation of the IPA–water azeotrope during extractive distillation.

Based on the published data, a significantly better performance of all tested entrainers could not have been expected. In the extractive distillation of a mixture of IPA and water, Zhang et al. measured the VLE experimentally for the dehydration of IPA with ChCl−Gly (molar ratio 1:2) [28]. According to their results, the azeotrope can be removed by the addition of 14.2 wt% DES. A similar study was carried out for ChCl−EG (molar ratios 1:2, 1:4, and 1:8) [27]. The minimum mass fraction of solvent required to break the azeotrope increases with the increase in EG content in the DES and was even higher for pure EG (thus proving our findings of immanent inefficiency of pure EG). On the other hand, the literature results cannot be directly compared with ours. The reported mass fractions of both DESs (ChCl−Gly (1:2) and ChCl−EG (1:2)) necessary to break the IPA–water azeotrope were evaluated for a single column with an appropriate number of separation stages, using the criterion of relative volatility always higher than 1. However, our experiments involved not more than two separation stages. Having this in mind, the results are quite comparable. Shivendara et al. simulated extractive distillation to separate IPA and water by adding EG [39]. Based on their calculations, this process is also feasible. In the extractive distillation of IPA–water mixture, Gomey et al. investigated the possible use of two DESs: ChCl−EG

1:2 and ChCl−Gly 1:2, 1-ethyl-3-methylimidazolium tetrafluoroborate as a representative of ionic liquids and dimethyl sulfoxide as a polar aprotic solvent [25]. According to their simulations, high-purity IPA can be produced with all the selected entraining agents. However, it is clear that simulation and VLE alone cannot be relied upon in the absence of experimental validation.

3.2. Liquid–Liquid Extraction

Since the selected solvents proved to be ineffective in separating the IPA–water mixture by extractive distillation in the applied experimental setup, the possibility of using DES for the separation of IPA and water by liquid–liquid extraction was investigated.

3.2.1. COSMO-RS Predictions

For the investigated two hydrophilic DESs, both involving sodium carbonate, the COSMO-RS model calculations with the VLE/LLE routine did not result in the LLE-type phase separation at 25 °C. On the other hand, all four hydrophobic DESs, DES 5–8, exhibited clear LLE phase behavior, depicted in Figure 2.

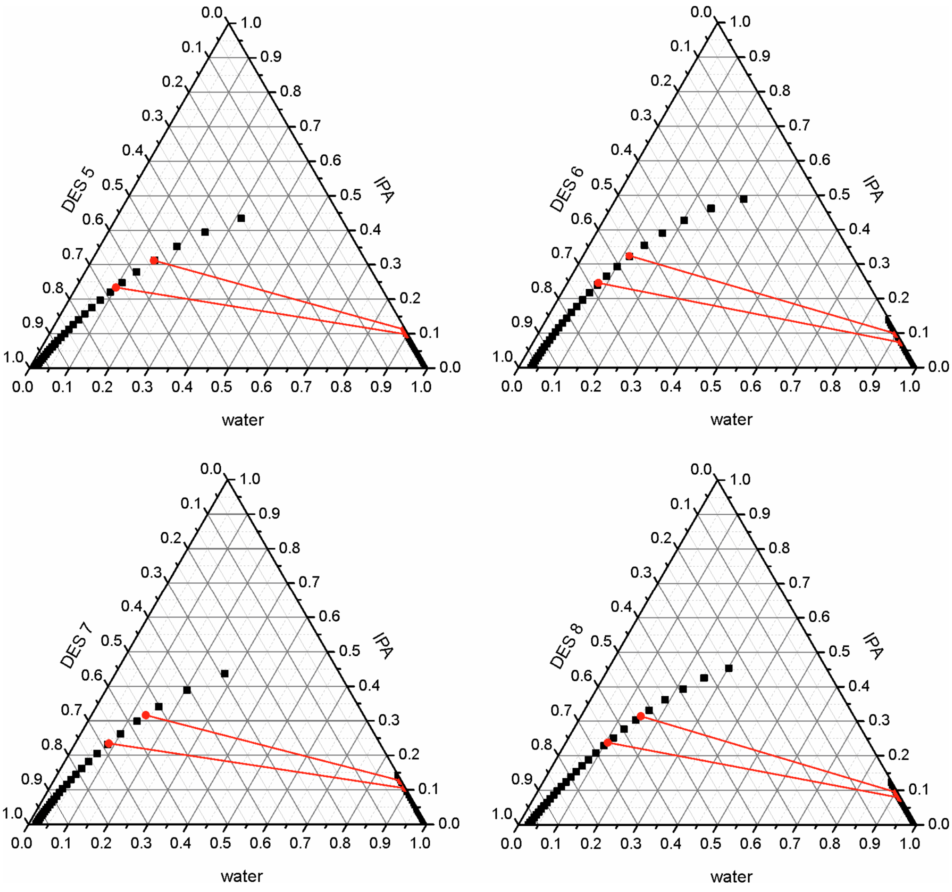

Figure 2. Ternary plots in mass fractions, showing the liquid–liquid equilibria phase diagrams, with two-phase regions bordered by the black squares and tie lines corresponding to the experiments in red, as calculated by the COSMO-RS model at 25 °C.

3.2.2. Experimental Validation

Since water is more polar than IPA, it was expected that the hydrophilic DESs would extract water preferentially. Of the two hydrophilic DESs, DES 4 was completely miscible with both feed mixtures, while DES 3 promoted phase separation, contrary to the COSMO-RS prediction. However, the measured refractive indices of the raffinate phase were higher than the maximum possible value for a solution of IPA and water, indicating partial miscibility of the phases. To confirm the presence of DES 3 in the raffinate phase, ^{1}H NMR spectra were measured; the spectra obtained are shown in Figure 3. The signals characteristic of DES 3 (multiplet from 3.67 to 3.87 ppm) are clearly visible in the enlarged spectra of both raffinate phases. Upfield shifts of these signals in the raffinate spectra, compared with DES 3, indicate changes in solvent environment, concentration, or subtle conformational changes that increase local electron density. This shift is more pronounced in feed solution with higher IPA concentration.

