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## Extraction of butanol and acetonitrile from aqueous solution using carboxylic acid based deep eutectic solvents

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### Abstract

The performance of three hydrophobic carboxylic acid based Deep Eutectic Solvents were evaluated for the extraction of 1-butanol and acetonitrile from aqueous solution. To do so, the phase diagrams of five ternary systems {[DL-menthol: lauric acid] + water + 1-butanol}, {[DL-menthol: capric acid] + water + 1-butanol}, {[DL-menthol: capric acid] + water + acetonitrile}, {[TBAMBr: capric acid] + water + 1-butanol} and {[TBAMBr: capric acid] + water + acetonitrile} were measured at 298.15 K at atmospheric pressure. Liquid-liquid equilibria data were used to determine distribution coefficient ( $\beta$ ) and selectivity ( $S$ ) of the solvents. It was found that DL-menthol based DESs is of interest for the extraction of 1-butanol and acetonitrile. NRTL and UNIQUAC models provide a good representation of the phase diagrams measured in this work. COSMO-RS enables to predict phase diagrams of systems containing DL-menthol based Deep Eutectic Solvents with good accuracy.

### Keywords

Deep eutectic solvent; Liquid-liquid equilibria; Extraction; COSMO-RS.

## **Introduction**

The exponential concern of scientists about the environmental issues highly pushed the development of new green solvents. In the early 2000s, the scientific community concentrated its research on ionic liquids (ILs), which also made it possible to demonstrate the high potential of these solvents in numerous industrial applications. Their specific properties enable their use in processes in a large range of temperature and the reduction of atmospheric pollution to almost zero. Promising results were observed with the use of ILs as electrolytes in Lithium-ion batteries [1], as corrosion inhibitors in different industries [2], as components of dye-sensitized solar cells [3] and as solvents for the greenhouse gases capture [4,5] as well as for the extraction of organic or inorganic compounds [6–10]. The high cost of ILs and their toxicity have restricted their industrial applications.

These last decades, scientists have focused their efforts on developing new green generation of solvents. Deep eutectic solvents (DESs) are easily produced by mixing at least two components which have the ability to form hydrogen bonds. Components of DESs are hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD). Abbott et al. [11] used the term of DES for the first time to explain the production of a liquid eutectic mixture from two solid compounds. The physico-chemical properties of DESs are quite similar to those observed with ILs. Moreover, the synthesis of these solvents is easy and fast. A long list of DESs based on natural products and presenting a high biodegradability and a low toxicity can be developed [12–14]. DESs were found to be efficient in numerous and diverse applications such as separation processes [15–20], organic synthesis [21–26], analytical chemistry [27,28] or biomass pretreatment [29–32]. Hydrophobic DESs (HDESs) were developed for the wastewater treatment. [33] Most HDESs are constituted of monoterpene or tetraalkylammonium as Hydrogen bond acceptor. Due to their low viscosity, monoterpene based HDESs are preferred in separation processes. A study on menthol based DESs shows that the extracting power of the

solvent is directly related to its polarity. A HDES constituted of menthol and levulinic acid has a high capacity for extracting phenolic compounds and flavonoids. [34] The extraction efficiency of phytocannabinoid extraction using DES (DL-menthol + acetic acid) is superior to those of conventional solvents. [35]

The solubility of water in HDESs based on DL-menthol and acids measured between 0.15% and 1% is lower than other HDESs [36]. The hydrophobicity increases with an increase of the alkyl chain length of the acid. The weak hydrogen bond observed in DL-menthol + carboxylic acid mixtures leads to HDESs presenting low viscosity (<100cP) and density lower than water [36]. The efficiency of DESs based on DL-menthol and carboxylic acids were evaluated on the extraction of alcohols [37], aromatics [38], pesticides [36,39] or metals such as Co, Zn, Ni, Mn or Li [40–42] from aqueous solutions. The development of separation processes for the extraction of high value compounds from biomass looks promising from recent studies [43–45].

Organic solvents such as acetonitrile or 1-butanol are strongly used in separation processes due to their selective miscibility. Due to its toxicity, acetonitrile has to be removed from aqueous waste.[46] Nevertheless, classical distillation of the binary system {water + acetonitrile} is not possible while the mixture presents an azeotrope. This last decade, the production of alternative biofuels such as biobutanol has attracted attention even though it suffers from the lack of efficient processes to separate butanol from fermentation broth.[47]

In the present work, three hydrophobic DESs constituted of DL-menthol or tetrabutylammonium bromide (TBAMBr) and a carboxylic acid (capric acid or lauric acid) were studied in order to evaluate their efficiency in liquid-liquid extraction of acetonitrile or 1-butanol from an aqueous solution. More precisely, phase diagrams of five ternary systems:

{ [DL-menthol : lauric acid ] + water + 1-butanol }, { [DL-menthol : capric acid ] + water + 1-butanol }, { [DL-menthol : capric acid ] + water + acetonitrile } , { [TBAMBr :capric acid ] + water + 1-butanol } and { [TBAMBr : capric acid ] + water + acetonitrile } were experimentally established. In this study, it must be pointed out that a DES, a mixture of two components, is defined as a pseudo-compound. Furthermore, the obtained experimental results were represented using NRTL and UNIQUAC thermodynamic models. Finally, the performance of COSMO-RS was also used to predict phase diagrams of the ternary systems studied in this work.

## **1. Experimental details**

### **1.1. Chemicals**

Tetrabutylammonium bromide ( $N_{4444}\text{-Br}$ ,  $\geq 99.0\%$ ), DL-menthol ( $C_{10}H_{20}O$ ,  $\geq 95.0\%$ ), capric acid ( $C_{10}$ ,  $\geq 98.0\%$ ), lauric acid ( $C_{12}$ ,  $\geq 98.0\%$ ), 1-butanol ( $C_4H_{10}O$ ,  $\geq 99.9\%$ ) and acetonitrile ( $CH_3CN$ ,  $\geq 98.0\%$ ), were supplied by Sigma-Aldrich. Before use, tetrabutylammonium bromide and DL-menthol were dried under vacuum at a temperature of 333.15 K for at least 24 h. Capric acid, lauric acid, 1-butanol and acetonitrile were used without further purification.

### **1.2. Synthesis of the hydrophobic DESs**

The three hydrophobic DESs (tetrabutylammonium bromide: capric acid), and (DL-menthol: capric acid), (DL-menthol : lauric acid) at molar ratios [1:2], [2:1] and [2:1 ] respectively were prepared by heating the [HBA: HBD] mixtures at 333.15 K, under a magnetic stirrer.

A homogeneous transparent liquid was obtained for the DL-menthol based DESs and a clear liquid was observed for the (TBAMBr) based DES. DESs ratios are shown in Table 1.

### **1.3. LLE Measurements**

The procedure for the determination of LLE was fully described in our previous works [9,48]. All of the aqueous samples containing 1-butanol and acetonitrile were prepared with ultrapure water. Precise amounts of aqueous solution and DES were introduced into a jacketed glass cell and the mixture was stirred during 24h. The experimental temperature was maintained constant at 298.15 K ( $\pm 0.02$  K) using a thermostatic bath Polystat 37 from FisherScientific. The temperature is measured using a Pt 100 with a calibration certificate supplied by Avantec. The compositions of the water-rich and the DES-rich phases were determined by gas chromatography (GC). An internal standard butan-2-one was added to the samples. The GC operating conditions used to quantify organic compounds or water contents are given in Tables 2 and 3. All experiments were repeated at least three times. The estimated uncertainties in the determination of mole fraction were 0.004.

