Effect of the type of ammonium salt on the extractive desulfurization of fuels using deep eutectic solvents

Citation for published version (APA):
Warrag, S. E. E., Adeyemi, I., Rodriguez, N. R., Nashef, I. M., van Sint Annaland, M., Kroon, M. C., & Peters, C. J. (2018). Effect of the type of ammonium salt on the extractive desulfurization of fuels using deep eutectic solvents. *Journal of Chemical and Engineering Data*, *63*(4), 1088-1095. https://doi.org/10.1021/acs.jced.7b00832

DOI:
10.1021/acs.jced.7b00832

Document status and date:
Published: 12/04/2018

Document Version:
Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Download date: 27. Aug. 2022

Effect of the Type of Ammonium Salt on the Extractive Desulfurization of Fuels using Deep Eutectic Solvents

Samah E.E Warrag[a,b], Idowu Adeyemi[c], Nerea R. Rodriguez[b], Inas M. Nashef[c], Martin van Sint Annaland[b], Maaike C. Kroon[a,*] and Cor J. Peters[a,d*]

[a] Khalifa University of Science and Technology, Petroleum Institute, Chemical Engineering Department, P.O. Box 2533, Abu Dhabi, United Arab Emirates

[b] Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, Process Intensification Group, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

[c] Khalifa University of Science and Technology, Masdar Institute, Department of Chemical and Environmental Engineering, P.O. Box 54224, Abu Dhabi, United Arab Emirates

[d] Colorado School of Mines, Chemical & Biological Engineering Dept.,
Center for Hydrate Research, Golden, CO 80401, United States

*Corresponding Authors: Maaike C. Kroon (mkroon@pi.ac.ae; +971-26075317) and Cor J. Peters (cpeters@pi.ac.ae; +971-26075492).

Abstract

In a previous work, we proved that the deep eutectic solvents (DESs) consisting of mixtures of tetraalkylammonium salts with polyols are promising candidates for oil desulfurization based on the obtained liquid-liquid equilibrium (LLE) data. In this study, the capability of DESs containing other salts (e.g. different alkyl chain lengths or different functional groups on the ammonium cation) for the extraction of thiophene from {*n*-hexane + thiophene} mixtures via LLE was evaluated. Therefore, four DESs composed of tetraethylammonium chloride or methyltriphenylphosphonium bromide as hydrogen bond acceptors and ethylene glycol or glycerol as hydrogen bond donors were prepared. Thereafter, the binary solubilities of the aliphatic hydrocarbon (*n*-hexane) and the thiophene in DESs were measured at 298.2 K and atmospheric pressure. Next, ternary liquid-liquid equilibrium (LLE) data for the four ternary systems {*n*-hexane + thiophene + DES} were measured at 298.2 K and atmospheric pressure. The Conductor-like Screening Model for Real Solvents (COSMO-RS) was used to better understand the extraction mechanism of thiophene. Experimentally obtained solute distribution coefficients and selectivities were calculated and compared to relevant literature. All DESs were found to be good candidates for extractive desulfurization with higher selectivities but somewhat lower distribution coefficients as compared to conventional ionic liquids. It was found that longer alkyl chain lengths on the cation yield higher distribution coefficients but lower selectivities, and the replacement of an alkyl group by a phenyl group on the cation generally yields lower distribution ratios but higher selectivities.

1. **Introduction**

Catalytic hydrodesulfurization (HDS) has been the conventional approach applied by oil refineries to capture sulfur and sulfur compounds.[1,2] This approach is based on hydrotreating the sulfur-containing fuel with Co-Mo/Al_2O_3 or Ni-Mo/Al_2O_3 catalysts under elevated temperatures (573.2 – 673.2 K), as well as elevated pressures (3.5 – 7.0 MPa),[3] which makes the method costly and energy-intensive. Moreover, the elimination of the family of thiophenes (i.e.: thiophene, methyl thiophene, benzothiophene, and dibenzothiophene, etc.) has been a real challenge as they exhibit steric hindrance with respect to the active sites of the catalyst; thereby, decreasing their reactivity towards desulfurization.[4] Thus, significant research efforts have been devoted to exploring effective and energy-saving alternatives to this technology. Aiming to reduce the energy requirement of this separation, many research studies have considered extractive desulfurization as alternative for sulfur capture. Liquid-liquid extraction is a simple operation, highly selective to specific compounds and often conducted at milder process conditions.[5] However, the solvent selection remains a challenging task. Traditional volatile organic compounds (VOCs) such as methanol, acetonitrile, and others has been applied successfully on extractive desulfurization.[6] Nevertheless, the environmental concerns associated with the volatility of the VOCs and difficultly of the solvent recovery made them undesirable for this separation.

Over the past two decades, ionic liquids (ILs) were proposed as potential candidates for extractive desulfurization agents.[7–13] The most pronounced physical property of ILs is their negligible vapor pressure. This would enable ILs to replace VOCs with much simpler solvent recovery steps.[14,15] However, the drawbacks associated with ILs are their high price, complex synthesis and several purification steps resulting in large waste streams. Thus, there is still a need to look for innovative alternative solvents for extractive desulfurization.

In 2003, a unique class of solvents, so-called deep eutectic solvents (DESs), was described.[16] DESs consist of at least one hydrogen bond donor (HBD) and at least one hydrogen bond acceptor (HBA) that form upon mixing a low melting mixture with very low vapor pressure. DESs have several unique properties, such as low flammability, thermal stability, wide liquid range, high solvation properties, often biodegradable and low-cost. More interestingly, the desired physicochemical properties of DESs can be achieved by perceptive and adequate selection of the DES constituents and their ratios, making them ‘objective-oriented’ solvents.[17–19] Due to these characteristics, DESs have attracted significant interest as promising alternatives for VOCs and ILs as ‘greener’ separation agents. DESs were investigated as an economical and sustainable solvent for several separation applications, among them, extractive desulfurization (EDS) of oil fuels.[20–26]

In previous work,[25] two DESs consisting of tetrahexylammonium bromide as HBA and ethylene glycol or glycerol as HBD with molar ratio equal to 1:2 were evaluated for their extraction properties of thiophene from *n*-hexane via liquid-liquid extraction. Based on the obtained distribution coefficients and selectivities, it was concluded that those DESs are promising solvents for desulfurization. However, the DESs applied were not (yet) further optimized.