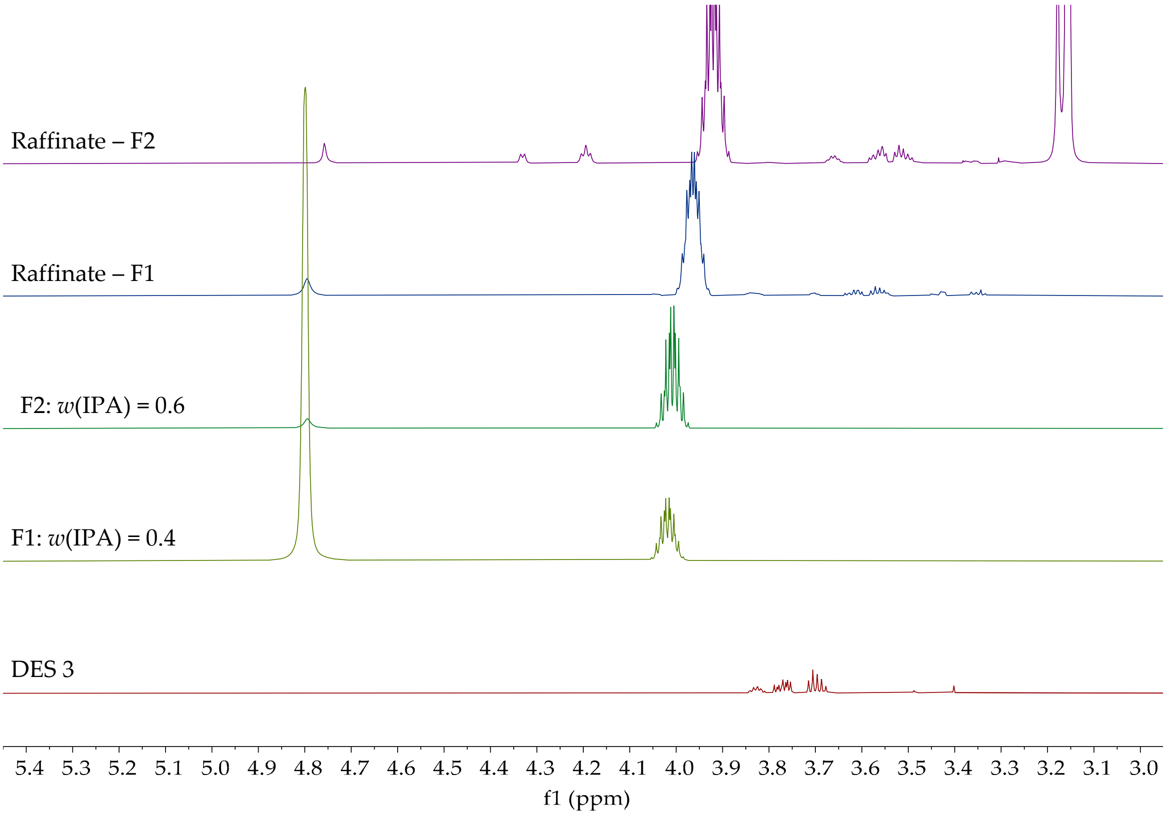

Figure 3. ^{1}H NMR spectra of feeds, DES 3, and extract phases.

Since hydrophilic DESs were not effective in separating IPA and water, four hydrophobic DESs were tested. DESs utilized for liquid–liquid extraction were selected based on their hydrophobic properties. Menthol–decanoic acid, with the same molar ratio, was already examined for the separation of *n*-hexane and ethanol [40]. DESs consisting of menthol and decanoic acid, as well as those made of decanoic and dodecanoic acid with different molar ratios of hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs), were assessed previously using experimentally derived LLE and selectivity data [5]. In addition, the feasibility of T:DA (1:1) and DDA:DA (1:1) was evaluated by liquid–liquid extraction and distribution coefficient [21]. On the other hand, DES comprising menthol and octanol has not been previously tested for the separation of isopropyl alcohol and water. This combination of HBA and HBD was chosen based on the findings of Audeh et al. [22] and Fan et al. [20]; menthol was identified as the most effective HBA, and the separation efficiency enhanced with the increase in the carbon chain length in alcohols.

The results obtained are shown in Table 8. For all hydrophobic DESs tested, increasing the concentration of IPA in the feed solution resulted in more effective separation. The best solvents for the separation of IPA and water were DES 6 and DES 5 for the feed solution with lower and higher IPA, respectively. The results show that the composition of the feed solution has a major influence on the extraction efficiency. All components of the feeds and DESs can act as donors and acceptors of hydrogen bonds. The efficiency of the solvent to be used for extraction can be explained by the affinity between selective solvent and key component (IPA in this case), including the strength of hydrogen bonds, availability of H-bonding sites, hydrophobicity, steric effects, etc.

For the lower IPA loading, the ability of DESs to compete with water for IPA and provide strong and readily available H-bonds is of great importance. For example, DES 7 had the lowest extraction performance. Both DES components are acids that tend to form dimers [41], which in turn reduces the number of available H-bonding sites for IPA. In contrast, the most efficient solvent, DES 6, combines the strongest H-bond donor (the phenolic -OH of thymol) with a strong HBD/HBA, which probably provides the most energetically favorable and numerous H-bond interactions with IPA. For the higher IPA loading, the competition for H-bonds in the aqueous phase is much stronger. The DES must be extremely efficient to break the existing IPA–water hydrogen bonds and form even stronger IPA-DES bonds [26]. The least efficient solvent was DES 8, which may be due to the insufficient strength of the H-bonds to effectively extract IPA from the highly concentrated aqueous solution. The most efficient solvent was DES 5, with decanoic acid providing strong H-bonds.

It is important to note that experimental IPA mass fractions in the water phase do not agree with COSMO-RS predictions. The mass fractions of IPA calculated by the model are much lower, ranging from 0.0937 to 0.1255 for the feed richer in IPA and from 0.0734 to 0.1053 for the feed leaner in IPA. The order of efficiency predicted by COSMO-RS is DES 7 < DES 5 < (DES 6 ≈ DES 8).

Table 8. The influence of the type of entrainer and the feed composition on the mass fraction of 2-propanol (IPA) in aqueous phase.

Entrainer	$w(\text{IPA})_\text{F}$, %	w(IPA), %	Efficiency, %
DES 5	0.4	16.55	58.64
	0.6	16.12	73.14
DES 6	0.4	14.62	63.46
	0.6	18.26	69.57
DES 7	0.4	16.97	57.57
	0.6	20.87	65.22
DES 8	0.4	16.12	59.71
	0.6	21.54	64.11

To investigate whether hydrophobic DESs are soluble in feed solutions, ^{1}H NMR spectra of DESs, feed solutions, raffinate, and extract phases were measured, and the spectra obtained are shown in Figures 4–7. Since IPA is less polar than water, it was expected that IPA would be extracted by hydrophobic DESs. The successful extraction of IPA from the aqueous phase is indicated by the presence of IPA signals and the expected reduction in water signal (4.7 ppm in Figure 4) in both extracts. The signals characteristic of DES 5 are not visible in the raffinate spectra, confirming the assumption that DES is not soluble in the feed solutions. This is in agreement with COSMO-RS predictions, where mass fractions of DES lower than 0.0021 were calculated. In addition, the relative intensity of the water signal is higher compared with the other IPA signals, indicating that the IPA concentration was significantly reduced. The upward shift of the hydroxyl protons of water and IPA (in the range of 1.2 to 2.2 ppm) in both raffinates compared with the chemical shifts in the feed solutions indicates a reduction in hydrogen bonding in the raffinate. In the feed solutions, IPA is dissolved in water due to the strong hydrogen bonding between

IPA and water molecules. The DES itself is formed by strong hydrogen bonds between its components. When DES is added to the feed solution, a highly interactive environment for IPA is created as both DES components can act as HBD and HBA. By establishing a subtle balance of hydrogen bonding and hydrophobic interactions between IPA and DES, IPA is effectively extracted from water. The DES components, particularly the acidic proton of decanoic acid, provide an energetically favorable environment for hydrogen bonding, while the hydrophobic parts of DES components can accommodate IPA molecules' hydrocarbon chains, so IPA interacts preferentially with DES. Similar considerations can be applied to the ^{1}H NMR spectra of other hydrophobic DESs.