## 2. Results and discussion

### 2.1. Experimental LLE data.

Experimental LLE data measured at 298.15 K for five ternary systems: {[DL-menthol : lauric acid] + water + 1-butanol}, {[DL-menthol: capric acid] + water + 1-butanol}, {[DL-menthol : capric acid] + water + acetonitrile} , {[TBAMBr :capric acid] + water + 1-butanol} and {[TBAMBr : capric acid] + water + acetonitrile} are given in Tables 4-5. LLE phase diagrams are shown in Figures 1 to 5. In order to check the reproducibility of the experimental results, the Othmer-Tobias [49] and Bachman [50] equations were applied. These two equations are respectively given by:

$$\ln\left(\frac{1-x_3^{\text{DES}}}{x_3^{\text{DES}}}\right) = a + b \ln\left(\frac{1-x_1^{\text{Aq}}}{x_1^{\text{Aq}}}\right) \quad (1)$$

$$x_2 = c + d \left(\frac{x_2^{\text{DES}}}{x_1^{\text{Aq}}}\right) \quad (2)$$

where subscripts 1, 2 and 3 stand for water, the solute (1-butanol or acetonitrile) and the DES, respectively. The values of the regressed parameters ( $a, b, c, d$ ) of equations 1 and 2 and of the coefficient of determination ( $R^2$ ) are reported in Table 6. The degree of the consistency of the LLE measurements are confirmed by the linearity of the plot. It can be noticed that  $R^2$  values are close to unity, which indicates a satisfactory reliability of the obtained data.

The ternary systems {DES + water + acetonitrile} have only one miscibility gap observed on the {Water + DES} binary system. Both systems have substantially the same amounts of DES in the aqueous solution. On the other hand, the properties of the hydrogen bond acceptor have a significant impact on the amount of water present in the DES phase. In this study, (TBAMBr) based DES present a lower miscibility gap than those observed with DL-menthol based DESs. In other words, the DES-rich phase contains a significant part of water. This will have a financial impact during the recycling of the DES since it requires more energy for the purification of the solvent before its reinjection in the extraction process. The ternary systems {DES + water + 1-butanol} present two miscibility gaps due to the low solubility of both 1-butanol and the DESs in water. In Figure 5, LLE data obtained with {DES3 + water + 1-butanol} are compared with those published by Verma and Banerjee [37]. Both sets of data are in good agreement. An increase of the acid carboxylic chain length increases the hydrophobicity of DESs. Replacing capric acid with lauric acid in DL-menthol based DES enables to reduce the DES molar fraction in the aqueous phase from 0.021 to 0.005 and the water molar fraction in the DES rich phase from 0.165 to 0.151. Solubility of water in DL-menthol based DESs are in good agreement with those measured by Martin et al. [51]. Indeed, the authors found a solubility of water in term of molar fraction of 0.148 (0.151 in this work) and 0.157 (0.165 in this work) in DESs 3 and 2, respectively.

The extraction efficiency can be evaluated through the distribution coefficient and the selectivity. The values of solute (1-butanol or acetonitrile) distribution coefficient  $\beta$  and selectivity  $S$ , reported in Tables 2 and 3, were calculated according to the equations 3 and 4:

$$\beta_i = \frac{x_i^{\text{DES}}}{x_i^{\text{Aq}}} \quad (3)$$

$$S = \frac{\beta_1}{\beta_2} \quad (4)$$

where  $x$  is the mole fraction of component  $i$  in the aqueous phase (Aq superscript) and in the DES-rich phase (DES superscript). Subscripts 1 and 2 stand for 1-butanol or acetonitrile and water, respectively. In order to obtain an efficient extraction, values of solute distribution coefficient have to be greater than 1. The trends of the solute distribution coefficient  $\beta$  and selectivity  $S$  versus the solute mole fraction are given in Figures 6 and 7. In the case of the extraction of 1-butanol from water, the selectivity values vary from 0.88 to 21.71, 111 to 979 and 14 to 708 for DES 1, DES 2 and DES 3, respectively. The distribution ratio values are found to be between 0.46 to 9.42, 24.66 to 138.07 and 6.31 to 99 for DES 1, DES 2 and DES 3, respectively. An analysis of data listed in tables 4 and 5 allows to conclude that the distribution ratio and selectivity values of DL-menthol based DESs are more important than those obtained with (TBAMBr) based DESs for the extraction of 1-butanol. Moreover, the efficiency of DESs in the extractions decreases with the increase of the alkyl chain length of the carboxylic acid. Table 7 gives the values of mass  $\beta$  et and  $S$  obtained at 298.15 K for the extraction of 1-butanol from aqueous solution using ionic liquids and traditional solvents [47,52–56]. In the case of ILs, the selectivity values and distribution coefficients are between 2.6 and 500 and 0.7 and 21, respectively. DESs 2 and 3 show remarkable efficiency for the extraction of 1-butanol while their  $\beta$  and  $S$  values are high. In table 8, distribution coefficient and selectivity observed with

DESs studied in this work and organic solvents for the extraction of acetonitrile from aqueous solution are presented [57–60]. The selectivity and distribution coefficient values of DES 1 are better than those calculated for DES 3. Their efficiency is close to alcohols or heptanoic acid but it still remains lower than aromatics.

## 2.2. Liquid-Liquid Equilibria Data correlation.

The LLE data of the investigated ternary systems were correlated using the Nonrandom Two-Liquid equation (NRTL) [61] and the universal quasi-chemical (UNIQUAC) models [62]. Interaction parameters and results are given in Tables 9 and 10.

### 2.2.1. NRTL Model

$$\ln \gamma_i = \frac{\sum_{j=1}^m x_j \tau_{ji} G_{ji}}{\sum_{k=1}^m x_k G_{ki}} + \sum_{j=1}^m \frac{x_j G_{ij}}{\sum_{k=1}^m x_k G_{kj}} \left( \tau_{ij} - \frac{\sum_{k=1}^m x_k \tau_{kj} G_{kj}}{\sum_{k=1}^m x_k G_{kj}} \right) \quad (5)$$

$$\text{with } G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \text{ and } \tau_{ij} = \frac{\Delta g_{ij}}{RT} = \frac{g_{ij} - \Delta g_{jj}}{RT} \quad (6)$$

Here,  $\Delta g_{ij}$  is the energy parameter characterizing the interaction between component  $i$  and  $j$ .

$\alpha_{ij} = \alpha_{ji} = \alpha$ . In this work, the non randomness parameter  $\alpha$  is taken equal to 0.3.

### 2.2.2. UNIQUAC Model

In the UNIQUAC Model, the activity coefficient for any component  $i$  in the mixture,  $\gamma_i$ , is given by:

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^m x_j l_j - q_i \ln (\theta_j \tau_{ji}) + q_i - q_i \sum_{j=1}^m \frac{\theta_j \tau_{ji}}{\sum_{k=1}^m \theta_k \tau_{kj}} \quad (7)$$

$$\text{Where } \Phi_i = \frac{r_i x_i}{\sum_{j=1}^m r_j x_j}, \theta_i = \frac{q_i x_i}{\sum_{j=1}^m q_j x_j}, l_j = \frac{z}{2} (r_j - q_j) - (r_j - 1) \text{ and } \tau_{ji} = \exp \left( \frac{-\Delta u_{ij}}{RT} \right) \quad (8)$$

Here, the lattice coordination number  $z$  is equal to 10. The molecular surfaces,  $q_i$ , and the molecular van der Waals volumes,  $r_i$  of the pure component  $i$  are calculated as the sum of the group volume and group area parameters  $R_k$  and  $Q_k$ :

$$r_i = \sum_k v_k^i R_k \text{ and } q_i = \sum_k v_k^i Q_k \quad (9)$$

where  $v_k^i$  is the number of groups of type  $k$  in molecule  $i$ . The group parameters  $R_k$  and  $Q_k$  are obtained from van der Waals group volumes and surface areas,  $V_k$  and  $A_k$  taken from the UNIFAC group contributions [63]:

$$R_k = \frac{V_k}{15.17} \text{ and } Q_k = \frac{A_k}{2.5 \times 10^9} \quad (10)$$

Values of  $r_i$  and  $q_i$  used in the UNIQUAC equation are listed in Table 11. Parameters of carboxylic acids are taken from the literature [64].

