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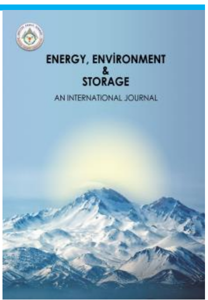

Deep Eutectic Solvents for Liquid-Liquid Extraction-Denitrification

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ABSTRACT. In this study, a new type of deep eutectic solvent was prepared and tested for the selective extraction of nitrogen compounds from model fuels. DES2 was made of triethylammonium acetate $[TEA]^+[AcO]^-$ and glycerol in a volume ratio of 1:6. The extraction capacity of DES2 was evaluated and compared to DES1a, and DES1b. The denitrification process was carried out at room temperature. The volume ratio of DESs to model fuels were taken 1:1. Obtained results showed, that DES2 was highly selective for all nitrogen compounds (pyridine, quinoline, indole, and pyridine/quinoline mixture) in a one-step liquid-liquid extraction (LLE). The purification rate of the pyridine, indole and pyridine/quinoline mixture was 100, 98 and 88% in one hour. Quinoline showed high-extraction efficiency (92%) in three hours of mixing time. All experiments were evaluated by NMR spectra.

Keywords: DES, denitrification, NMR, glycerol, separation

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The abbreviations:

DESs -Deep eutectic solvents
DES1a - NH_4Cl:Glycerol (1:12)
DES1b - NH_4Cl:Glycerol (1:6)
DES2 - Triethylammonium acetate:Glycerol (1:6)
$[TEA]^+[AcO]^-$ -triethylammonium acetate
HBD -hydrogen bond donor
HBA -hydrogen bond acceptor
LLE -liquid-liquid extraction

1. INTRODUCTION

The fundamental principles of green chemistry aim to design less consumption of energy, use non-toxic chemical reagents, decrease environmental pollution, and include waste prevention [1]. For this reason, new types of green solvents called ionic liquids, invested as alternatives to classical organic solvents. ILs have been widely used due to their remarkable properties such as high thermal stability, low vapor pressure, nonflammability, recycling, etc[2-4]. However, some disadvantages of ILs limited their application. The poor biodegradability, toxicity, complexity, and highly costly synthesis are considerable drawbacks to the use of these solvents [5].

Deep eutectic solvents, analogs to ionic liquids have emerged as a new generation of eco-friendly solvents. DESs are typically easy to synthesize. It is prepared by

The current work reports the selective separation of nitrogen compounds with a new deep eutectic solvent DES2. Pyridine, quinoline, indole, and pyridine/quinoline mixture with 1,7% were the content of model fuel (mixtures of n-decane and n-hexadecane). The purification of model fuels by DESs was investigated and evaluated at room temperature.

The results showed the extraction capacity of DES2 was higher than DES1a and DES1b for all nitrogen components. For the pyridine, quinoline, indole, and pyridine/quinoline mixtures high results were obtained in 1 hour by DES2. The experiments were evaluated by ^{1}H NMR analysis.

2. EXPERIMENTAL

2.1 Materials and methods

Chemicals
All chemicals used in this paper were obtained from Sigma-Aldrich (Germany). Pyridine, quinoline, and indole with ≥ 99% high purity were used to prepare new model

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fuel samples. Triethylammonium acetate [TEA]$^+$[AcO]$^-$ was synthesized in the laboratory.

Synthesis of DESs

DES2 was synthesized by mixing triethylammonium acetate [TEA]$^+$[AcO]$^-$ as a hydrogen bond acceptor and glycerol as a hydrogen bond donor. The volume ratio of HBA:HBD was taken 1:6.

Experimental procedure

Pyridine, quinoline, pyridine/quinoline and indole with 1,7% content were added to the mixture of n-decane and hexadecane (model fuel). LLE process was investigated in a volume ratio of DESs to model fuels 1:1. All experiments were carried out at room temperature (Figure 1 and 2).

Fig. 1. Preparation of the DES2

Fig. 2. LLE of nitrogen compounds from the model fuel

NMR analysis

LLE evaluation was by the integral intensity of 1H NMR spectra. NMR experiments have been performed on a BRUKER FT NMR spectrometer (UltraShieldTM Magnet) AVANCE 300 (300.130 MHz) with a BVT 3200 variable temperature unit in 5 mm sample tubes using Bruker Standard software (TopSpin 3.1). The ^{1}H chemical shifts were referenced to internal tetramethylsilane (TMS); the experimental parameters for ^{1}H: digital resolution = 0.23 Hz, SWH = 7530 Hz, TD = 32 K, SI = 16 K, 90^0 pulse-length = 10 μs, PL1 = 3 dB, ns-= 1, ds= 0, d1 =1 s; for ^{13}C: digital resolution = 0.27 Hz, SWH = 17985 Hz, TD = 64 K, SI = 32 K, 90^0 pulse-length = 9 μs, PL1 = 1.5 dB, ns= 100, ds= 2, d1= 3 s. NMR-grade $CDCl_3$ was used for the analysis of model fuel blends.