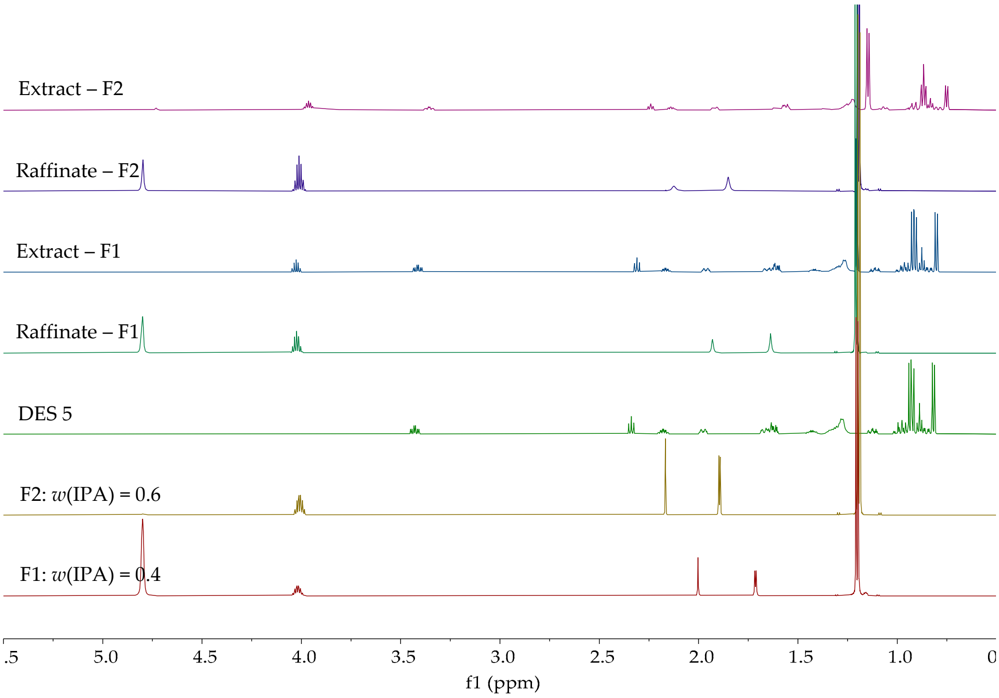

Figure 4. ^{1}H NMR spectra of feed, DES 5, raffinate, and extract.

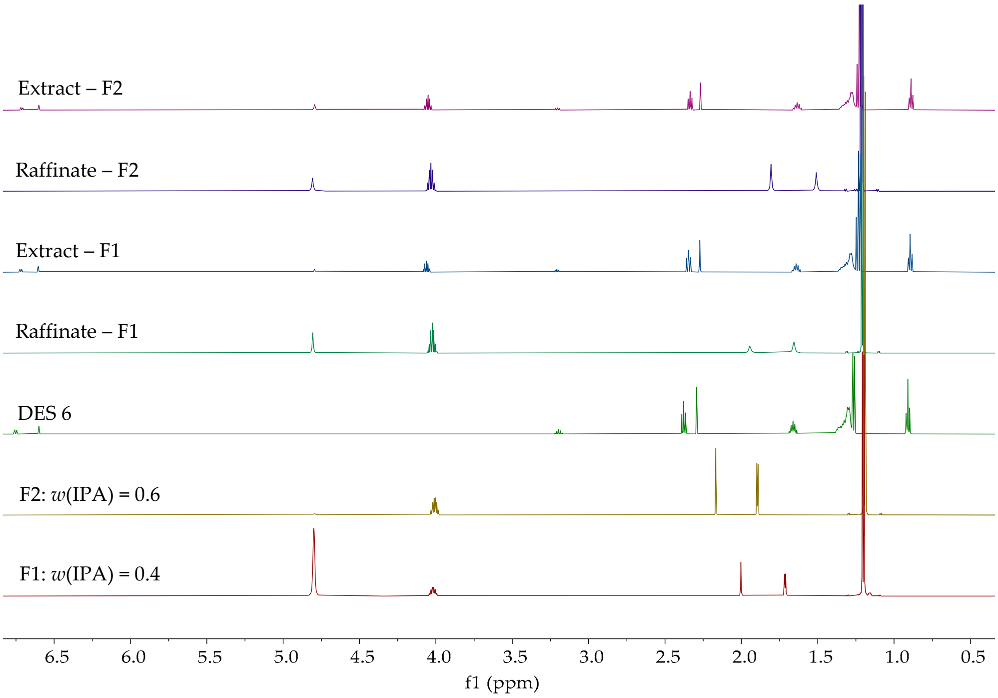

Figure 5. ^{1}H NMR spectra of feed, DES 6, raffinate, and extract.

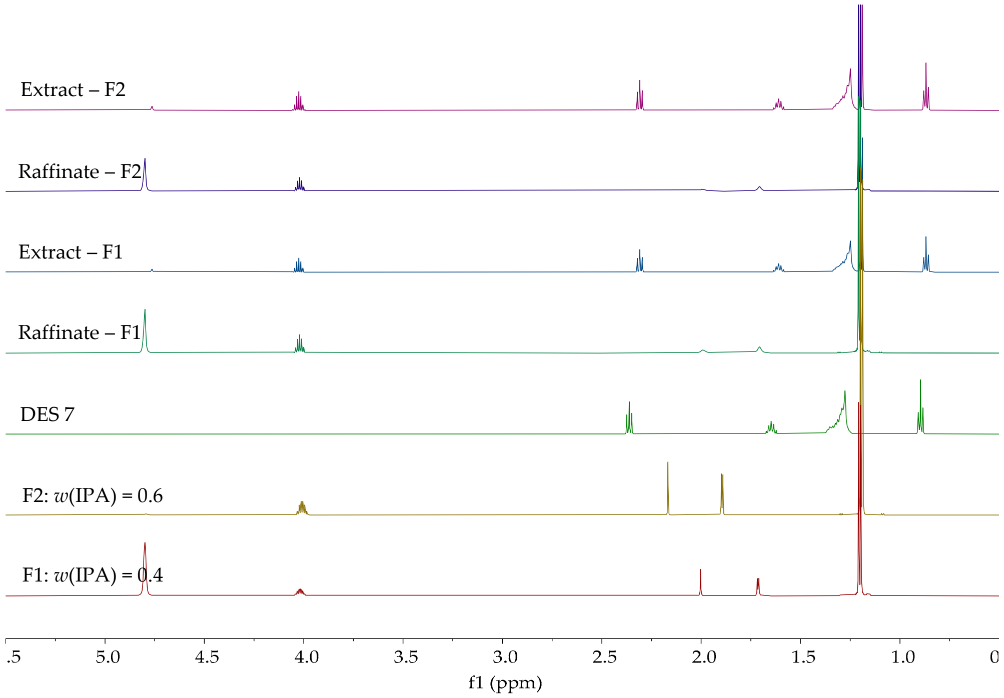

Figure 6. ^{1}H NMR spectra of feed, DES 7, raffinate, and extract.