Binary interaction parameters for both thermodynamic models are determined by minimizing the function (11):

$$F_{obj} = \sum_{k=1}^N \sum_{i=1}^3 \left\{ (x_i^{\text{Aq,exp}} - x_i^{\text{Aq,cal}})^2 + (x_i^{\text{DES,exp}} - x_i^{\text{DES,cal}})^2 \right\} \quad (11)$$

where  $N$  is the number of experimental points and  $x_i^{\text{Aq,exp}}$ ,  $x_i^{\text{Aq,cal}}$  are the experimental and calculated mole fractions. Aq and DES stand for aqueous phase and DES -rich phase, respectively. The binary interaction parameters and root mean-square deviation (rmsd) calculated using equation 12 are given in Tables 9 and 10.

$$rmsd = \sqrt{\frac{\sum_{k=1}^N \sum_{i=1}^3 \{(x_i^{\text{HC,exp}} - x_i^{\text{HC,cal}})^2 + (x_i^{\text{IL,exp}} - x_i^{\text{IL,cal}})^2\}}{6N}} \quad (12)$$

### 2.2.3. Conductor-like Screening model for Real solvent (COSMO-RS)

The Conductor-like Screening Model for Real Solvents (COSMO-RS) approach developed by Klamt and Eckert [65–67] was used to represent the phase diagrams of the ternary systems studied in this work. COSMO models were found to be suitable tools to predict thermodynamic properties and phase equilibrium for the pure fluids and their mixtures. Indeed, COSMO-RS has been previously used to predict the thermodynamic behavior of systems containing ionic liquids [68–70] or DESs [71,72]. Phase diagrams of pseudo-ternary systems were predicted using the COSMOtherm software, version C30. The LLE calculations were performed using the BP\_TZVP\_C30\_1601 parameterization in the COSMOtherm software [73]. In this work, DESs were represented using the electroneutral approach. Phase diagrams obtained with COSMO-RS and experimental data are plotted in Figures 1-5. Phase diagrams of {water + 1-butanol + DL-menthol based DESs} ternary systems are predicted with good accuracy with COSMO-RS and a ARD of less than 10% is obtained. Two miscibility gaps for the {water + acetonitrile +DES2} ternary system are predicted by COSMO-RS. Predicted values for low acetonitrile concentrations follow the same trend than experimental data but the observed ARD is larger than 20%. Larger deviations are observed with DES1. Zawadski et al [59] show that LLE containing ILs were well predicted when the ions of the ILs are both hydrophobic or

hydrophilic. Our results seem to follow the same trend. Indeed, COSMO-RS predicts with good accuracy the phase diagrams of systems containing DESs constituted of hydrophobic components such as DL-menthol with a carboxylic acid. This is not the case of DESs containing a hydrophilic component (TBAMBr) and a hydrophobic component (carboxylic acid).

Sigma profiles represent the probability of finding a surface segment of charge density  $\sigma$  in the studied component (Figure 8). In particular, atoms with negative polarities such as oxygen end up surrounded by positive charge densities  $\sigma$ , and will likely display peaks in the positive area of the sigma profile. And vice versa for polar atoms. Additionally, sigma potentials account for how much a component 'likes' and is attractive for a molecular surface of polarity sigma (see Figures 9-11). The more negative the potential is, the stronger the attraction is.

Water has a very wide and almost symmetrical sigma profile. It comprises one peak in each hydrogen bonding region. The symmetry of this profile concurs with the fact that water likes itself and is a solvent with a high boiling temperature. The sigma potential presents a flat region surrounded by curves with high slope (and negative values). It indicates that hydrogen bonds are possible in these regions. For sigma values over  $0.01 \text{ e.A}^{-2}$ , the solvent (in this case water) has a high affinity with surface of positive sigma values, i.e. hydrogen bonds acceptors, and conversely for surface of sigma values under  $-0.01 \text{ e.A}^{-2}$  and hydrogen bonding donors.

Decanoic and dodecanoic acids have very similar sigma profiles. They display a high peak centered on 0 because of the alkyl chain. The peak in the hydrogen bond donor area is smaller than the one of water ( $\sigma < -0.01 \text{ e.A}^{-2}$ ). They also have a peak in the hydrogen bond acceptor area. Their sigma potentials are lower than water one at  $\sigma = 0$ , which is congruent with the fact that they are less lipophobic than water. They also have more affinity than water for hydrogen bond acceptors but are less attracted by hydrogen bond donors.

In the hydrogen-bond donor area of the sigma profile of the 1-butanol, there is a peak about half the one of water in term of height. The hydrogen-bond acceptor peak is around the same polarity as the water one but at a higher polarity than the peaks of the two acids. Regarding the sigma potential, in the area displaying how attractive the solvent is for acceptors the values are higher than the values of the potential of water. A 1-butanol molecule does not desire as many acceptors as a water one would since water has twice the number of hydrogen atoms susceptible to undergo hydrogen bonds. Thus, the alcohol requires stronger acceptors.

DL-menthol peaks are similar to the ones of 1-butanol. The shape of the sigma potential is also similar to the one of the other alcohol. In particular, it indicates that menthol and 1-butanol can perform hydrogen bonds with the acids: the acid will provide the hydrogen which will form a bond with the oxygen of the alcohol. This matches the descriptions of DESs provided by Ribeiro et al. [36] and Krizek et al. [35] in which menthol plays the role of hydrogen bond acceptor and acids are the hydrogen bond donors.

The molecule of acetonitrile has an asymmetric sigma profile. The nitrogen causes a peak around  $0.01 \text{ e.A}^{-2}$ . The three hydrogen atoms generate the peak at  $-0.01 \text{ e.A}^{-2}$  while the carbon atoms are responsible for the peak closer to 0. This asymmetry implies that acetonitrile molecules cannot interact as efficiently as water can with itself. The nitrogen atom lacks more fitting polar hydrogen atoms to interact with. Thus, the boiling point of acetonitrile is lower than the one of water. The asymmetry is also notable in the sigma potential. It leads to acetonitrile being attractive for strong hydrogen donors but non attractive for acceptors.

Tetrabutylammonium sigma profile presents two peaks, one involving the hydrogen atoms around  $-0.003 \text{ e.A}^{-2}$  and one at  $0.002 \text{ e.A}^{-2}$  because of the nitrogen atom, very close to 0 in accordance with the fact that the nitrogen cannot perform hydrogen bonds. The sigma potential is an off-centred parabola. This suggests a better affinity for surface of null polarity.

The sigma profile of the bromide anion shows a single narrow peak at 0.018 e.A<sup>-2</sup>. Both sigma profile and sigma potential suggest that the anion is a good acceptor of hydrogen bonds. This is consistent with the anion of the tetrabutylammonium bromide forming a hydrogen bond with capric acid within the DES mixture [74].