In order to study the effect of the chain length of the alkyl group and the effect of the functional group on the ammonium cation, the capability of other salts on the extraction of thiophene from {*n*- hexane + thiophene} mixtures via liquid-liquid extraction was investigated for the first time in this work. It is known that the crude contains a series of hydrocarbon and a variety of sulfur spices, however for simplicity the mixture of {*n*-hexane + thiophene} will be considered as an oil model. Therefore, the following DESs were selected: (i) tetraethylammonium chloride: ethylene glycol in molar ratio (1:2), (ii) tetraethylammonium chloride: glycerol (1:2), (iii) methyltriphenylphosphonium bromide:ethylene glycol (1:3), and (iv) methyltriphenylphosphonium bromide: glycerol (1:3). More information on the DES selection can be found in the Supporting Information. To validate the workability of the selected DES for the desulfurization, the binary solubilities of thiophene/ DES and *n*-hexane/ DES were measured first at 298.2 K and atmospheric pressure. Thereafter, ternary liquid-liquid equilibrium (LLE) data for the four ternary systems {*n*-hexane + thiophene + DES} were measured at 298.2 K and atmospheric pressure. Also, COSMO-RS was used to better understand the extraction mechanism of thiophene. The solute distribution coefficients and selectivities were calculated and compared to the relevant literature to evaluate the performance of the studied DESs.

We would like to draw the attention of the readers that; since the DES is a mixture of two compounds, it would preferably be considered as a pseudo-compound. Consequently, in this work the systems {*n*-hexane/thiophene + DES} and {*n*-hexane+ thiophene + DES} were considered as pseudo-binary systems and pseudo-ternary systems, respectively.

2. Experimental and modeling procedures

2.1 Materials

All the chemicals were purchased at the highest purity available and used as obtained. The source and purity (as stated by the suppliers) of all the chemicals are presented in Table 1.

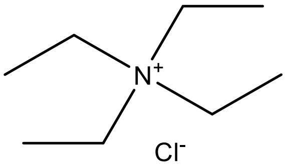
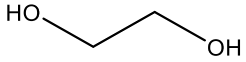
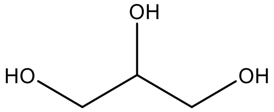
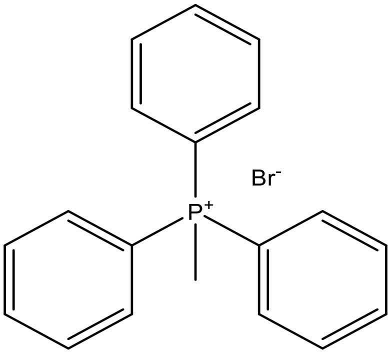
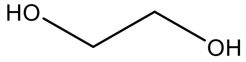
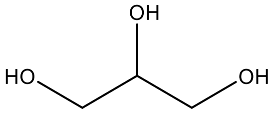
Table 1: Source and purity (as stated by the suppliers) of the chemicals used in this work

Chemical	**CAS number**	**Source**	**Purity (*wt %*)**
Thiophene	110-02-1	Sigma-Aldrich	≥ 99
Hexane	110-54-3	Sigma-Aldrich	≥ 95
Methyltriphenylphosphonium bromide	1779-49-3	Merck KGaA	≥ 99
Tetraethylammonium chloride	56-34-8	Merck KGaA	≥ 99
Glycerol	56-81-5	Merck KGaA	≥ 99
Ethylene glycol	107-21-1	Sigma-Aldrich	≥ 99
Ethanol	64-17-5	TechniSolv	≥ 99.5

2.2 DESs preparation

The DESs were prepared using a Mettler AX205 balance with uncertainty in measurements of 0.2 mg. Adequately weighted masses of the HBA (the salts) and the HBD (the polyols) were mixed in a closed flask and heated at 333 K under stirring until a clear liquid was formed. The temperature was controlled using a thermostatic bath with a temperature controller (IKA ETS-D5) with uncertainty in the measurement of ±0.1 K. The HBA, HBD, and HBA:HBD molar ratio for the DESs used in this work are presented in Table 2. The DES structure was verified by 400 Bruker nuclear magnetic resonance (NMR) spectrometer for ^{1}H-NMR (see Figures S.1 to S.4).

Table 2: The HBA, HBD, and HBA:HBD molar ratio for the DESs used in this work

DESs	HBA	Molar ratio	HBD
TEACl:EG		1:2	
TEACl:Gly			
MTPPBr:EG		1:3	
MTPPBr:Gly			

2.3 Experimental determination of the pseudo-binary and pseudo-ternary LLE data

The LLE data of the pseudo-binary systems {*n*-hexane + DES} and {thiophene + DES}, and the pseudo-ternary systems {*n*-hexane + thiophene + DES} were experimentally determined at a temperature of 298.2 K and at atmospheric pressure. Initial mixtures of *n*-hexane, thiophene, and DES with known composition within the immiscibility region were prepared and placed in 20 mL headspace vials. The vials were vigorously mixed for at least 2 h at 500 rpm in a temperature-controlled incubated shaker (IKA KS 4000 *i*-control) kept at 298.2 K with temperature stability of ±0.1 K. Then, the mixtures were left to settle and reach equilibrium overnight in a heating block. The heating block was kept at 298.2 K on a hot plate (IKA RCT basic) with a temperature controller (IKA ETS-D5). Then, a sample from the top "aliphatic-rich" phase and another one from the bottom "DES-rich" phase was taken using needled syringes. The samples were diluted using pure ethanol for analysis.

The concentrations of thiophene and *n*-hexane in the diluted samples were analyzed using a Varian 430 GC equipped with a flame ionization detector (T = 473.2 K) and a Varian CP-SIL 5CB column (25 m × 0.25 mm × 1.25 μm). The oven temperature was set at T = 313.2 K for 2 min, then increased to T = 353.2 K at a rate of 12.5 K min^{-1}. The temperature was kept constant for 2 min at T = 353.2 K. The injector temperature was T = 548.2 K. The carrier gas was helium with a constant flow rate of 3 mL min^{-1}. Due to the low vapor pressure of the DESs, their concentrations were obtained from a mass balance calculation. It should be mentioned that for each system the GC liner "whereby the inert and/or non-volatile materials are collected" was replaced to avoid the column contamination.

2.4 Modeling of the LLE data

The COSMO-RS model is a quantum chemistry-based method with the purpose of predicting chemical potentials (μ) in liquids. In COSMO-RS, the molecules are placed in a conductor as the reference state, then the screening charge density ($\boldsymbol{\sigma}$) on the surface of each molecule is calculated and stored in a *.cosmo file*. The electrostatic misfit energy (E_{misfit}), hydrogen bond interaction (E_{hb}), and van der Waals interaction (E_{vdW}) represent the molecular interactions in COSMO-RS.[27–29] The surface of the molecules in the liquid is divided into segments each with a certain surface charge density. Then, a probability function "σ-profile" can be obtained by applying a local averaging algorithm on the surface charge densities over effective contact segments. The σ-profile can help to understand the properties and the solvation of the compounds and their mixtures in terms of charge interactions.[27–29]

All compounds were generated with the TMoleX tool. [30] The geometry was optimized with Hartree-Fock method for higher accuracy and using the 6-31 G basis set to allow for polarization effects of the species in the complexes.[31] After the optimization, a single point estimation was conducted and the *.cosmo file* was generated for use in the analysis. Each DES was represented by three different species, e.g. HBD, HBA cation and HBA anion, whereby the electro-neutrality between HBA cation and anion was guaranteed.[32] The TMoleX tool also provided the *COSMOThermX file*,[30] which was used for the analysis of the extraction capacity for thiophene and *n*-hexane of each DES.