3. RESULTS AND DISCUSSION

3.1 Characterization of DESs

Some physical properties of DESs have shown in Table 1. The value of solvent viscosity and density are considerable factors for the separation process. The energy consumption of the mixing process and the mixing regime is determined due to viscosity and density. On the other side, the rate of stratification also depends on the solvent density [17].

Table 1 Some physical properties of DESs

Type of DES (HBA: HBD)	Density at 20° C, g/sm³	Viscosity, at 20°C, mm²/s	Viscosity, at 40°C, mm²/s
DES 1a	**1,2307**	**97,384**	**32,647**
DES 1b	**1,2309**	**81,656**	**27,829**
DES 2	**1,1949**	**120,812**	**36,780**

In addition, the stability data was tested at 298,15 K, 1 atm. over a month. All DESs showed high results and remained as homogenous liquid at room temperature.

3.2. Liquid-liquid extraction process

From our previous research, it is obvious that DES1a and DES1b were checked for the selective extraction of pyridine, quinoline, indole and pyridine/quinoline mixture. In this work, we studied the separation of all indicated nitrogen compounds by DES2, based on triethylammonium acetate [TEA]$^+$[AcO]$^-$ and the selectivity compared to DES1a and DES1b. All experiments were carried out at room temperature.

As can be seen from Table 2 and Table 3, the optimal separation efficiencies of indole were observed in 3 hours of mixing time. DES1b (94%) was more selective than DES1a (80%) in the same molar ratio and reaction conditions. However, in three hours of mixing time, the maximum separation results of quinoline were 60% by DES1a and 50% by DES1b.

Pyridine was completely separated in one hour of mixing time by DES1b. The pyridine/quinoline mixture was purified from the model fuel in one-hour mixing time by DES1a. The high extraction efficiency was 72%.

Table 2 Extraction of nitrogen compounds by DES1a at room temperature

DES [NH$_4$Cl (1): Glycerol (12)]			
Amount of nitrogen compounds	**DES: fuel (volume ratio)**	**Time (hour)**	**Separation efficiency, (%)**
Pyridine (1,7%)	1:1	1	87
Pyridine (1,7%)	1:1	3	92
Pyridine (1,7%)	1:1	5	85
Indole (1,7%)	1:1	1	38
Indole (1,7%)	1:1	3	80
Indole (1,7%)	1:1	5	71
Quinoline (1,7%)	1:1	1	40
Quinoline (1,7%)	1:1	3	60
Quinoline (1,7%)	1:1	5	46
Pyridine/Quinoline (1,7%)	1:1	1	72
Pyridine/Quinoline (1,7%)	1:1	3	58
Pyridine/Quinoline (1,7%)	1:1	5	45

Table 3 Extraction of nitrogen compounds by DES1b at room temperature

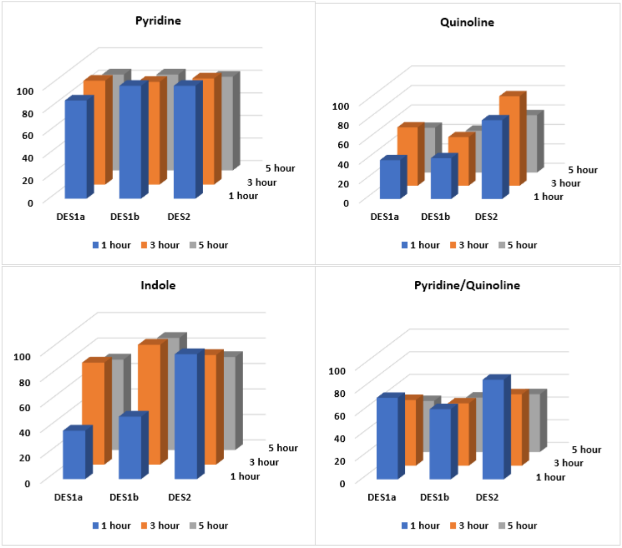
DES [NH$_4$Cl (1): Glycerol (6)]			
Amount of nitrogen compounds	**DES: fuel (volume ratio)**	**Time (hour)**	**Separation efficiency, (%)**
Pyridine (1,7%)	1:1	1	100
Pyridine (1,7%)	1:1	3	91
Pyridine (1,7%)	1:1	5	85
Indole (1,7%)	1:1	1	49
Indole (1,7%)	1:1	3	94
Indole (1,7%)	1:1	5	88
Quinoline (1,7%)	1:1	1	42
Quinoline (1,7%)	1:1	3	50
Quinoline (1,7%)	1:1	5	43
Pyridine/Quinoline (1,7%)	1:1	1	62
Pyridine/Quinoline (1,7%)	1:1	3	55
Pyridine/Quinoline (1,7%)	1:1	5	48