#### **4. Conclusions**

This paper presents phase diagrams of ternary systems composed of {water + acetonitrile or 1-butanol + DES}. Results indicate that menthol based DESs are particularly efficient for the extraction of 1-butanol or acetonitrile. Their performance is better than most ILs while the obtained distribution coefficients are 10 to 20 times more important than ILs. Moreover, they present the highest selectivity. The efficiency of the DES composed of tetrabutylammonium bromide and decanoic acid is very low compared to menthol based DESs and functionalized ILs. NRTL and UNIQUAC models enable to represent such ternary systems with high accuracy. COSMO-RS can predict with good accuracy ternary systems composed of menthol based DESs. In the case of TBAMBr based DESs, the solubility of water is overestimated and phase diagrams are not predicted with sufficient accuracy.

**Table 1.** DESs composition.

Abbreviation	HBAs	HBDs	Ratio (HBA:HBD)
DES 1	TBAMBr	Capric Acid	[1:2]
DES 2	DL-menthol	Capric Acid	[2:1]
DES 3		Lauric Acid	[2:1]

**Table 2.** GC operating conditions for the quantification of 1-butanol or acetonitrile in samples.

Element	Operation variable	Specification
Column	Type	CP-Wax 52 CB (New Agilent J&W))
	dimension	30m x 0.32mm x 0.5 $\mu$ m
	Carrier gas	Helium
	Gas flow rate	1 mL/min
Oven	Temperature	383.15 – 573.15 K at 10 K. min <sup>-1</sup>
Injector	Injected volume	0.1 $\mu$ L
	Split ratio	50
	Temperature	523.15 K
Detector	Type	Flame Ionisation Detector (FID)
	Temperature	523.15 K

**Table 3.** GC operating conditions for the quantification of water in samples.

Element	Operation variable	Specification
Column	Type	GSQ FILM THK. (J&W SCIENTIFIC)
	Dimension	30 m x 0.53 mm
	Gas flow rate	5 mL/min
	Carrier gas	Helium
Oven	Temperature	353.15 K-513.15 K at 10 K. min <sup>-1</sup>
Injector	Injected volume	5.0 $\mu$ L
	Split ratio	1
	Temperature	523.15 K
Detector	Type	Thermal Conductivity Detector (TCD)
	Temperature	523.15 K

**Table 4.** Experimental LLE data and Distribution Coefficients  $\beta$ , selectivity  $S$  for the ternary systems {DL-menthol DES (1) – water (2) – 1-butanol / acetonitrile (3)} at 298.15K and 0.1 MPa.

Aqueous-rich phase			DL-menthol DES-rich phase			$\beta$	$S$
{[DL-menthol : lauric acid ] (1) - water (2) – 1-butanol (3)}							
$x_1^I$	$x_2^I$	$x_3^I$	$x_1^{II}$	$x_2^{II}$	$x_3^{II}$		
0.005	0.995	0.000	0.849	0.151	0.000		
0.000	0.897	0.103	0.000	0.455	0.545		
0.026	0.973	0.001	0.765	0.136	0.099	99.00	708.29
0.026	0.972	0.002	0.747	0.138	0.115	57.50	405.00
0.03	0.966	0.004	0.62	0.156	0.224	56.00	346.77
0.032	0.961	0.007	0.514	0.169	0.317	45.29	257.51
0.029	0.962	0.009	0.486	0.162	0.352	39.11	232.25
0.029	0.954	0.017	0.445	0.154	0.401	23.59	146.12
0.027	0.95	0.023	0.402	0.158	0.44	19.13	115.02
0.023	0.936	0.041	0.201	0.269	0.530	12.93	44.98
0.011	0.901	0.088	0.062	0.383	0.555	6.31	14.84
{[DL-menthol : capric acid ] (1) - water (2) – 1-butanol (3)}							
0.011	0.989	0.000	0.835	0.165	0.000		
0.011	0.988	0.001	0.723	0.139	0.138	138.07	979.09
0.012	0.986	0.002	0.651	0.148	0.201	100.5	669.50
0.013	0.984	0.003	0.610	0.156	0.234	78.00	492.00
0.013	0.983	0.004	0.583	0.149	0.268	66.98	442.64
0.014	0.982	0.004	0.553	0.184	0.263	65.82	351.02
0.014	0.979	0.007	0.474	0.186	0.340	48.60	255.95
0.016	0.966	0.018	0.275	0.235	0.490	27.22	111.90
0.015	0.960	0.025	0.224	0.160	0.617	24.66	148.21
{[DL-menthol : lauric acid ] (1) - water (2) – acetonitrile (3)}							
0.005	0.995	0.000	0.849	0.151	0.000		
0.017	0.978	0.005	0.831	0.157	0.012	2.40	14.95
0.013	0.954	0.033	0.656	0.221	0.123	3.73	16.09
0.011	0.951	0.038	0.628	0.229	0.143	3.76	15.63
0.010	0.944	0.046	0.556	0.258	0.186	4.04	14.79
0.010	0.940	0.050	0.519	0.260	0.221	4.42	15.98
0.028	0.904	0.068	0.314	0.394	0.292	4.29	9.85

**Table 5.** Experimental LLE data and Distribution Coefficients  $\beta$ , selectivity  $S$  for the ternary systems {TBAMBr DES (1) – water (2) – 1-butanol or acetonitrile (3)} at 298.15K and 0.1 MPa.

Aqueous-rich phase			TBAMBr DES-rich phase			$\beta$	$S$
$x_1^I$	$x_2^I$	$x_3^I$	$x_1^{II}$	$x_2^{II}$	$x_3^{II}$		
{{TBAMBr :capric acid }} (1) - water (2) – 1-butanol (3)							
0.028	0.972	0.000	0.490	0.510	0.000		
0.025	0.967	0.008	0.487	0.509	0.004	0.46	0.880
0.018	0.965	0.020	0.422	0.455	0.123	6.18	13.12
0.023	0.960	0.016	0.403	0.452	0.145	8.89	18.89
0.020	0.961	0.019	0.388	0.432	0.180	9.50	21.15
0.018	0.960	0.022	0.379	0.423	0.197	8.98	20.37
0.017	0.960	0.023	0.367	0.417	0.217	9.42	21.71
0.018	0.959	0.023	0.361	0.415	0.224	9.76	22.57
0.017	0.955	0.028	0.324	0.409	0.267	9.52	22.21
0.015	0.948	0.037	0.210	0.386	0.404	10.93	26.85
0.010	0.916	0.074	0.044	0.372	0.583	7.88	19.40
0.011	0.901	0.088	0.024	0.359	0.617	7.01	17.60
{{TBAMBr : capric acid }} (1) - water (2) – acetonitrile (3)							
0.028	0.972	0.000	0.490	0.510	0.000		
0.029	0.966	0.005	0.470	0.510	0.020	4.00	7.58
0.028	0.960	0.012	0.409	0.538	0.053	4.42	7.88
0.025	0.956	0.019	0.384	0.541	0.075	3.95	6.98
0.023	0.948	0.029	0.351	0.553	0.096	3.31	5.67
0.037	0.915	0.048	0.180	0.703	0.117	2.44	3.17
0.037	0.918	0.045	0.168	0.722	0.110	2.44	3.11

**Table 6.** Othmer-Tobias and Bachman constants for the ternary systems studied in this work.

Ternary System	Othmer-Tobias			Bachman		
	a	b	$R^2$	c	d	$R^2$
H <sub>2</sub> O + 1-butanol + DES1	3.178	10.640	0.990	0.900	0.010	0.999
H <sub>2</sub> O + acetonitrile + DES1	1.528	4.110	0.982	0.905	0.003	0.997
H <sub>2</sub> O + 1-butanol + DES2	1.787	6.940	0.999	0.952	0.007	0.999
H <sub>2</sub> O + acetonitrile + DES2	1.530	4.110	0.985	0.906	0.005	0.999
H <sub>2</sub> O + 1- butanol + DES3	2.779	8.796	0.989	0.908	0.013	0.998

**Table 7.** Distribution coefficient ( $\beta$ ) and selectivity (S) of DESs and ILs obtained for the extraction of 1-butanol from aqueous solution.