4. Results and discussion

4.1 Pseudo-Binary LLE experiments

The equilibrium compositions of the pseudo-binary systems consisting of {*n*-hexane + DES} and {thiophene + DES} were experimentally determined at 298.2 K and atmospheric pressure as described in section 3.3. The obtained values are listed in Table 3.

Table 3: Equilibrium compositions (weight fraction) measured at 298.2 K and 1.01 bar, of the DES-rich phase for the pseudo-binary mixtures of {*n*-hexane or thiophene + DES}*

DES	w_{hexane}	$w_{thiophene}$
TEACl:EG	0.0036 ± 0.0014	0.3253 ± 0.0027
TEACl:Gly	0.0008 ± 0.0003	0.1527 ± 0.0015

MTPPBr:EG	0.0034 ± 0.0001	0.4968 ± 0.0040
MTPPBr:Gly	0.0091 ± 0.0003	0.1165 ± 0.0010

*The standard uncertainties in the measurements are *u* (p) = 0.04 bar, *u* (T) = 0.1 K, and standard uncertainties for the mass fractions are reported in the table

From Table 3 the following can be observed: (i) the solubilities of thiophene are always greater compared to those of *n*-hexane in all the studied DESs, and (ii) thiophene was found to be more soluble in DESs containing ethylene glycol as HBD than the glycerol-based DESs for the same HBA. The increased solubility of thiophene in the DESs over *n*-hexane is commonly explained by the favorable electrostatic interactions between the DES' cations and the π-electrons available in the thiophene. The higher solubility of thiophene in ethylene glycol-based DESs as compared to glycerol-based DESs is presumably due to the polarity difference between glycerol and ethylene glycol. The glycerol-based DESs are more polar, making the solubility of the weakly polar or apolar compounds lower.

The role of the HBA "salt" was also observed from the solubility difference of thiophene in MTPPBr:EG and TEACl:EG. Thiophene was found to be more soluble in MTPPBr:EG than in TEACl:EG. The presence of a phenyl ring in the MTPPBr:EG provided a preferred environment for thiophene through π-π interactions. However, the solubility of thiophene in TEACl:Gly is slightly higher than that in MTPPBr:Gly. This is presumably due to the dominating role of glycerol "increased polarity" that exists in a ratio of 1:3 in MTPPBr:Gly (while ethylene glycol is only present in the ratio 1:2 in the DES TEACl:EG). It worth to mention that the experimental results obtained in this section are in line with our findings in a previous work on the extraction of the thiophene using other DESs consisting of salts as HBA and polyols as HBD.[25]

4.2 Pseudo-Ternary LLE experiments

The LLE data of the four pseudo-ternary systems {*n*-hexane + thiophene + DES} were experimentally determined at 298.2 K and atmospheric pressure. The obtained equilibrium compositions of the ternary systems as listed in Table 4 and depicted graphically in Figure 1 by means of triangular diagrams. Considering the studied system as pseudo-ternary, according to the Sørensen et al. classification,[33] the four systems showed a type II ternary behavior. This is one completely miscible pair {*n*-hexane + thiophene} and two partially miscible ones {aliphatic + DES} and {thiophene + DES} with only one large immiscibility region.

From Figure 1, it can be observed that the aliphatic-rich (raffinate) phase is free of DES. This observation was verified via ^{1}H NMR that, within the detection limits of the equipment, only *n*-hexane and thiophene were detected in the aliphatic-rich phase. The ^{1}H NMR spectra are available Supporting

Information (see Figures S.5 to S.8). It can be seen from the spectra that the aliphatic-rich phase only contains *n*-hexane and thiophene. Similar behavior was observed in other systems of {aliphatic + thiophene + DESs} [24,25] and {aliphatic + thiophene + ILs}.[8–11,13] This observation is remarkable from an industrial point of view. It means that no solvent recovery column is needed for the aliphatic-rich stream. This will contribute to reducing the operational costs of the process.

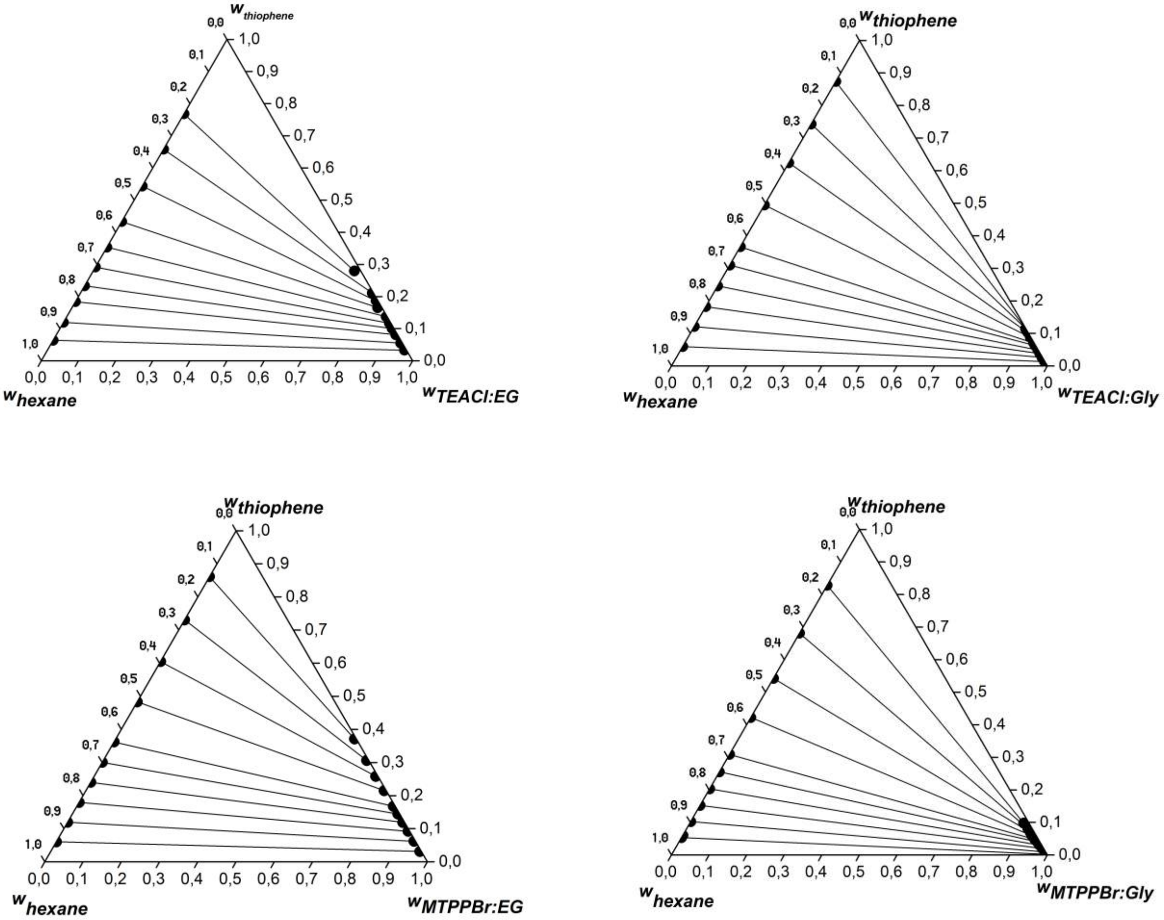


Figure 1: Experimental tie lines (● circle, solid line) in weight fractions for the pseudo-ternary systems {*n*-hexane + thiophene + DES} at 298.2 K and 1.01 bar