The extraction capacity of DES2 for each nitrogen component was listed in Table 4. NMR analysis for pyridine, quinoline, indole, and pyridine/quinoline mixture showed, that high results were in 1 hour mixing time. Pyridine was completely separated from model fuel (Figure 3). The purification rate of the indole and pyridine/quinoline mixture was 98% and 88%. Quinoline showed high-extraction efficiency in three hours of mixing time. We could receive 92% separation at a single-stage LLE.

Table 4 Extraction of nitrogen compounds by DES2 at room temperature

DES [triethylammonium acetate (1): Glycerol (6)]			
Amount of nitrogen compounds	**DES: fuel (volume ratio)**	**Time (hour)**	**Separation efficiency, (%)**
Pyridine (1,7%)	1:1	1	100
Pyridine (1,7%)	1:1	3	94
Pyridine (1,7%)	1:1	5	83
Indole (1,7%)	1:1	1	98
Indole (1,7%)	1:1	3	86
Indole (1,7%)	1:1	5	73
Quinoline (1,7%)	1:1	1	81
Quinoline (1,7%)	1:1	3	92
Quinoline (1,7%)	1:1	5	59
Pyridine/Quinoline (1,7%)	1:1	1	88
Pyridine/Quinoline (1,7%)	1:1	3	63
Pyridine/Quinoline (1,7%)	1:1	5	51

It is also evident from Scheme 1, DES2 is more selective for the denitrification process than DES1a and DES1b. In one hour of mixing time, DES2 showed very high extraction for each nitrogen compound. The separation efficiency decreased linearly with increasing mixing time for the pyridine, indole, and pyridine/quinoline mixture. In contrast to other compounds, the best result for quinoline was reached in three hours of mixing time by DES2. DESs can be ranked according to the ability of removing nitrogen compounds from model fuel like that: *DES1a<DES1b<DES2*.



Scheme 1. The separation efficiency of nitrogen compounds by DES1a, DES1b, and DES2

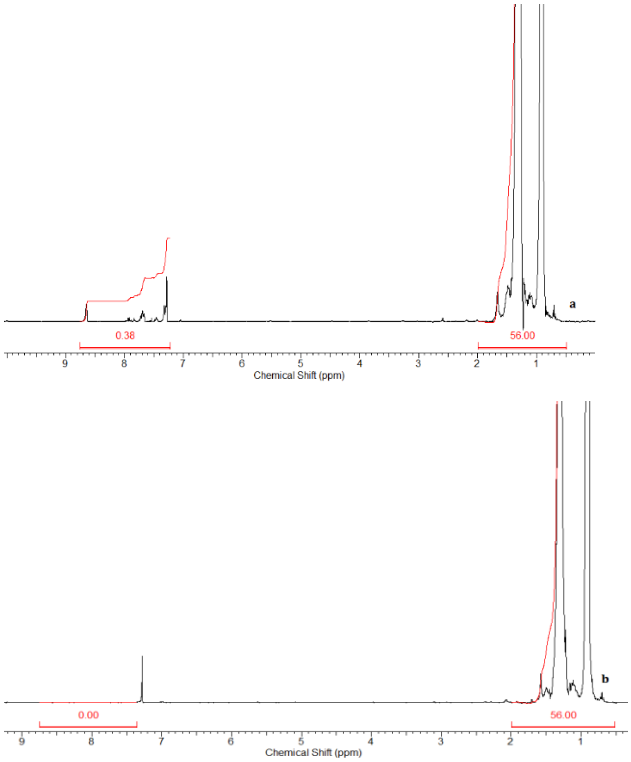


Fig. 3. ^{1}H NMR analysis for pyridine of before (***a***) and after (***b***) LLE

4. CONCLUSION

In this study, we investigated the selectivity of a new type of deep eutectic solvent for the separation of nitrogen compounds from model fuel. DES2 was synthesized by mixing triethylammonium acetate as HBA and glycerol as HBD. The denitrification process was carried out at room temperature, and the results were compared between DES1a, DES1b, and DES2. From the obtained results, it is obvious that DES2 is more selective for all nitrogen components. In one hour of mixing, the maximum separation efficiencies of the indole and pyridine/quinoline mixture were 98% and 88%, respectively, by using DES2. High-efficiency separation for quinoline was 92% in three hours of mixing time. Pyridine was completely separated from model fuel at a single-stage LLE by DES1b and DES2. DES1a showed a lower selectivity capacity for the most of nitrogen components than DES1b and DES2.