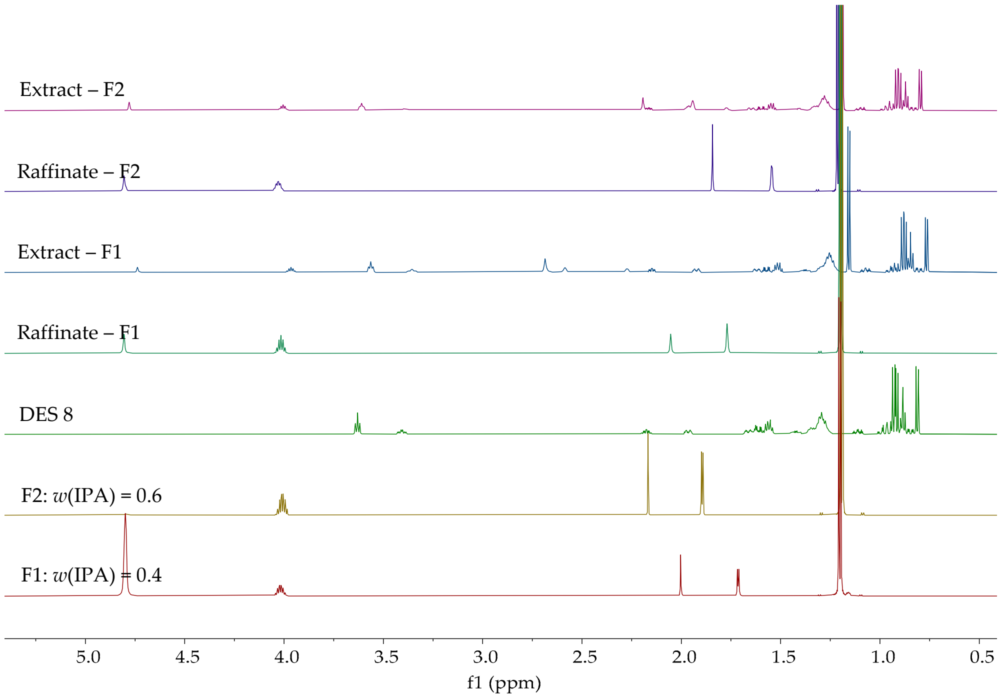

Figure 7. ^{1}H NMR spectra of feed, DES 8, raffinate, and extract.

3.2.3. Reusability of DESs and Multistage Extraction

Since one of the most important properties of DESs is their high capacity for different types of solutes, the reusability of hydrophobic DESs without regeneration was experimentally investigated. The most efficient DESs for both feeds were selected, and the results obtained are shown in Table 9. The DES-to-feed ratio was reduced to 0.5:1 kg/kg to save chemicals. Only two cycles were performed for both DESs. When DES 5 was used in the second cycle, a homogeneous mixture was obtained. After the first cycle, DES 5 contains not only menthol and decanoic acid, but also a considerable amount of IPA. As a result, the polarity of the solvent is increased to such an extent that DES 5 becomes completely miscible with the fresh feedstock F1. Thus, it can be concluded that reusability is hindered by the loss of phase separation. On the other hand, DES 6 contains a considerable amount of IPA after the first extraction cycle so that many of the active H-binding sites of DES are already occupied by the previously extracted IPA molecules. In contrast with DES 5, DES 6 still forms a separate phase, indicating that the overall polarity change is not sufficient to cause complete miscibility with the aqueous solution. This suggests that the combination of thymol and decanoic acid (perhaps due to the stronger hydrophobicity of thymol or the introduction of another H-bonding network associated with the phenolic –OH group) is more robust in maintaining immiscibility, even when loaded with IPA and some water. Thus, the reusability of DES 6 is compromised by a reduction in solvent capacity due to prior loading of IPA at the active hydrogen bonding sites.

These different reusability challenges highlight the importance of not only the initial extraction efficiency, but also the long-term stability and phase behavior of DESs in the development of sustainable extraction processes. An effective reuse of both DESs would require a regeneration step to remove the extracted IPA and restore their original properties. Since both menthol and thymol are volatile, re-extraction of IPA or cooling may serve as a method to regenerate the DESs.

Table 9. Reusability of DESs (DES-to-feed mass ratio = 0.5:1 kg/kg).

Entrainer	w(IPA)$_F$, %	Cycle	w(IPA), %	Efficiency, %
DES 5	0.6	1	33.52	44.13
	0.6	2	-	-
DES 6	0.4	1	22.67	43.90
	0.4	2	33.67	15.81

Since reuse was not successful, a multistage extraction was performed. Fresh DES was used in each stage. The results are presented in Table 10. After three stages, the IPA concentration in the raffinate had decreased significantly. However, phase separation became more difficult the less IPA the feed solution contained. Several centrifugation cycles were required for both DESs.

Table 10. Multistage extraction (DES-to-feed mass ratio = 0.5:1 kg/kg).

Entrainer	w(IPA)$_F$, %	Stage	w(IPA), %	Efficiency, %
DES 5	0.6	1	33.52	44.13
		2	18.04	69.93
		3	10.88	81.86
DES 6	0.4	1	22.21	43.90
		2	11.11	72.23
		3	5.08	87.30

3.3. Salting-Out

Experimental determination of the solubility of selected solid compounds in water and IPA was performed to evaluate their potential to improve water–IPA separation (Table 11). The results confirmed the expected much higher solubility of all inorganic salts in water, in comparison with organic compounds, suggesting that these solids could more effectively displace IPA from its aqueous solution. The low solubility of caffeine, piperine, and pentaerythritol in both solvents suggests that they will not induce the desired phase separation.

Table 11. Solubility of compounds in water and IPA at 25 °C and atmospheric pressure (standard uncertainties: $u(X) \leq 4.18 \cdot 10^{-3}$ g, $u(T) = 0.2$ K, $u(P) = 5$ kPa).

Entrainer	***X* (Solubility), g/g**	
	Water	**IPA**
Caffeine	0.0248	0.0382
Glycine	0.2564	0.0031
Piperine	0.0002	0.0415
Pentaerythritol	0.0786	0.0172
Potassium carbonate	1.8008	0.0009
Potassium chloride	0.3582	0.0067
Potassium iodide	1.4964	0.1089
Potassium sulfate	0.1245	0.0005
Sodium carbonate	0.2163	0.0004
Sodium bicarbonate	0.0566	0.0013
Sodium chloride	0.3611	0.0070
Sodium sulfate	0.2779	0.0011
Sodium thiosulfate	0.8870	0.0002
Sorbitol	1.3181	0.0623
Dodecanoic acid	0.0041	1.2000
Choline chloride	4.3661	0.1638

3.3.1. COSMO-RS Predictions

As expected, different types of phase diagrams were obtained, including complete miscibility of the compounds, solid–liquid (SLE) equilibria ternaries without LLE demixing, those with ATPS-type LLE demixing, and those with simple LLE-type demixing originating from the partial miscibility of water with piperine and dodecanoic acid, respectively. The observed phase diagrams fitted reasonably well with the calculated solubilities of all the salting-out agents in pure water and IPA. However, the results will not be presented here due to the simple fact that COSMO-RS-based solubilities, in particular those of the ionic compounds, did not confirm the experimental observations. As a direct consequence, the experimental findings on the phase behavior did not match the calculated ones. The possible reasons were discussed elsewhere [35,42], and include, in brief, the neglected solvation (hydration) of small ions, such as potassium, sodium, and chloride, as well as the neglected hydrolysis of carbonate and hydrogencarbonate anions. Of course, one cannot forget the fact that COSMO-RS was developed primarily for non-ionic species. This fact was confirmed by a much better correspondence of the calculated and experimental solubilities of caffeine, glycine, piperine, pentaerythritol, ChCl, and dodecanoic acid in water, as well as those of caffeine, piperine, and pentaerythritol in IPA. Interestingly enough, the solubility order of magnitude of some inorganic salts such as Na_2CO_3, $NaHCO_3$, NaCl, and Na_2SO_4 in IPA was fairly predicted, corroborating the hydration and salt hydrolysis (absent in IPA) as probable reasons for the discrepancy.