Table 4: Experimental LLE data measured at 298.2 K and 1.01 bar. All the compositions are in weight fractions for the pseudo-ternary systems {*n*-hexane *(1)* + thiophene *(2)* + DES *(3)*}. β and S are the calculated distribution and selectivity values, respectively. The DES concentration (w_3) in both phases can be calculated from mass balance.*

Aliphatic phase		**DES phase**			
w_1	w_2	w_1	w_2	β	S
{*n*-hexane *(1)* + thiophene *(2)* + TEACL:EG *(3)*}					

0.9359	±0.0016	0.0641	±0.0016	0.0054	±0.0019	0.0328	±0.0021	0.512	±0.035	87.994	±31.633
0.8803	±0.0021	0.1197	±0.0021	0.0044	±0.0019	0.0551	±0.0034	0.461	±0.029	91.567	±40.428
0.8160	±0.0019	0.1840	±0.0019	0.0049	±0.0014	0.0813	±0.0026	0.442	±0.015	73.321	±21.628
0.7665	±0.0063	0.2335	±0.0063	0.0053	±0.0028	0.1003	±0.0031	0.430	±0.018	61.816	±33.154
0.7083	±0.0063	0.2917	±0.0063	0.0039	±0.0017	0.1171	±0.0019	0.402	±0.011	72.154	±31.940
0.6464	±0.0040	0.3536	±0.0040	0.0027	±0.0006	0.1373	±0.0035	0.388	±0.011	92.676	±21.776
0.5667	±0.0029	0.4333	±0.0029	0.0118	±0.0025	0.1652	±0.0044	0.381	±0.010	18.326	±3.858
0.4563	±0.0046	0.5437	±0.0046	0.0052	±0.0009	0.1927	±0.0066	0.343	±0.012	30.833	±5.647
0.3417	±0.0037	0.6583	±0.0037	0.0033	±0.0009	0.2109	±0.0057	0.320	±0.009	33.296	±9.299
0.2316	±0.0049	0.7684	±0.0049	0.0175	±0.0007	0.2791	±0.0104	0.363	±0.014	4.813	±0.275
{*n*-hexane *(1)* + thiophene *(2)* + TEACl:Gly *(3)*}											
0.9403	±0.0018	0.0597	±0.0018	0.0008	±0.0001	0.0135	±0.0004	0.226	±0.009	257.734	±37.059
0.8786	±0.0047	0.1214	±0.0047	0.0013	±0.0009	0.0263	±0.0010	0.217	±0.012	145.239	±100.429
0.8178	±0.0027	0.1822	±0.0027	0.0006	±0.0001	0.0382	±0.0016	0.210	±0.009	276.892	±45.503
0.7540	±0.0052	0.2460	±0.0052	0.0009	±0.0004	0.0488	±0.0019	0.198	±0.009	171.839	±86.262
0.6904	±0.0027	0.3096	±0.0027	0.0014	±0.0009	0.0624	±0.0052	0.202	±0.017	101.361	±64.406
0.6337	±0.0043	0.3663	±0.0043	0.0010	±0.0003	0.0701	±0.0030	0.191	±0.009	124.598	±37.945
0.5054	±0.0072	0.4946	±0.0072	0.0012	±0.0004	0.0874	±0.0030	0.177	±0.007	77.065	±24.281
0.3759	±0.0049	0.6241	±0.0049	0.0007	±0.0002	0.1022	±0.0015	0.164	±0.003	88.027	±20.021
0.2565	±0.0078	0.7435	±0.0078	0.0006	±0.0001	0.1143	±0.0013	0.154	±0.002	62.634	±9.500
0.1261	±0.0052	0.8739	±0.0052	0.0004	±0.0001	0.1137	±0.0016	0.130	±0.002	42.681	±6.870
{*n*-hexane *(1)* + thiophene *(2)* + MTPPBr:EG *(3)*}											
0.9397	±0.0002	0.0603	±0.0002	0.0035	±0.0002	0.0314	±0.0008	0.521	±0.014	140.381	±7.927
0.8805	±0.0006	0.1195	±0.0006	0.0038	±0.0002	0.0617	±0.0013	0.517	±0.012	119.478	±5.869
0.8206	±0.0008	0.1794	±0.0008	0.0042	±0.0002	0.0921	±0.0031	0.513	±0.018	100.916	±6.165
0.7597	±0.0023	0.2403	±0.0023	0.0044	±0.0002	0.1189	±0.0032	0.495	±0.014	85.662	±4.214
0.6996	±0.0012	0.3004	±0.0012	0.0046	±0.0002	0.1443	±0.0035	0.480	±0.012	73.511	±3.755
0.6380	±0.0013	0.3620	±0.0013	0.0049	±0.0003	0.1676	±0.0059	0.463	±0.016	60.748	±4.620
0.5167	±0.0027	0.4833	±0.0027	0.0053	±0.0002	0.2149	±0.0039	0.445	±0.009	43.423	±2.024
0.3950	±0.0018	0.6050	±0.0018	0.0054	±0.0003	0.2581	±0.0073	0.427	±0.012	31.032	±2.149
0.2694	±0.0025	0.7306	±0.0025	0.0054	±0.0002	0.3060	±0.0097	0.419	±0.013	20.928	±1.043
0.1388	±0.0007	0.8612	±0.0007	0.0048	±0.0002	0.3708	±0.0107	0.431	±0.012	12.365	±0.633
{*n*-hexane *(1)* + thiophene *(2)* + MTPPBr:Gly *(3)*}											
0.9468	±0.0002	0.0532	±0.0002	0.0010	±0.0001	0.0016	±0.0002	0.031	±0.004	29.303	±4.982
0.8975	±0.0003	0.1025	±0.0003	0.0018	±0.0003	0.0089	±0.0001	0.087	±0.001	43.940	±7.700
0.8478	±0.0002	0.1522	±0.0002	0.0033	±0.0017	0.0195	±0.0008	0.128	±0.005	33.017	±17.194
0.7970	±0.0007	0.2030	±0.0007	0.0064	±0.0015	0.0304	±0.0002	0.150	±0.001	18.690	±4.335
0.7449	±0.0018	0.2551	±0.0018	0.0069	±0.0020	0.0404	±0.0009	0.158	±0.004	17.016	±4.949
0.6911	±0.0018	0.3089	±0.0018	0.0097	±0.0012	0.0483	±0.0003	0.156	±0.001	11.089	±1.319
0.5777	±0.0014	0.4223	±0.0014	0.0117	±0.0012	0.0595	±0.0006	0.141	±0.001	6.954	±0.736
0.4575	±0.0018	0.5425	±0.0018	0.0107	±0.0020	0.0697	±0.0011	0.128	±0.002	5.482	±1.033
0.3188	±0.0013	0.6812	±0.0013	0.0113	±0.0015	0.0808	±0.0007	0.119	±0.001	3.336	±0.432
0.1720	±0.0016	0.8280	±0.0016	0.0142	±0.0012	0.0974	±0.0009	0.118	±0.001	1.423	±0.120