Solvent	$\beta$	S	Ref.
DES 1	2.92	22.57	This work
DES 2	21.0	979	This work
DES 3	15.5	708	This work
DL-menthol + palmitic acid [12:1]	3.4	81.2	[52]
[Im10,1][TCB]	3.2	100	[53]
[P <sub>6,6,6,14</sub> ][TCB]	2.0	500	[53]
[MO <sub>10,1</sub> ][TCB]	4.8	70	[53]
[Im <sub>8,1</sub> ][FAP]	0.8	420	[53]
[Bmim][PF <sub>6</sub> ]	0.74	21.03	[47]
[Hmim][PF <sub>6</sub> ]	0.97	37.48	[47]
[Omim][PF <sub>6</sub> ]	1.11	49.23	[47]
[Im <sub>10,1</sub> ][Tf <sub>2</sub> N]	5.7	90	[54]
[MO <sub>10,1</sub> ][Tf <sub>2</sub> N]	2.1	99.7	[54]
[Bmim][Tf <sub>2</sub> N]	1.03	39.07	[47]
[Hmim][Tf <sub>2</sub> N]	1.25	66.12	[47]
[Omim][Tf <sub>2</sub> N]	1.37	78.89	[47]
[Hmim][TfO]	0.90	2.62	[47]
[N <sub>8,2,2,2</sub> ][Tf <sub>2</sub> N]	2.78	68.8	[56]
[N <sub>8,2,2,2</sub> ][Tf <sub>2</sub> N]	2.58	96.2	[56]
[DoMIM][Tf <sub>2</sub> N]	2.71	73.4	[56]
[C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> MIM][Tf <sub>2</sub> N]	1.94	55.1	[56]
[Omim][TfO]	1.03	3.56	[47]
[Pmim][TfO]	1.05	4.96	[47]
[HMIM]BF <sub>4</sub>	0.90	3.91	[47]
[OMIM][BF <sub>4</sub> ]	2.18	12.24	[47]
[Cyphos 104]	9.21	55	[55]
[MTOA][Oct]	11.29	49	[55]
[TDAMCH]	8.49	130	[55]
[TOAMNaph]	21	274	[55]

**Table 8.** Distribution coefficient ( $\beta$ ) and selectivity (S) of DESs and organic solvents obtained for the extraction of acetonitrile from aqueous solution.

Solvent	T/K	$\beta$	S	Ref.
DES 1	298.15	8	0.85	This work
DES 3	298.15	15	0.34	This work
1-butanol	303.15	4.96	1.27	[58]
2-Methylpropan-1-ol	303.15	5.81	1.25	[58]
n-propyl chloride	303.15	168	1.15	[59]
heptanoic acid	323.15	10.56	0.72	[57]
nonanone	323.15	10.25	0.47	[57]
benzene	298.15	315	2.17	[60]
toluene	298.15	298.8	1.7	[60]
m-xylene	298.15	419	0.3	[60]
ethylbenzene	298.15	1931	1.05	[60]

**Table 9.** Values of binary parameters for the NRTL equation for the ternary mixtures.

Ternary system	ij	$\Delta g_{ij}$ (J.mol <sup>-1</sup> )	$\Delta g_{ji}$ (J.mol <sup>-1</sup> )	rmsd
H <sub>2</sub> O (1) + 1-butanol (2) + DES1 (3)	12	7718	20654	0.0038
	13	10070	-528	
	23	8470	-900	
H <sub>2</sub> O (1) + 1-butanol (2) + DES2 (3)	12	7572	2409	0.0045
	13	8032	3460	
	23	-3795	5570	
H <sub>2</sub> O (1) + 1-butanol (2) + DES3 (3)	12	5852	1778	0.0091
	13	6428	3806	
	23	-1450	-1780	
H <sub>2</sub> O (1) + acetonitrile (2) + DES2 (3)	12	11520	-1032	0.0029
	13	9112	3048	
	23	10552	3392	
H <sub>2</sub> O (1) + acetonitrile (2) + DES1 (3)	12	13471	-3085	0.0020
	13	9521	-245	
	23	16931	2491	

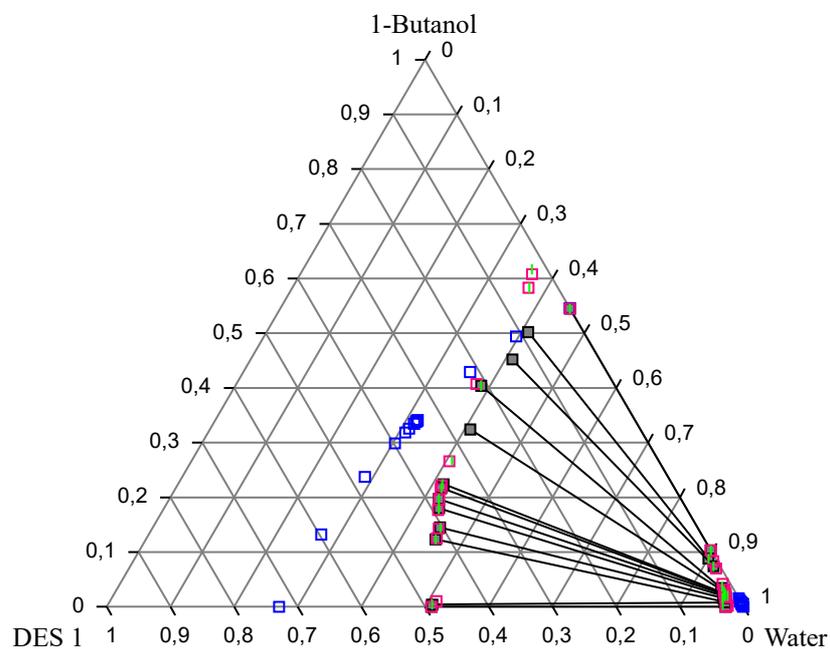
**Table 10.** Values of binary parameters for the UNIQUAC equation for the ternary mixtures.