However, another calculation was performed for the salting-out systems selected for further experimental validation, i.e., those that induced LLE phase separation in the targeted composition region. For the experimental compositions, the entraining effect of the selected solids on the separation of IPA and water was estimated again in terms of the ratio of activity of IPA and water in the system with an entrainer, divided by the same ratio in the system without an entrainer, this time at 25 °C. Hopefully, this ratio can be linked, via activity coefficients, to the tendency towards LLE phase separation, salting-out efficiency, and difference between liquid equilibrium phases' compositions. The results are presented in Figure 8. The figure shows that dodecanoic acid (DDA) pushes the system in the direction opposite of other entrainers, keeping IPA primarily in the liquid phase containing the entrainer. This fact may be easily explained by the hydrophobicity of both the entrainer and IPA. All the other entrainers are producing the aimed effect of increasing the activity ratio of IPA and water. The corresponding entraining order is $K_2CO_3 < Na_2S_2O_3 < Na_2SO_4 < Na_2CO_3$ and does not depend on the initial IPA-to-water ratio. The more entrainer is added, the larger is the effect, regardless of its cause or direction.

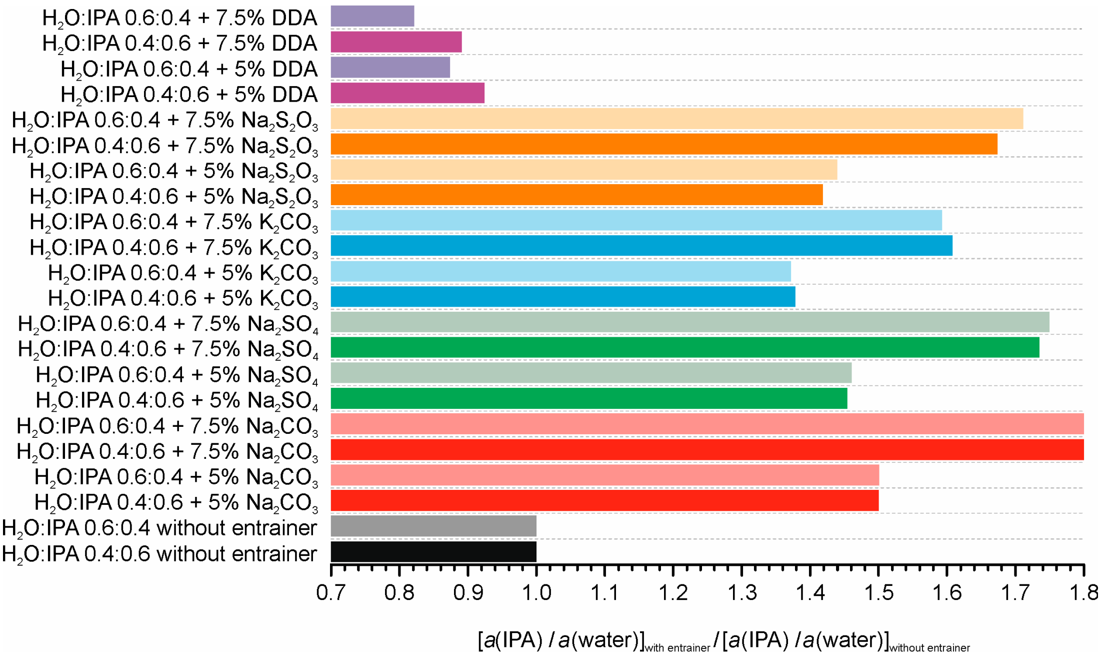

Figure 8. Ratio of activity of IPA and water in the system with an entrainer, divided by the same ratio in the system without an entrainer, as calculated by the COSMO-RS model at 25 °C. IPA—isopropanol; DDA—dodecanoic acid.

3.3.2. Experimental Validation

Solid compounds that induce phase separation and the corresponding salting-out efficiency are shown in Table 12. It can be observed that the increase in mass fraction of IPA in feed solution and the amount of the entrainer added increases the salting-out efficiency. The effect of the entrainer amount was found by COSMO-RS calculations as well, but the calculation results are not that definite regarding the effect of feed solution composition. A higher concentration of the target component (IPA) provides a greater driving force for its separation. This is expected, as more ions provide a stronger salting-out effect. However, as seen with Na_2SO_4, this trend can reach an optimum and then decline due to thermodynamic factors such as saturation, or kinetic factors, such as increased viscosity (in poorly designed experiments). The best entrainer was Na_2CO_3, just as with COSMO-RS. By adding 7.5 wt% to the feed with higher amount of IPA, an organic phase with the concentration of IPA higher than that of the azeotropic point was obtained. Opposite to the inorganic salts, DDA dissolves in feed solution and induces phase separation by dissolving in an IPA-rich phase, again in line with the COSMO-RS model predictions.

Table 12. The influence of the type and concentration of entrainer in the mixture on the mass fraction of 2-propanol (IPA) in a newly formed phase.

Entrainer	$w(\mathrm{IPA})_F$, %	w(Entrainer), %	w(IPA), %	Efficiency, %
K_2CO_3	40	5.0	63.24	38.73
		7.5	70.59	50.99
	60	5.0	82.44	56.09
		7.5	87.84	69.59
Na_2CO_3	40	5.0	65.00	41.67
		7.5	66.82	44.69
	60	5.0	85.48	63.71
		7.5	90.25	75.63
Na_2SO_4	40	5.0	57.69	29.49
		7.5	61.52	35.87
	60	5.0	80.95	52.38
		7.5	79.49	48.73
$Na_2S_2O_3$	40	5.0	66.21	43.68
		7.5	69.31	48.85
	60	5.0	81.69	54.23
		7.5	85.48	63.71
Dodecanoic acid	40	5.0	36.88	7.79
		7.5	33.98	15.04

The maximum solubility of Na_2SO_4 in the feed solution with 60 wt% IPA was 2.33%, so some of the added salt remained undissolved.

Inorganic salts improve separation due to the salting-out effect. When these salts dissolve in the aqueous IPA mixture, their ions interact intensively with water molecules due to strong ion–dipole forces resulting in classical solvation (hydration), in particular of Na^+ and K^+ cations [43]. This phenomenon “binds” the water molecules and reduces their availability for interaction with IPA. As a result, the solubility of IPA in the aqueous phase decreases, leading to its “salting-out” and promoting its separation into a newly formed, IPA-rich phase. Carbonates have the highest separation efficiencies of all the entrainers tested. Na_2CO_3 has the highest efficiency at 75.63%, closely followed by K_2CO_3 at 69.59%, the latter being underpredicted by COSMO-RS. In a study conducted by Wang et al., Na_2CO_3 proved to be more efficient than K_2CO_3 in the separation of IPA and water [30]. Based on the experimentally obtained equilibrium data, they evaluated the scaled effective excluded volume and the salting-out coefficient. Both values were higher for Na_2CO_3. This strong performance can also be attributed to the highly kosmotropic nature (strong water structuring ability) of the carbonate ion ($CO_3{}^{2-}$) [43], in addition to the already-mentioned salt hydrolysis effect. The high charge density of these ions leads to a very effective competition with IPA for water molecules. In salting-out, Na_2CO_3 generally performs slightly better than K_2CO_3 due to the smaller ionic radius of Na^+ in comparison with K^+ and thus the higher charge density. $Na_2S_2O_3$ also shows good separation performance, achieving up to 63.71%. Although its performance is effective, it is generally somewhat lower than that of carbonates. Thiosulfate is also a kosmotropic anion [43], but perhaps its interaction with water is not as strong or as exclusive as that of the carbonate ion in this particular system. Additionally, as conjugate bases of a strong acid, thiosulphate anions are not involved in salt hydrolysis. Among the inorganic salts, Na_2SO_4 exhibited the lowest separation efficiency at 52.38%. Although sulfate is a known kosmotropic ion [44], its effectiveness here is lower than that of carbonates and thiosulphate. Even at the highest concentration (7.5% entrainer at 60% IPA feed), the efficiency drops from 52.38% to 48.73%, indicating possible limitations such as saturation and lower effective interaction at higher loading.