* The standard uncertainties in the measurements are *u* (p) = 0.04 bar, *u* (T) = 0.1 K, and standard uncertainties for the mass fractions are reported in the table

In order to evaluate the performance of the studied DESs on the extraction of thiophene, the solute distribution coefficients β and the selectivities S were calculated from the experimental data using Eq. (1) and (2), respectively:[34]

$$\boldsymbol{\beta_2} = \frac{\boldsymbol{w_{2,E}}}{\boldsymbol{w_{2,R}}} \qquad \text{(Eq. 1)}$$

where $w_{2,E}$ is the weight fraction of thiophene in the extract “DES-rich” phase and $w_{2,R}$ is the weight fraction of thiophene in the raffinate “aliphatic-rich” phase.

$$\boldsymbol{S} = \frac{\boldsymbol{\beta_2}}{\boldsymbol{\beta_1}} \qquad \text{(Eq. 2)}$$

and where β_1 and β_2 refer to the distribution coefficients of *n*-hexane and thiophene, respectively. The solute distribution coefficient β allows quantifying the solvent capacity to extract the solute. Therefore, high β value implies that less solvent is needed to achieve the targeted extraction efficiency. Contrarily, the selectivity allows quantifying the affinity of the solvent to the solute in comparison to the carrier. High selectivity means that smaller equipment size is sufficient for the targeted separation.

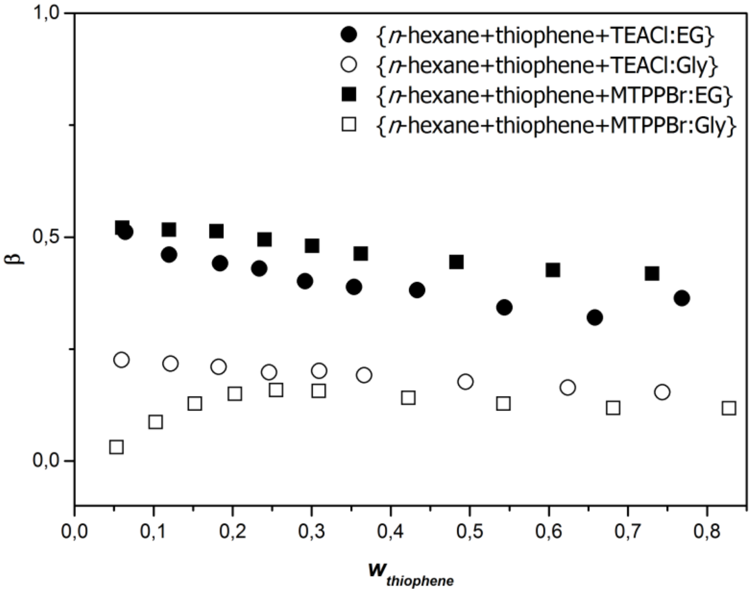


Figure 2: Solute distribution coefficient as a function of the weight fraction of thiophene in the aliphatic-rich phase.

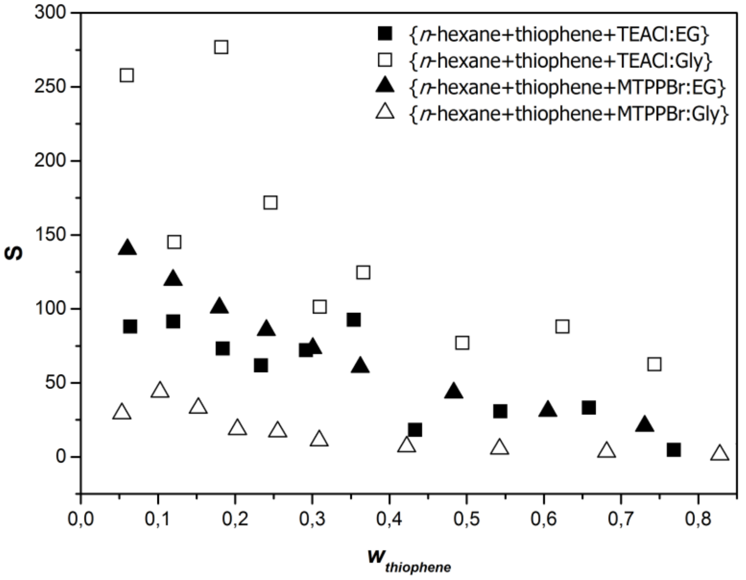


Figure 3: Selectivity as a function of the weight fraction of thiophene in the aliphatic-rich phase.

The numerical values for the distribution coefficients are presented in Table 4 and graphically shown in Figure 2. For all the measuring systems, the distribution coefficient was found to be less than unity. As shown in **Error! Reference source not found.**, the distribution coefficient for the ethylene glycol-based DESs was found to be greater than for the glycerol-based DESs. This behavior was expected based on the higher solubility of thiophene in ethylene glycol-based-DESs (see Table 3). Thus, the use of ethylene glycol-based DESs is preferable in comparison with glycerol-based DESs due to the higher distribution coefficient. In general, the obtained distribution coefficients slightly decreased with an increase in the thiophene concentration, but the effect of thiophene concentration on the distribution coefficient was small. This means that the thiophene concentration in the system does not significantly affect the extraction efficiency of all the considered DESs. The low distribution ratios are compensated by the absence of the DESs in the aliphatic-rich phase and the low volatility of the DESs, which facilitate the solvent recovery after the extraction. Also, the effect of the HBA "salt" on the distribution coefficient was found to be minor. Apparently, HBD is the dominant factor determining the distribution coefficient.