System	ij	$\Delta u_{ij}$ (J.mol <sup>-1</sup> )	$\Delta u_{ji}$ (J.mol <sup>-1</sup> )	rmsd
H <sub>2</sub> O (1) + 1-butanol (2) + DES1 (3)	12	-385	3609	0.0133
	13	2632	460	
	23	2094	-778	
H <sub>2</sub> O (1) + 1-butanol (2) + DES2 (3)	12	448	3180	0.0120
	13	-504	5280	
	23	-920	2636	
H <sub>2</sub> O (1) + 1-butanol (2) + DES3 (3)	12	-42	2410	0.0205
	13	2228	2550	
	23	-640	1456	
H <sub>2</sub> O (1) + acetonitrile (2) + DES1 (3)	12	-4822	228	0.0036
	13	1428	1002	
	23	-2664	13205	
H <sub>2</sub> O (1) + acetonitrile (2) + DES2 (3)	12	1237	2649	0.0067
	13	-1102	6278	
	23	993	1747	

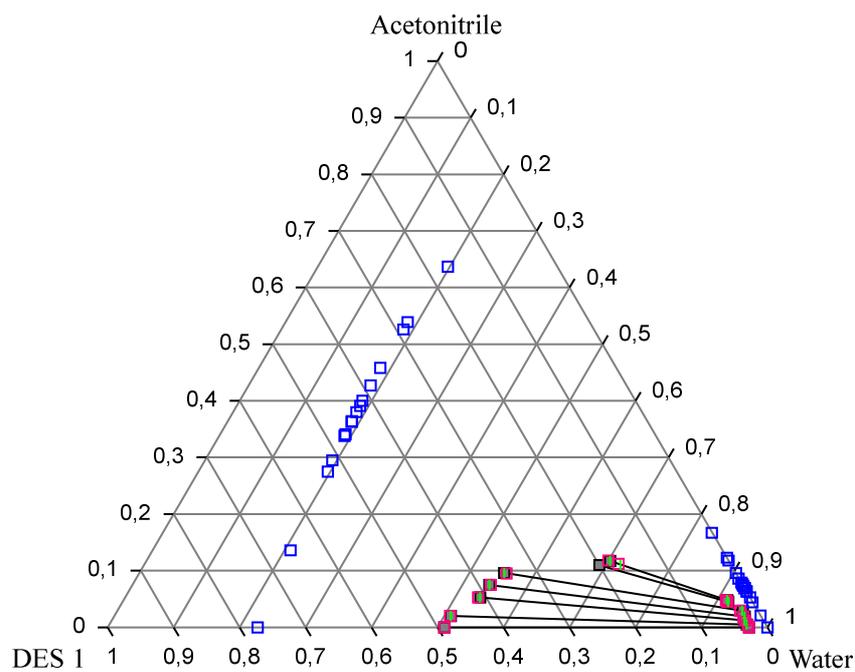
**Table 11.** UNIQUAC parameters of pure compounds and DESs.

Compounds	$r_i$	$q_i$
H <sub>2</sub> O	0.920	1.400
Capric acid	7.580	6.392
Lauric acid	8.932	7.472
DL-menthol	6.742	5.388
TBAMBr	15.930	14.023
DES 1	10.363	8.936
DES 2	7.021	5.722
DES 3	7.472	6.082
1-butanol	3.454	3.048
acetonitrile	1.870	1.724

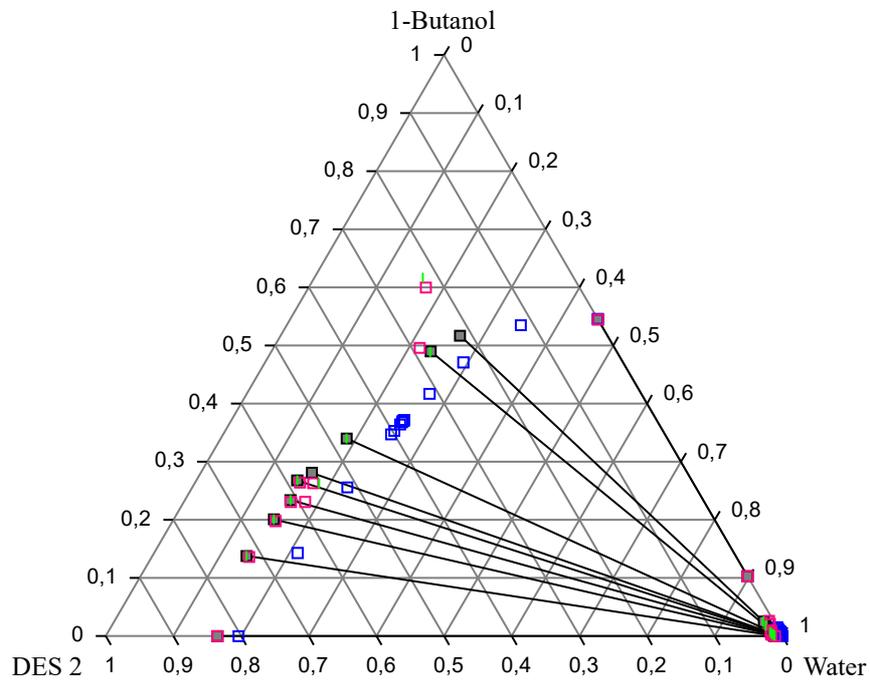
**Figure 1.** Results of the prediction in the ternary system {water + 1-butanol + DES1}. ■, Experimental bimodal curve; □, COSMO-RS model; □, NRTL model; |, UNIQUAC model.



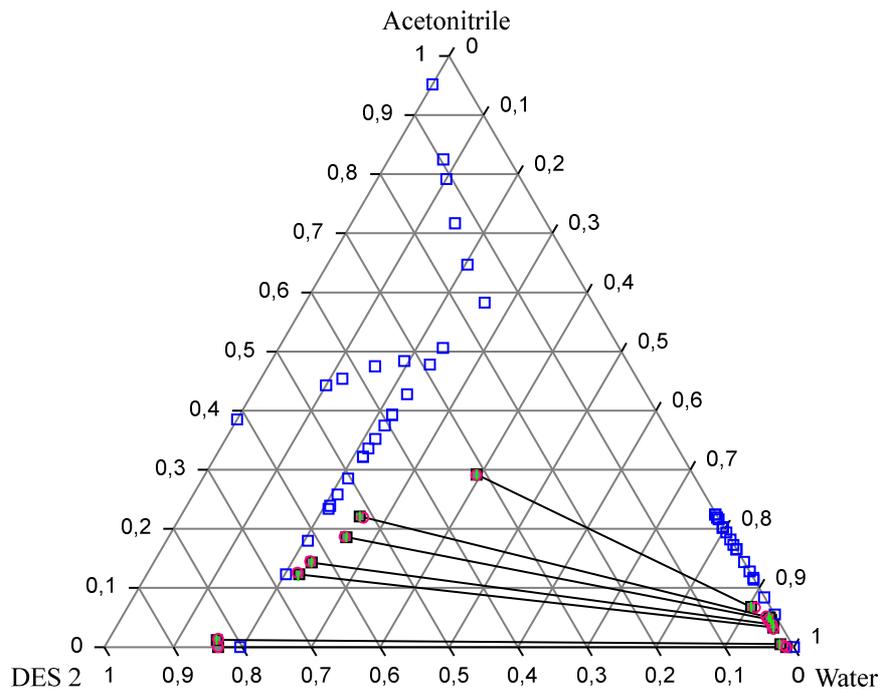
**Figure 2.** Results of the prediction in the ternary system {water + acetonitrile + DES1}. ■, Experimental bimodal curve; □, COSMO-RS model; □, NRTL model; |, UNIQUAC model.



**Figure 3.** Results of the prediction in the ternary System {water + 1-butanol + DES2}. ■, Experimental bimodal curve; □, COSMO-RS model; □, NRTL model; |, UNIQUAC model.