In contrast with the inorganic salts, DDA does not act as a salting-out agent due to its hydrophobic nature. Although DDA dissolves in the IPA-rich phase, it has a significantly lower separation efficiency. DDA can dissolve IPA, but its affinity for IPA is not strong or selective enough to efficiently pull a large amount of IPA from the aqueous phase. IPA still has a strong tendency to remain dissolved in water. The hydrophobic nature of DDA means that it does not contribute to the salting-out effect of water. Its contribution is solely its miscibility with IPA driven by a combination of hydrophobic and hydrogen-bonding interactions, and this mechanism proved to be inefficient for the effective phase separation of IPA from water compared with the strong ionic effects of salts. In fact, the experiment with DDA at 60 wt% IPA did not result in phase separation at all. The small amount of dissolved DDA (5% or 7.5%) did not induce a well-defined phase separation.

In order to check whether inorganic salts and DDA were present in both phases, the FTIR spectra of both phases were recorded (Figures 9–13). In the organic phase spectra, an increase in the intensity of the peaks characteristic of IPA and a decrease in the intensity of the peaks characteristic of water can be observed compared with the spectra of the feed mixtures. No bands specific for carbonates (Na_2CO_3 [45] and K_2CO_3 [46]) or Na_2SO_4 [47] were detectable in the spectra of the IPA-rich phase. The band characteristic of the S–O stretching of the thiosulfate anion is seen at 1011.89 cm^{-1} in the IPA-rich phase spectra, indicating the solubility of $Na_2S_2O_3$ [48] in both phases. Bands characteristic of DDA were not detected in the aqueous phase spectra. To confirm the results obtained by FTIR analysis, ^1H NMR spectra were recorded, as the bands characteristic of DDA may overlap with the peaks of the initial mixture. The spectra obtained confirmed the solubility of DDA only in the IPA-rich phase (Figure 14).

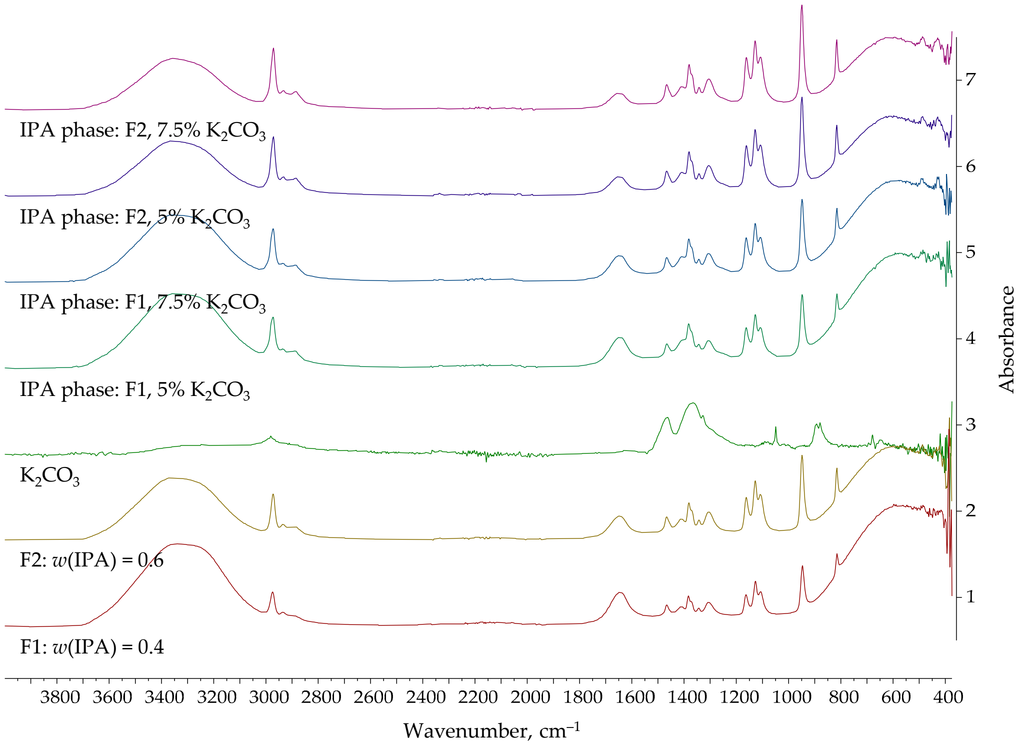

Figure 9. FTIR spectra of feeds, K_2CO_3, aqueous, and 2-propanol (IPA)-rich phases.

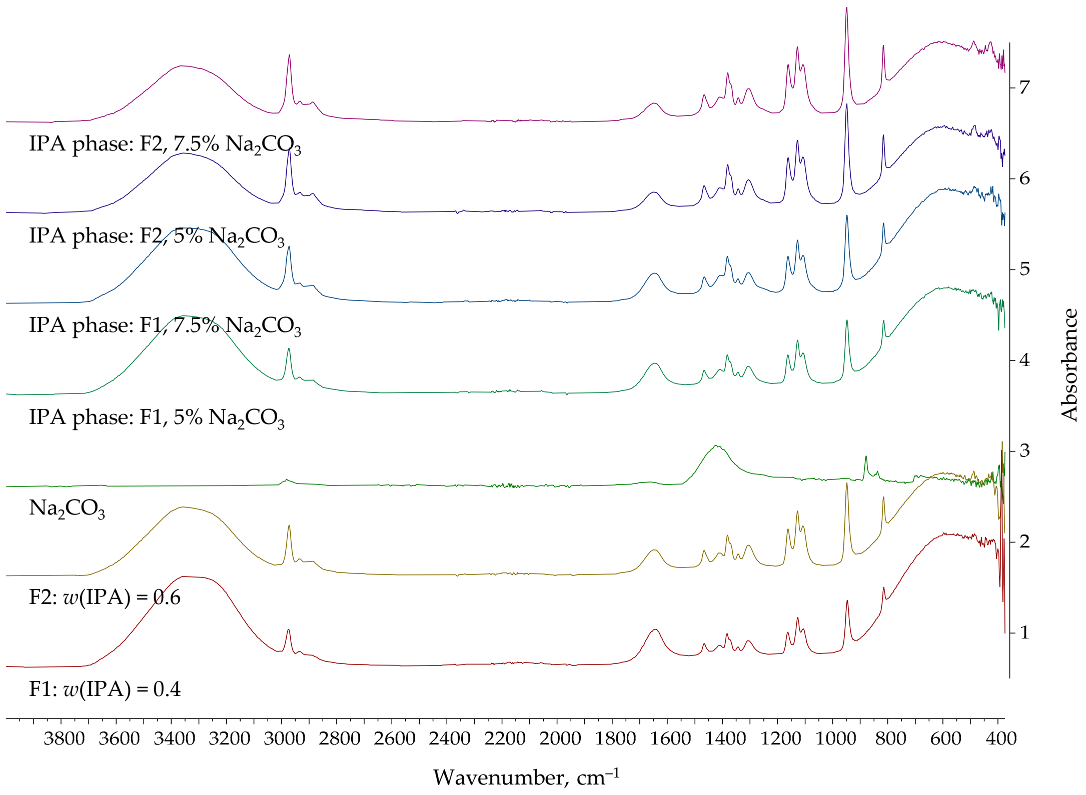

Figure 10. FTIR spectra of feeds, Na_2CO_3, aqueous, and 2-propanol (IPA)-rich phases.