The calculated selectivity values are also presented in Table 4 and graphically depicted in **Error! Reference source not found.**. In all four studied systems, the selectivity was found to be greater than unity. This implies that the extraction of thiophene using DESs is feasible. The trend observed in Figure 3 is a decrease in selectivity with an increase in thiophene concentration (even though some data was somewhat scattered in some cases). The data scattering in the DESs with high selectivity “i.e. TEACl:Gly”, is a result of error propagation due to the low concentration of *n*-hexane and benzene on the DES rich phase. Also, it can be observed that TEACl: Gly has the highest selectivity among the studied DESs. The selectivity order observed was: TEACl:Gly (1:2) > MTPPBr:EG (1:3) > TEACl:EG (1:2) > MTPPBr:Gly (1:3). This order could be expected on basis of the pseudo-binary solubilities presented in the previous section (you get the same order when calculating $w_{\text{thiophene}}/w_{\text{hexane}}$ using the values in Table 3). This shows that selectivities are much more dependent on the HBA “salt” than the distribution coefficients.

On the basis of the obtained LLE results (S > 1), it can be concluded that all studied DESs are potential candidates for the desulfurization of fuels. Moreover, it can be concluded that the type of ammonium salt used to form the DES does not have a major effect on the distribution coefficient, but has some effect on the selectivity.

4.3 Modeling of the LLE data

The analysis of the sigma profiles obtained with COSMO-RS can provide an in-depth understanding of the interactions between the DESs and thiophene. The threshold value for the hydrogen bonding interactions applied was: $\sigma_{\text{hb}} = \pm 0.0084$ eA^{-2}. From Figure 4, it can be clearly seen that the four DESs have peaks on both sides beyond the threshold value, which confirms the formation of hydrogen bonding within the DES. It can also be deduced that thiophene is a non-basic compound due to its location that is barely exceeding the lower limit of $\sigma_{\text{hb}} = -0084$ eA^{-2}.[32] This means that the thiophene is a weak HBD. Instead, it is showing a very small peak above the upper limit (at $\sigma > +\sigma_{\text{hb}}$) indicating the ability to be a HBA. However, based on the σ-profiles, the pronounced interaction between thiophene and DESs is the electrostatic interaction, with negligible and/or absent hydrogen bonding interaction. Thus, thiophene is extracted by the DESs mainly on the basis of electrostatic interactions, which confirms our observations for thiophene solubilities in the DESs presented in Table 3.

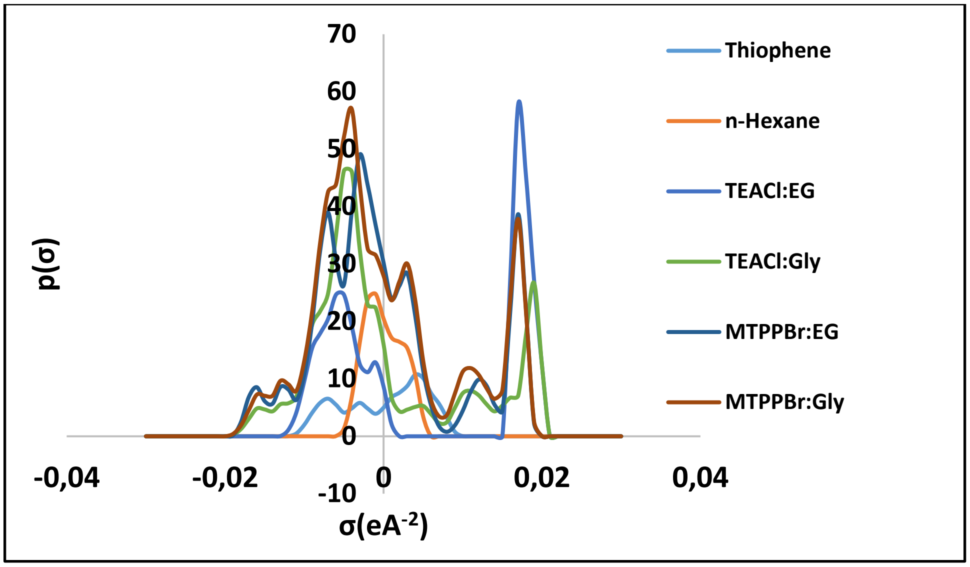


Figure 4: Sigma profile of thiophene, *n*-hexane and the four DESs studied

4.4 Literature comparison

The solute distribution coefficients and selectivities calculated at 298.2 K and atmospheric pressure were compared to systems using other previously studied DESs and ILs as extracting agents. The distribution coefficients and the selectivities for the LLE systems {*n*-hexane + thiophene + DES/IL} can be found in Figures 5 and 6, respectively. From Figure 5, it can be seen that the distribution coefficients of the studied DESs (TEACl:EG, TEACl:Gly, MTPPBr:EG, MTPPBr:Gly) in this work were lower than those of the ILs except for [C_2mim][NTf_2].[10] Also, they were found to be lower than for the THABr:EG and THABr:Gly DESs studied previously.[25]

Remarkably, the selectivity of the TEACl:Gly, studied in this work, was found to be the highest among all the ILs and DESs as shown in Figure 6. The selectivities of the other three DESs were found to be only slightly higher or similar to those of the previously studied ILs and DESs.

Regarding the effect of the type of ammonium salt of the DES on the extraction performance, the following conclusions can be made: (i) longer alkyl chain lengths on the cation (e.g. see results for THABr:EG versus TEACl:EG, and THABr:Gly versus TEACl:Gly) yield higher distribution coefficients but lower selectivities, and (ii) the replacement of an alkyl group by a phenyl group on the cation (e.g. see results for THABr:EG versus MTPPBr:EG, and THABr:Gly versus MTPPBr:Gly) generally yields lower distribution ratios but higher selectivities, but in both cases the differences are only minor.

It should be noted that all comparisons were done on a mass basis due to the differences in the molecular weight of the solvents, which is more fair and practical for large scale/industrial solvent selection. The selectivity affects the extractor size. High selectivity values (as obtained here for TEACl:Gly) imply that smaller equipment is needed, which results in a lower initial investment of capital cost. The smaller initial capital investment and the ease of solvent recovery, coupled with the cheap price of the DESs are all added values that could compensate the slightly higher amount of solvent needed due to the lower distribution coefficient (as obtained for TEACl:Gly).