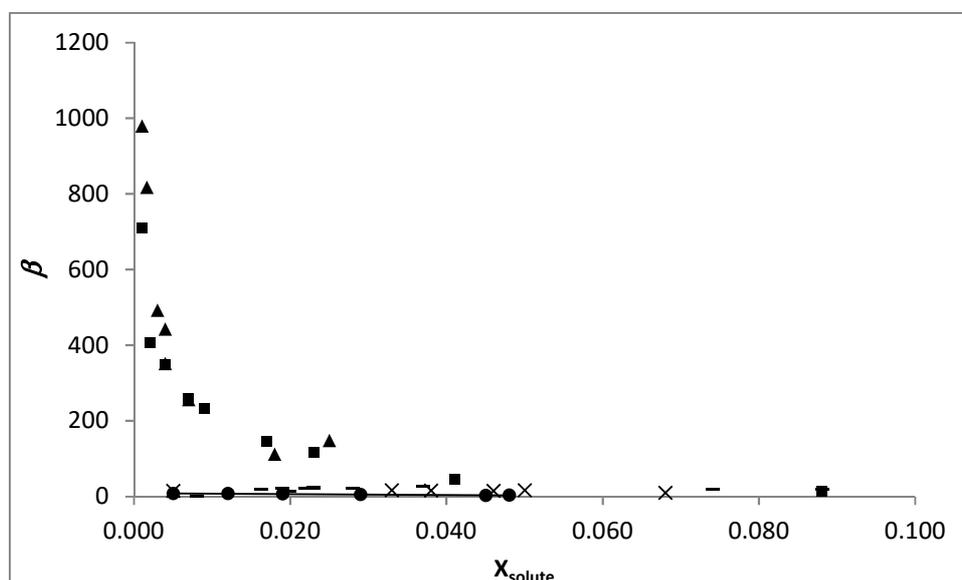


**Figure 4.** Results of the prediction in the ternary System {water + acetonitrile + DES2}. ■, Experimental bimodal curve; □, COSMO-RS model; □, NRTL model; |, UNIQUAC model.

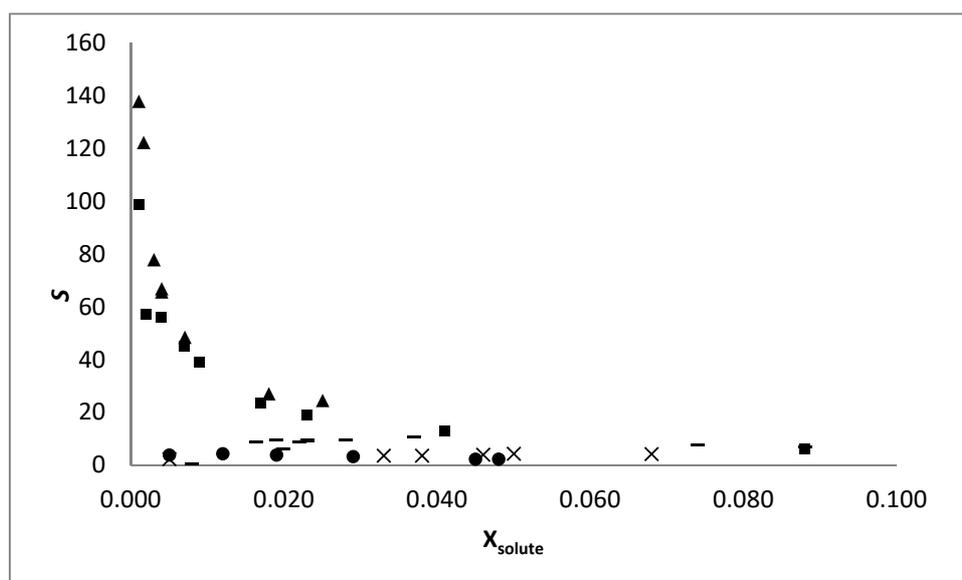




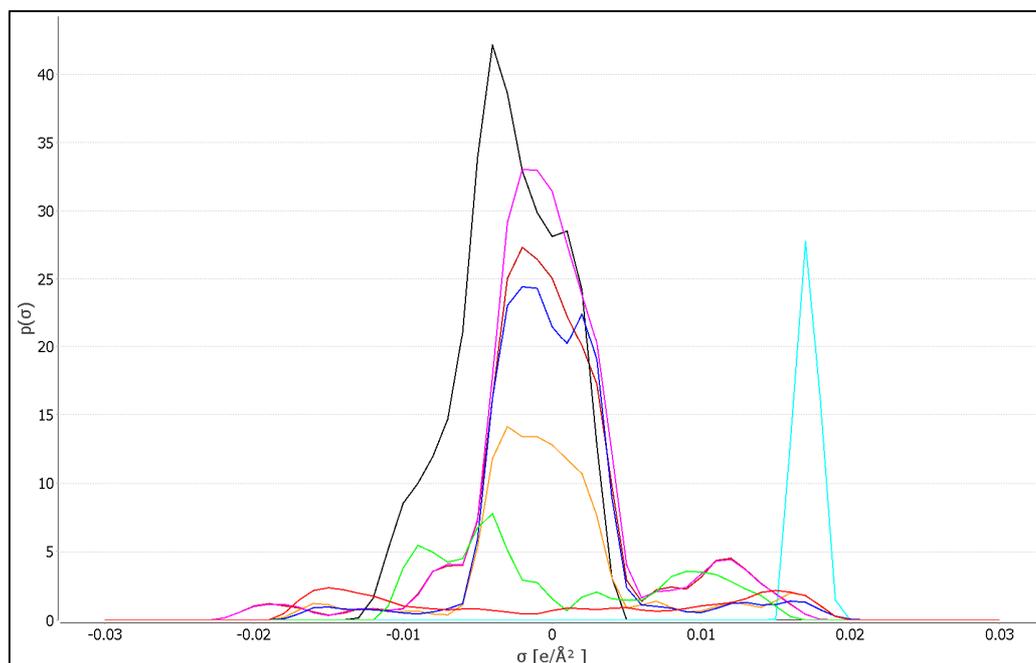
**Figure.6.** Plot of Distribution Coefficients of 1-butanol or acetonitrile as function of the mole fraction in the aqueous phase for the studied systems: – {water + 1-butanol + DES 1}; ▲ {water + 1-butanol + DES 2}; ■ {water + 1-butanol + DES 3}; ● {water + acetonitrile + DES 1}; × {water + acetonitrile + DES 2}.