REFERENCES

[1] Anastas, P.T., Warner, J.C. Principles of green chemistry. *Green chemistry: Theory and practice*, 1998, 135p.

[2] Ghandi, K. A review of ionic liquids, their limits and applications. *Green and sustainable chemistry*, 4, 44-53, 2014.

[3] Walkoli, A.T., Sonawane, P.D. Ionic liquids: Eco-friendly solvent, *Research & Reviews in Biotechnology & Biosciences*, 9(1), 9-13, 2022.

[4] Welton, T. Room-temperature ionic liquids. Solvents for synthesis and catalysis, *Chemical reviews*, 99(8), 2071-2084, 1999.

[5] Peric, B., Sierra, J., Martí, E., Cruañas, R., Garau, M.A, Arning, J., Bottin-Weber, U., Stolte, S. (Eco) toxicity and biodegradability of selected protic and aprotic ionic liquids, *Journal of hazardous materials*, 261, 99-105, 2013.

[6] Zhang, Q., Vigier, K.D., Royer, S., Jérôme, F. Deep eutectic solvents: syntheses, properties and applications, *Chemical Society Reviews*, 41(21), 7108-7146, 2012.

[7] Abbott, A.P., Boothby, D., Capper, G., Davies, D.L., Rasheed, R.K. Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids, *Journal of the American Chemical Society*, 126(29), 9142-9147, 2004.

[8] Hansen, B.B., Spittle, S., Chen, B., Poe, D., Zhang, Y., Klein, J.M., Horton, A., Adhikari, L., Zelovich, T., Doherty, B.W., Gurkan, B. Deep eutectic solvents: A review of fundamentals and applications, *Chemical reviews*, 121(3), 1232-1285, 2020.

[9] Elachkar, T., Greige-Gerges, H., Fourmentin, S. Basics and properties of deep eutectic solvents: a review, *Environmental chemistry letters*, 19, 3397-3408, 2021.

[10] Tang, B., Row, K.H. Recent developments in deep eutectic solvents in chemical sciences. *Monatshefte für Chemie-Chemical Monthly*, 144, 1427-1454, 2013.

[11] Chen, J., Li, Y., Wang, X., Liu, W. Application of deep eutectic solvents in food analysis: A review, *Molecules*, 24(24), 4594-4604, 2019.

[12] Shahbaz, K., Mjalli, F.S., Hashim, M.A., Alnashef, I.M. Using deep eutectic solvents based on methyl triphenyl phosphunium bromide for the removal of glycerol from palm-oil-based biodiesel, *Energy & Fuels*, 25(6), 2671-2678, 2011.

[13] Warrag, S.E., Darwish, A.S., Abuhatab, F.O., Adeyemi, I.A., Kroon, M.C., Alnashef, I.M. Combined extractive dearomatization, desulfurization, and denitrogenation of oil fuels using deep eutectic solvents: A parametric study, *Industrial & Engineering Chemistry Research*, 59(25), 11723-11733, 2020.

[14] Warrag, S.E., Darwish, A.S., Adeyemi, I.A., Hadj-Kali, M.K., Kroon, M.C., Alnashef I.M. Extraction of pyridine from n-alkane mixtures using methyltriphenylphosphonium bromide-based deep eutectic solvents as extractive denitrogenation agents, *Fluid Phase Equilibria*, 517, 112622, 2020.

[15] Sudhir, N., Yadav, P., Nautiya,l B.R., Singh, R., Rastogi, H., Chauhan, H. Extractive desulfurization of fuel with methyltriphenyl phosphonium bromide-tetraethylene glycol-based eutectic solvents, *Separation Science and Technology*, 55(3), 554-563, 2020.

[16] Niftullayeva, S., Mamedov, I. Extraction of nitrogen compounds from model fuel by DES, Modern problems of theoretical & experimental chemistry, *International conference*, 168-169, 2022.

[17] Rogošić, M., Kučan, K.Z. Deep eutectic solvent based on choline chloride and propylene glycol as a potential medium for extraction denitrification of hydrocarbon fuels, *Chemical Engineering Research and Design*, 161, 45-57, 2020.