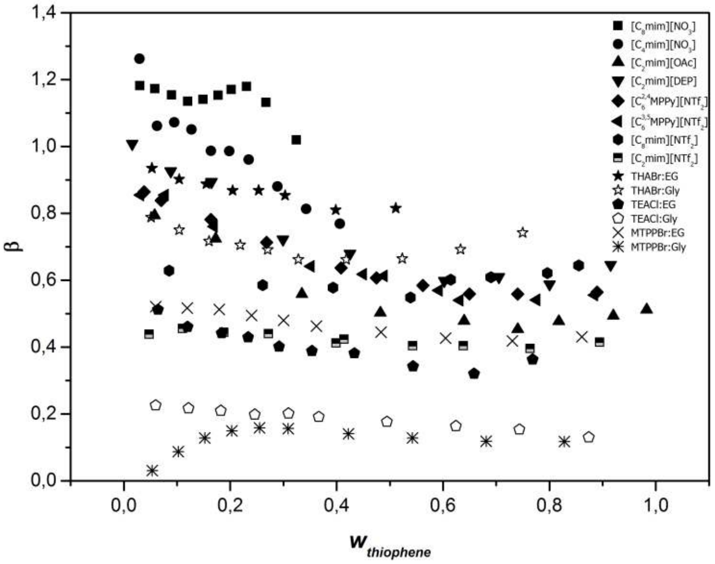


Figure 5: Solute distribution coefficients as function of the thiophene mass fraction in the aliphatic-rich phase for the {*n*-hexane + thiophene + solvent} systems.[7–11,26,35]

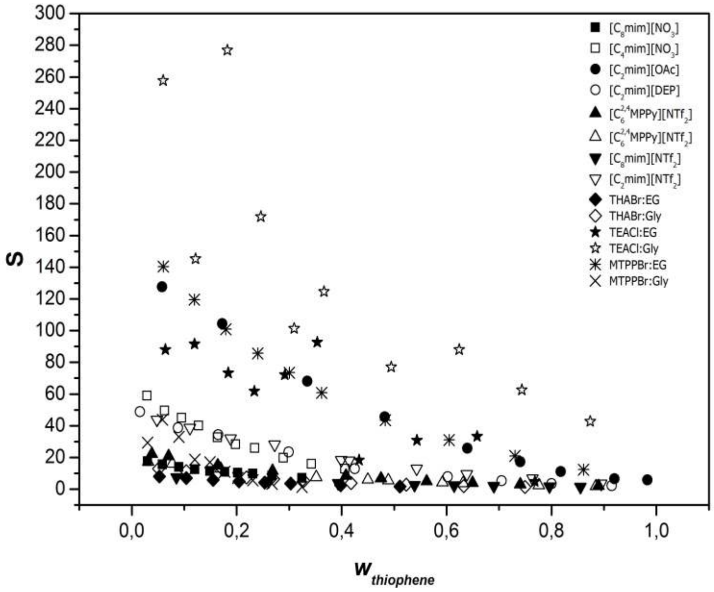


Figure 6: Selectivities as function of the thiophene mass fraction in the aliphatic-rich phase for the {*n*-hexane + thiophene + solvent} systems.[7–11,26,35]

5. Conclusions

In this work, four deep eutectic solvents (DESs) consisting of mixtures of ammonium salts with polyols were evaluated for their extraction properties of thiophene from *n*-hexane via liquid-liquid extraction. The DESs selected were: (i) tetraethylammonium chloride: ethylene glycol in molar ratio (1:2), (ii) tetraethylammonium chloride: glycerol (1:2), (iii) methyltriphenylphosphonium bromide:ethylene glycol (1:3), and (iv) methyltriphenylphosphonium bromide: glycerol (1:3). First, the binary solubilities of {thiophene + DES} and {*n*-hexane + DES} at 298.2 K and atmospheric pressure were determined. Then, the liquid-liquid equilibrium (LLE) data of the ternary systems {*n*-hexane + thiophene + DES} were determined at 298.2 K and atmospheric pressure. COSMO-RS was used to predict the ternary LLE data and to understand the extraction mechanism. Further, solute distribution coefficients and selectivities were calculated and compared to relevant literature. It can be concluded that the type of ammonium salt used to form the DES does not have a major effect on the distribution coefficient, but has some effect on the selectivity. The solute distribution coefficients obtained for the ethylene glycol-based DESs are always higher than those of glycerol-based DESs. Thus, the polyol was found to be dominantly affecting the extraction of thiophene. All DESs were found to be good candidates for extractive desulfurization with higher selectivities but somewhat lower distribution coefficients as compared to conventional ionic liquids.

Associated Content

Supporting information available presents selection of the DES used in this work, the ^{1}H-NMR spectra of the DESs, and the absence of DES in the system {*n*-hexane + thiophene + DES}, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

Author Information

Corresponding Authors: Maaike C. Kroon (mkroon@pi.ac.ae; +971-26075317) and Cor J. Peters (cpeters@pi.ac.ae; +971-26075492).

ORCID:

Maaike C. Kroon: 000-0002-5985-986X

Samah E. E. Warrag: 0000-0002-5928-8833

Funding

Petroleum Institute Research Center (PIRC) grant "Advanced *PVT*-Properties and Molecular Modeling of Complex Fluids in Support of Safe and Green Hydrocarbon Production" (project code: LTR14009).

Notes

The authors declare no competing financial interest.

Acknowledgments

We would like to gratefully acknowledge the financial support from the Petroleum Institute Research Center (PIRC) through a grant entitled "Advanced *PVT*-Properties and Molecular Modeling of Complex Fluids in Support of Safe and Green Hydrocarbon Production" (project code: LTR14009).

References

(1) Brunet, S.; Mey, D.; Perot, G.; Bouchy, C.; Diehl, F. On the Hydrodesulfurization of FCC Gasoline: A Review. *Appl. Catal. A Gen.* **2005**, *278*, 143–172.

(2) Shafi, R.; Hutchings, G. J. Hydrodesulfurization of Hindered Dibenzothiophenes: An Overview. *Catal. Today* **2000**, *59*, 423–442.

(3) Debajyoti, B. Design Parameters for a Hydro Desulfurization (HDS) Unit for Petroleum Naphtha at

3500 Barrels per Day. *World Sci. News* **2015**, *3*, 99–111.

(4) Song, C. An Overview of New Approaches to Deep Desulfurization for Ultra-Clean Gasoline , Diesel Fuel and Jet Fuel. *Catal. Today* **2003**, *86*, 211–263.

(5) Zhang, J.; Hu, B. Liquid-Liquid Extraction (LLE). In *Separation and Purification Technologies in Biorefineries*; **2013**, 61–78.

(6) Ali, S. H.; Hamad, D. M.; Albusairi, B. H.; Fahim, M. A. Removal of Dibenzothiophenes from Fuels by Oxy-Desulfurization. *Energy and Fuels* **2009**, *23*, 5986–5994.

(7) Alonso, L.; Arce, A.; Francisco, M.; Soto, A. Phase Behaviour of 1-Methyl-3-Octylimidazolium Bis[trifluoromethylsulfonyl]imide with Thiophene and Aliphatic Hydrocarbons: The Influence of N-Alkane Chain Length. *Fluid Phase Equilib.* **2008**, *263*, 176–181.

(8) Francisco, M.; Arce, A.; Soto, A. Ionic Liquids on Desulfurization of Fuel Oils. *Fluid Phase Equilib.* **2010**, *294*, 39–48.

(9) Rodríguez-Cabo, B.; Francisco, M.; Soto, A.; Arce, A. Hexyl Dimethylpyridinium Ionic Liquids for Desulfurization of Fuels. Effect of the Position of the Alkyl Side Chains. *Fluid Phase Equilib.* **2012**, *314*, 107–112.