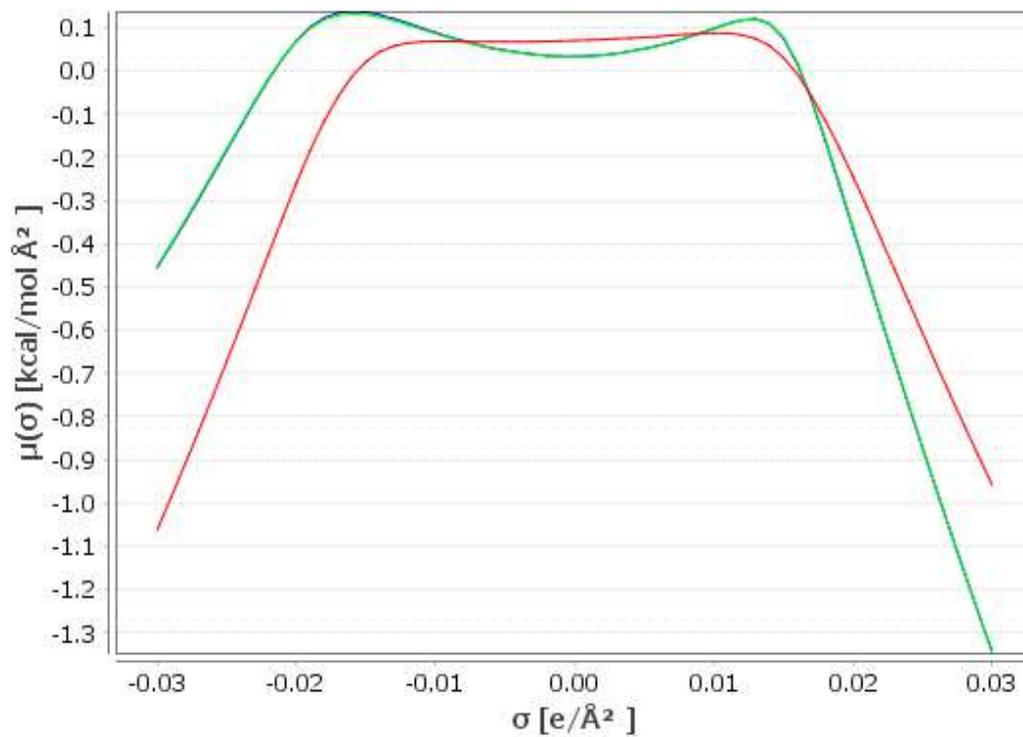
**Figure 7.** Plot of the selectivity of 1-butanol or acetonitrile as function of the mole fraction in the aqueous phase for the studied systems: – {water + 1-butanol + DES 1}; ▲ {water + 1-butanol + DES 2}; ■ {water + 1-butanol + DES 3}; ● {water + acetonitrile + DES 1}; × {water + acetonitrile + DES 2}.



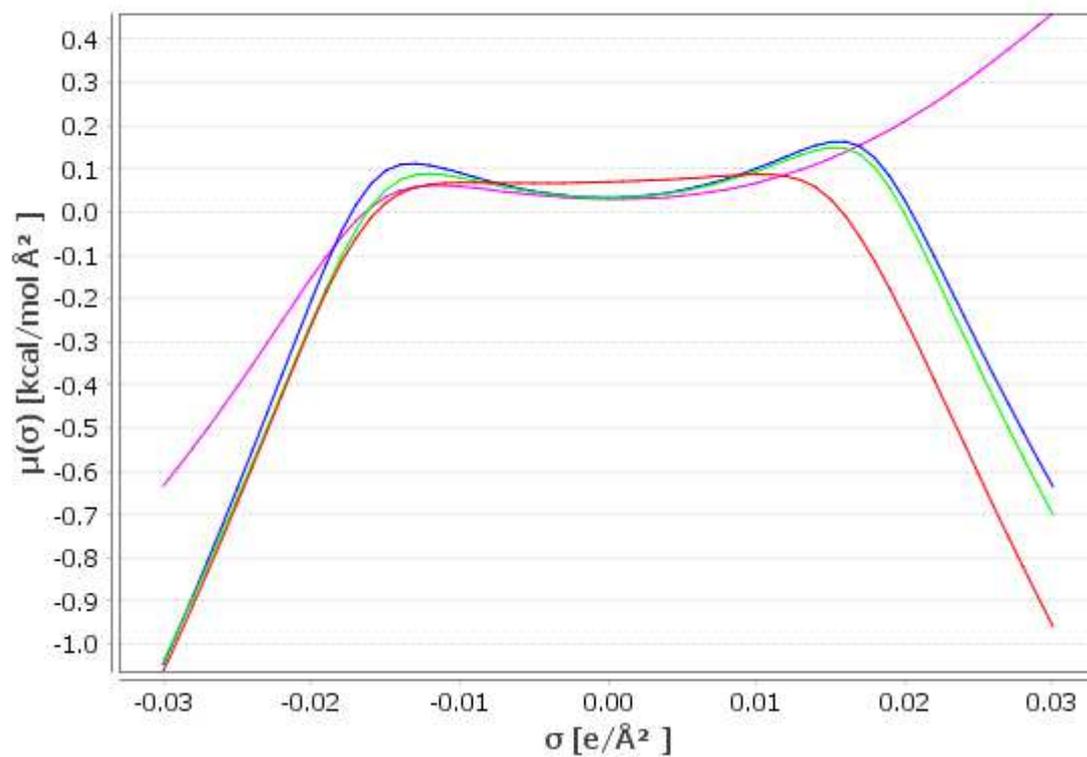
**Figure 8.**  $\sigma$ -profiles of — water, — decanoic acid, — dodecanoic acid, — 1-butanol, — acetonitrile, — DL-menthol, — bromide and — tetrabutylammonium.



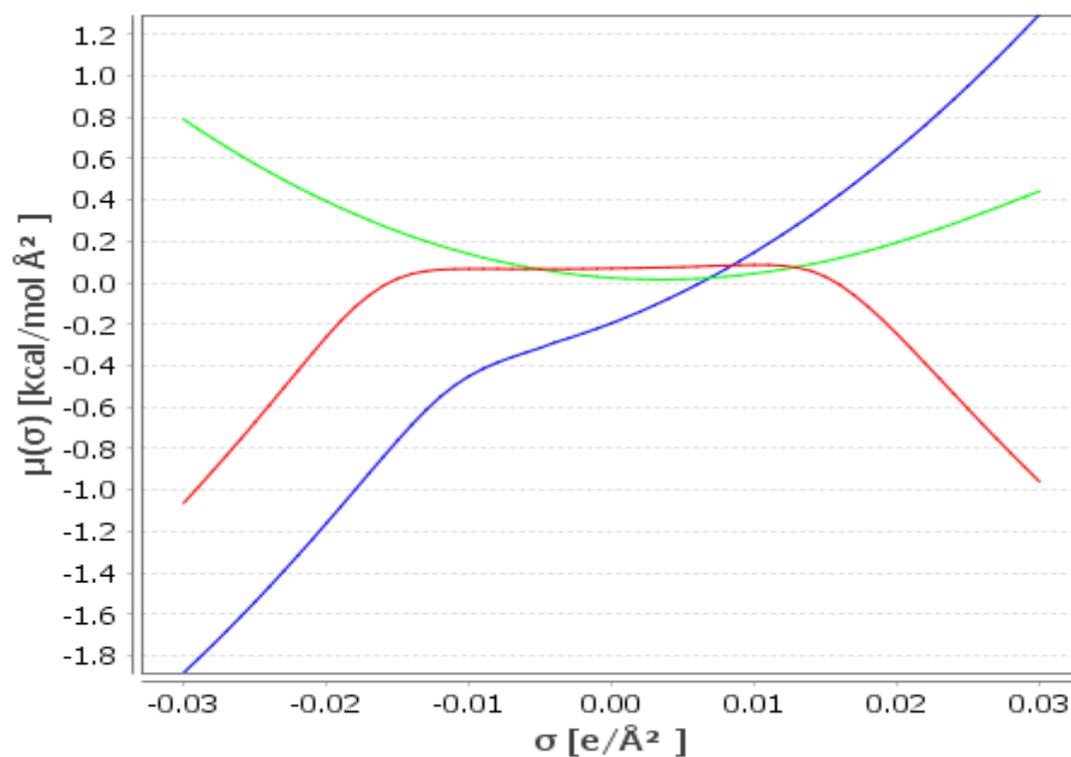
**Figure 9.**  $\sigma$ -potentials of — water, — decanoic acid and — dodecanoic acid.



**Figure 10.**  $\sigma$ -potentials of - water, - 1-butanol, - menthol and - acetonitrile.



**Figure 11.**  $\sigma$ -potentials of - water, - tetrabutylammonium cation and - bromide anion.



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