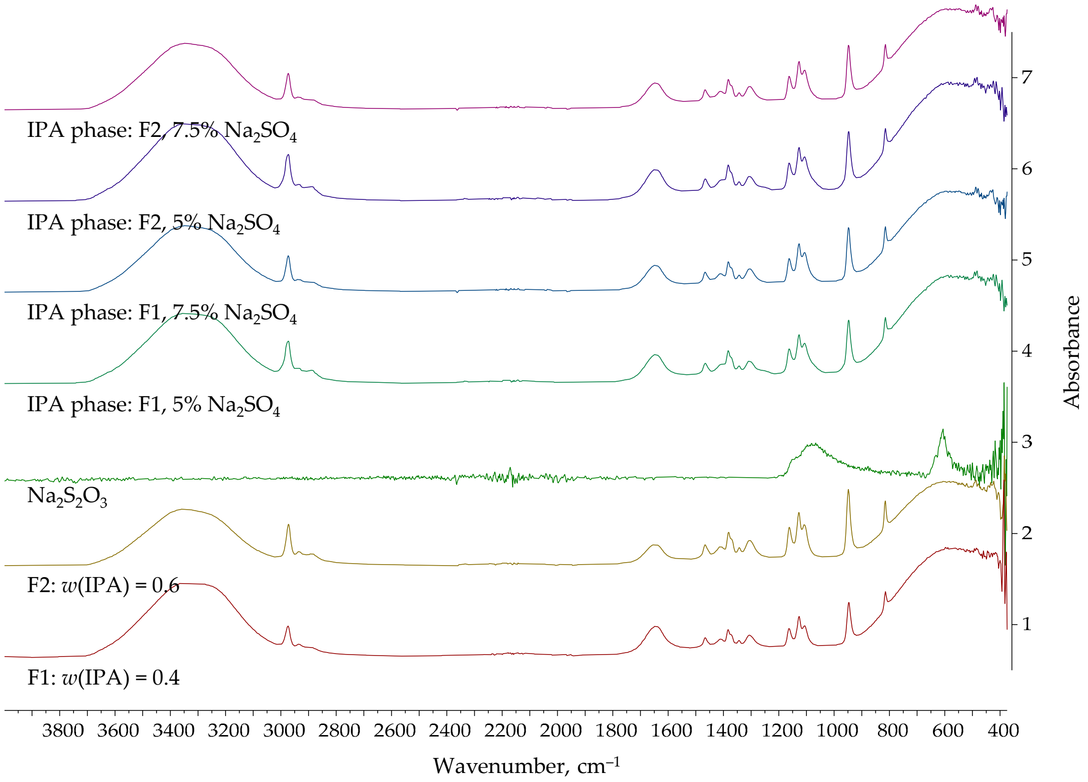

Figure 11. FTIR spectra of feeds, Na_2SO_4, aqueous, and 2-propanol (IPA)-rich phases.

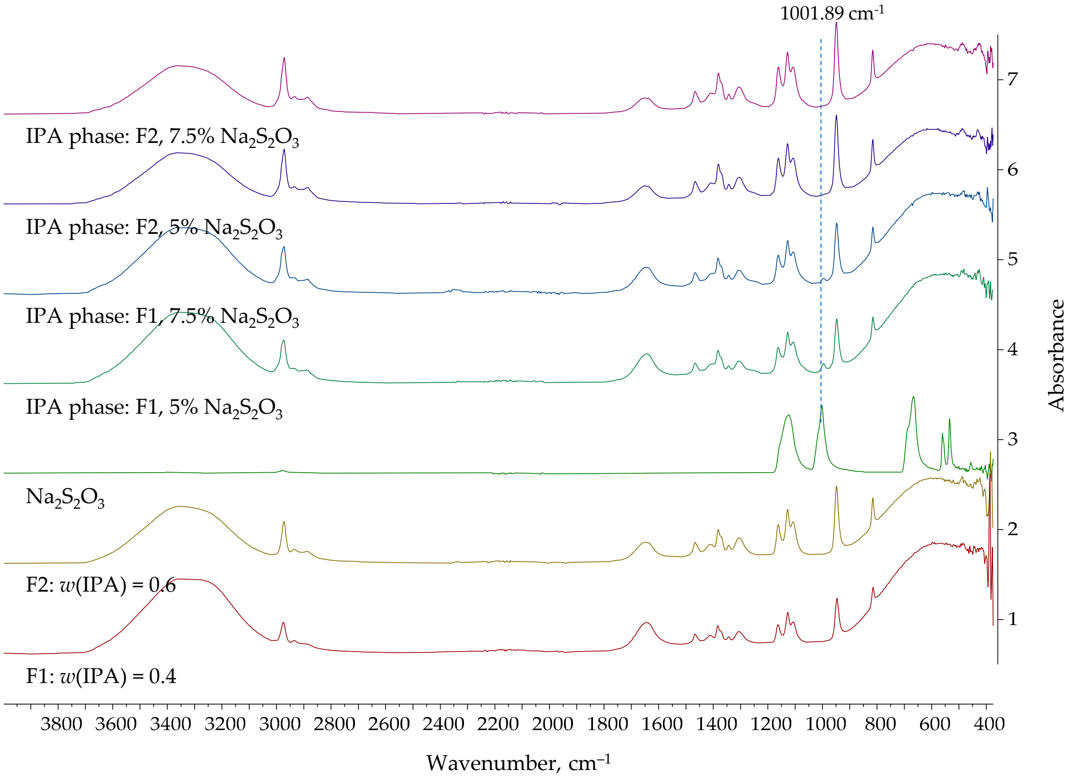

Figure 12. FTIR spectra of feeds, $Na_2S_2O_3$, aqueous, and 2-propanol (IPA)-rich phases.