(10) Rodríguez-Cabo, B.; Soto, A.; Arce, A. Desulfurization of Fuel-Oils with [C_2mim][NTf_2]: A Comparative Study. *J. Chem. Thermodyn.* **2013**, *57*, 248–255.

(11) Rodríguez-Cabo, B.; Arce, A.; Soto, A. Desulfurization of Fuels by Liquid-Liquid Extraction with 1-Ethyl-3-Methylimidazolium Ionic Liquids. *Fluid Phase Equilib.* **2013**, *356*, 126–135.

(12) Mokhtarani, B.; Mansourzareh, H.; Mortaheb, H. R. Phase Behavior of Nitrate Based Ionic Liquids with Thiophene and Alkanes. *Ind. Eng. Chem. Res.* **2014**, *53*, 1256–1261.

(13) Ma, M.; Reza, M.; Mokhtarani, B. Novel Liquid E Liquid Equilibrium Data for Six Ternary Systems Containing IL , Hydrocarbon and Thiophene at 25°C. *Fluid Phase Equilib.* **2016**, *412*, 21–28.

(14) Gordon, C. M. New Developments in Catalysis Using Ionic Liquids. *Appl. Catal. A Gen.* **2001**, *222*, 101–117.

(15) Welton, T. Ionic Liquids in Catalysis. *Coord. Chem. Rev.* **2004**, *248*, 2459–2477.

(16) Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. Novel Solvent Properties of Choline Chloride/urea Mixtures. *Chem. Commun. (Camb).* **2003**, 70–71.

(17) Francisco, M.; Van Den Bruinhorst, A.; Kroon, M. C. Low-Transition-Temperature Mixtures (LTTMs): A New Generation of Designer Solvents. *Angew. Chemie - Int. Ed.* **2013**, *52*, 3074–3085.

(18) Zhang, Q.; De Oliveira Vigier, K.; Royer, S.; Jérôme, F. Deep Eutectic Solvents: Syntheses, Properties and Applications. *Chem. Soc. Rev.* **2012**, *41*, 7108–7146.

(19) Domínguez de María, P.; Maugeri, Z. Ionic Liquids in Biotransformations: From Proof-of-Concept to Emerging Deep-Eutectic-Solvents. *Curr. Opin. Chem. Biol.* **2011**, *15*, 220–225.

(20) Li, C.; Li, D.; Zou, S.; Li, Z.; Yin, J.; Wang, A.; Cui, Y.; Yao, Z.; Zhao, Q. Extraction Desulfurization Process of Fuels with Ammonium-Based Deep Eutectic Solvents. *Green Chem.* **2013**, *15*, 2793–2799.

(21) Li, J. J.; Xiao, H.; Tang, X. D.; Zhou, M. Green Carboxylic Acid-Based Deep Eutectic Solvents as Solvents for Extractive Desulfurization. *Energy and Fuels* **2016**, *30*, 5411–5418.

(22) Gano, Z. S.; Mjalli, F. S.; Al-wahaibi, T.; Al-wahaibi, Y. The Novel Application of Hydrated Metal Halide ($SnCl_2.2H_2O$) – Based Deep Eutectic Solvent for the Extractive Desulfurization of Liquid Fuels. *Int. J. Chem. Eng. Appl.* **2015**, *6*, 367-271.

(23) Tang, X. dong; Zhang, Y. fen; Li, J. jing; Zhu, Y. qiang; Qing, D. yong; Deng, Y. xin. Deep Extractive Desulfurization with Arenium Ion Deep Eutectic Solvents. *Ind. Eng. Chem. Res.* **2015**, *54*, 4625–4632.

(24) Hadj-Kali, M. K.; Mulyono, S.; Hizaddin, H. F.; Wazeer, I.; El-Blidi, L.; Ali, E.; Hashim, M. A.; AlNashef, I. M. Removal of Thiophene from Mixtures with *N* -Heptane by Selective Extraction Using Deep Eutectic Solvents. *Ind. Eng. Chem. Res.* **2016**, *55*, 8415–8423.

(25) Warrag, S. E. E.; Rodriguez, N. R.; Nashef, I. M.; van Sint Annaland, M.; Siepmann, J. I.; Kroon, M. C.; Peters, C. J. Separation of Thiophene from Aliphatic Hydrocarbons Using Tetrahexylammonium-Based Deep Eutectic Solvents as Extracting Agents. *J. Chem. Eng. Data* **2017**, *62*, 2911–2919.

(26) Warrag, S. E. E.; Peters, C. J.; Kroon, M. C. Deep Eutectic Solvents for Highly Efficient Separations in Oil and Gas Industries. *Curr. Opin. Green Sustain. Chem.* **2017**, *5*, 55–60.

(27) Klamt, A. Conductor-like Screening Model for Real Solvents : A New Approach to the Quantitative Calculation of Solvation Phenomena. *J. Phys. Chem.* **1995**, *99*, 2224–2235.

(28) Klamt, A.; Eckert, F. COSMO-RS: A Novel and Efficient Method for the a Priori Prediction of

Thermophysical Data of Liquids. *Fluid Phase Equilib.* **2000**, *172*, 43–72.

(29) Klamt, A.; Eckert, F. Erratum to " COSMO-RS : A Novel and Efficient Method for the a Priori Prediction of Thermophysical Data of Liquids " [Fluid Phase Equilib . 172 (2000) 43 – 72]. *Fluid Phase Equilib.* **2003**, *205*, 357.

(30) COSMOtherm. A Graphical User Inerface to the COSMOtherm Program, User Guide. COSMOlogic GmbH & Co KG: Leverkusen, Germany 2013.

(31) Lin, H.; Wu, D.; Liu, L.; Jia, D. Theoretical Study on Molecular Structures , Intramolecular Proton Transfer Reaction , and Solvent Effects of 1-Phenyl-3-. *J. Mol. Struct. THEOCHEM* **2008**, *850*, 32–37.

(32) Hizaddin, H. F.; Ramalingam, A.; Hashim, M. A.; Hadj-kali, M. K. O. Evaluating the Performance of Deep Eutectic Solvents for Use in Extractive Denitri Fi Cation of Liquid Fuels by the Conductor-like Screening Model for Real Solvents. *J. Chem. Eng. Data* **2014**, *59*, 3470–3487.

(33) Sørensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, A. Liquid-Liquid Equilibrium Data: Their Retrieval, Correlation and Prediction Part I: Retrieval. *Fluid Phase Equilib.* **1979**, *2*, 297–309.

(34) McKetta, J. J. *Encyclopedia of Chemical Processing and Design: Volume 21 - Expanders to Finned Tubes*, 1st ed.; M. Dekker, 1984.

(35) Mokhtarani, B.; Mansourzareh, H.; Mortaheb, H. R. Phase Behavior of Nitrate Based Ionic Liquids with Thiophene and Alkanes. *Ind. Eng. Chem. Res.* **2014**, *53*, 1256–1261.

For Table of Contents Only