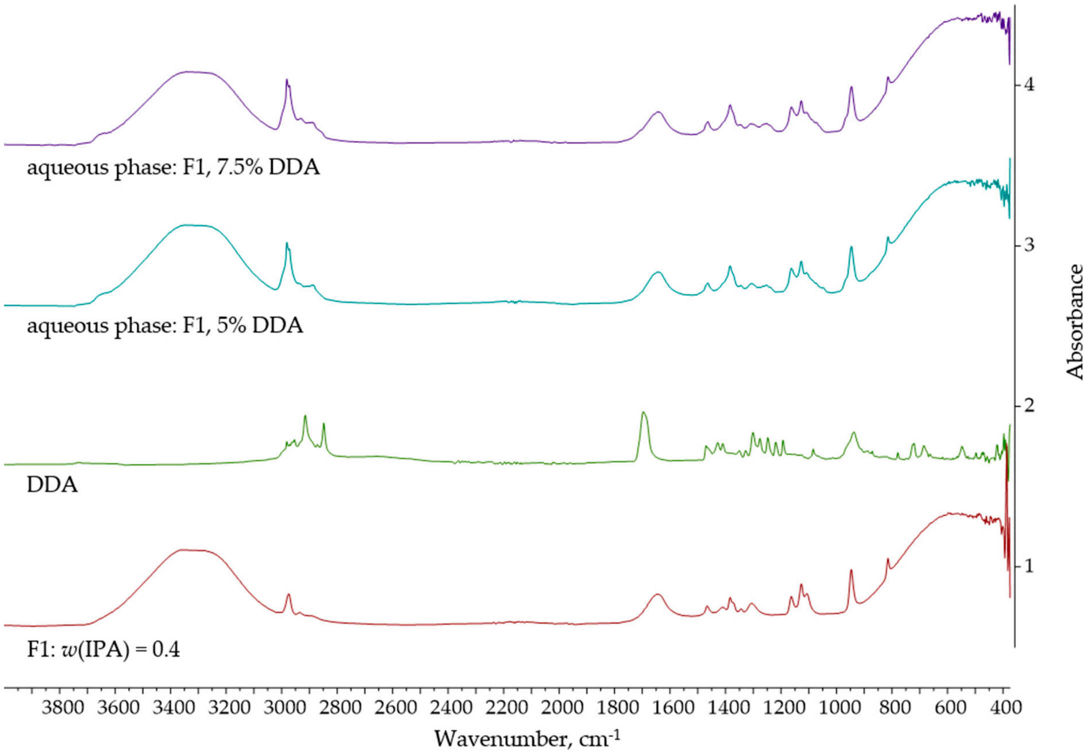

Figure 13. FTIR spectra of feed, dodecanoic acid (DDA), aqueous, and 2-propanol (IPA)-rich phases.

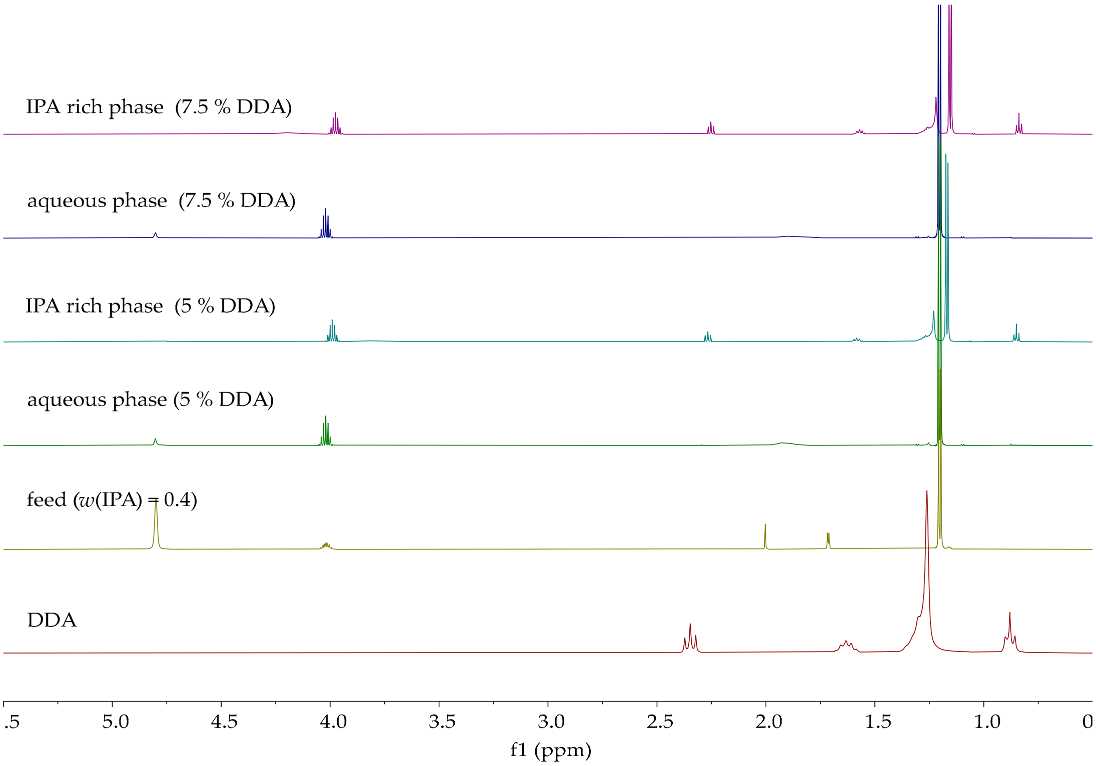

Figure 14. ^{1}H NMR spectra of feed, dodecanoic acid (DDA), aqueous, and 2-propanol (IPA)-rich phases.

4. Conclusions

In this article, the separation of IPA–water mixtures was studied, using DESs for extractive distillation and liquid–liquid extraction as well as various solid compounds for salting-out.

Simple distillation and extraction experiments were performed and compared with the COSMO-RS model predictions. Regarding extractive distillation with pure multivalent alcohols, neither ethylene glycol nor glycerol was found to affect relative volatility and related quantities, both with experiments and calculations, despite the fact that EG is often quoted as the “efficient entrainer” for the studied system. Although the separation efficiency is slightly higher when DESs are used as entrainers, it can be concluded that the selected solvents were not effective for the separation of IPA and water by extractive distillation in the investigated experimental setup.

Regarding LLE experiments and separation by extraction, four hydrophobic DESs were tested to check their performance. The thermodynamic model used successfully predicted the general shapes of the experimental phase diagrams but failed in predicting the experimentally confirmed order of DES efficiencies. Extract phases were found to be richer in IPA than feed solution, and the used DESs were proven, by ^{1}H NMR, not to dissolve in the raffinate phases. The problems of reusability of the extractants and multistage extraction are tackled as well. However, the conclusions are not definite there, and the downstream separation of the extract is about to be conceived too.

As for the salting-out experiments, 16 candidates were tested, both inorganic salts and organic compounds. The predictions of the COSMO-RS model were interesting, however, not in accordance with the experimental findings for inorganic salts, probably due to an inadequate or non-existing description of ion solvation (hydration) and salt hydrolysis. Five salting-out agents were found to induce LLE phase separation in the desired composition range. However, dodecanoic acid exhibited an effect that was rather poor and acting contrary to the intention. Among the four inorganic salt-based entrainer candidates, sodium carbonate was found to be the best, which was confirmed by COSMO-RS model predictions too. The desired composition of the separate liquid phases was confirmed by FTIR and ^{1}H NMR.

The potential employment of DESs in industrial extraction and/or extractive distillation processes remains untested, particularly regarding their long-term stability and environmental implications. Additional investigation into alternative hydrophilic and hydrophobic DES combinations may reveal novel prospects for enhancing separation procedures.

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Abbreviations

The following abbreviations are used in this manuscript:

ATPS	aqueous two-phase system
CAS	Chemical Abstracts Service
ChCl	choline chloride
COSMO-RS	conductor-like screening model for real solvents
DA	decanoic acid
DDA	dodecanoic acid
DES	deep eutectic solvent
DMSO	dimethyl sulfoxide
EG	ethylene glycol
[EMIM][BF$_4$]	1-ethyl-3-methylimidazolium tetrafluoroborate
[EMIM][DCA]	1-ethyl-3-methylimidazolium dicyanamide
FTIR	Fourier-transform infrared spectroscopy
Gly	glycerol
HBA	hydrogen bond acceptor
HBD	hydrogen bond donor
HDES	hydrophobic deep eutectic solvent
HPLC	high-performance liquid chromatography
NMR	nuclear magnetic resonance spectroscopy
IPA	2-propanol (isopropanol)
LLE	liquid–liquid equilibria
M	menthol
NRTL	non-random two-liquid activity coefficient model
O	1-octanol
PHI-IR	partial heat-integrated intermediate evaporator
T	thymol
TAC	total annual cost
VLE	vapor–liquid equilibria

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