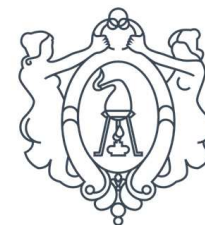




Extraction of sulfur compounds from liquid fuels with the addition of oxidizing agent



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ABSTRACT:

Hydrosulfurization (HDS), a widely employed method in industries for the desulfurization of fuel oils, such as gasoline and diesel fuel, is faced with the challenge of producing lower-sulfur or sulfur-free fuel oils, which are required by more and more countries. However, HDS is not very effective for the removal of thiophenic sulfur compounds, unless operated under harsh conditions, such as high temperature, high pressure, and requirement of a noble catalyst and hydrogen. Extractive desulfurization (EDS) and oxidative desulfurization (ODS) of fuel oils using ionic liquids (ILs) has been intensively studied in recent years by our team and has a good future as an alternative or complementary method to HDS.

In this study, we present experimental data of liquid-liquid phase equilibrium (LLE) for the ternary systems [BMMOR][TCM] or [HMMOR][TCM] (1) + thiophene, or benzothiophene (2) + heptane (3) at temperature $T = 308.15$ K and at atmospheric pressure. High solubility of sulfur compounds and practical complete immiscibility of heptane in ionic liquids have been observed. Selectivity and solute distribution ratio, derived from the experimental equilibrium data, were calculated and used to determine the efficiency of these ionic liquid as a solvent for the extraction of sulfur compounds from model fuels. The experimental data were correlated using the NRTL equation [1], and the binary interaction parameters have been reported.

In the second part of our experiment, the oxidative desulfurization of model fuels has been studied using tricyanometanide-based ionic liquid. Model liquid fuel was prepared by dissolving aromatic sulfur compounds in alkane. Oxidation in this process was achieved by adding hydrogen peroxide and acetic acid to the mixture. Different parameters such as oil to IL, or DES ratio, oxidant to sulfur ratio, temperature were optimized.

Based on our research, we can conclude that EDS and ODS using ILs are a potentially preferable methods to remove thiophenic S compounds compared to traditional HDS technology.

MATERIALS

Ionic liquids

1-hexyl-1-methylmorpholinium tricyanometanide, [HMMOR][TCM],
synthesis in our laboratory

1-butyl-1-methylpyrrolidinium tricyanometanide, [BMPYR][TCM],
CAS No. 878027-72-6, supplied by IOLTec GmbH.

1-butyl-1-methylmorpholinium tricyanometanide, [BMMOR][TCM],
CAS No. 1620828-20-7, supplied by IOLTec GmbH.

sulfur compounds

benzothiophene,
CAS No. 95-15-8, supplied by Sigma-Aldrich

thiophene,
CAS No. 110-02-1, supplied by Sigma-Aldrich

model fuel

n-heptane,
CAS No. 142-82-9, supplied by Sigma-Aldrich

oxidizing agent

hydrogen peroxide,
CAS No. 7722-84-1, supplied by Sigma-Aldrich

acetic acid,
CAS No. 64-19-7, supplied by Sigma-Aldrich

Fig. 1. Experimental tie-lines (●, black lines) for the LLE of the ternary system {[HMMOR][TCM] (1) + thiophene (2) + heptane (3)} at $T = 308.15$ K and $p = 0.1$ MPa. The corresponding tie-lines correlated by means of the NRTL equation (○, blue lines).

Fig. 2. Experimental tie-lines (●, black lines) for the LLE of the ternary system {[HMMOR][TCM] (1) + benzothiophene (2) + heptane (3)} at $T = 308.15$ K and $p = 0.1$ MPa. The corresponding tie-lines correlated by means of the NRTL equation (○, blue lines).

Fig. 3. Experimental tie-lines (●, black lines) for the LLE of the ternary system {[BMMOR][TCM] (1) + thiophene (2) + heptane (3)} at $T = 308.15$ K and $p = 0.1$ MPa. The corresponding tie-lines correlated by means of the NRTL equation (○, blue lines).

Fig. 4. Experimental tie-lines (●, black lines) for the LLE of the ternary system {[BMMOR][TCM] (1) + benzothiophene (2) + heptane (3)} at $T = 308.15$ K and $p = 0.1$ MPa. The corresponding tie-lines correlated by means of the NRTL equation (○, blue lines).

Table 1. Binary interaction parameters and root mean square deviation (σ_{ij}) for the NRTL equation for ternary systems {[BMMOR][TCM] or [HMMOR][TCM] (1) + thiophene or benzothiophene (2) + heptane (3)} at $T = 308.15$ K, $p = 0.1$ MPa. Parameter $\alpha_{ij} = \alpha_{ji} = 0.2$

Components <i>i-j</i>	NRTL parameters		RMSD σ_{ij}
	$g_{ij}^E - g_{ij}^E$ (J mol ⁻¹)	$g_{ij}^E - g_{ij}^E$ (J mol ⁻¹)	
[BMMOR][TCM] (1) + thiophene (2) + heptane (3)			
1-2	1930.4	58458	0.006
1-3	5659.7	15880	
2-3	3023.3	1378.3	
[BMMOR][TCM] (1) + benzothiophene (2) + heptane (3)			
1-2	4703.9	68148	0.008
1-3	7127.3	15240	
2-3	756.20	5067.7	
[HMMOR][TCM] (1) + thiophene (2) + heptane (3)			
1-2	-861.03	60820	0.005
1-3	4123.0	15883	
2-3	5056.2	-1327.2	
[HMMOR][TCM] (1) + benzothiophene (2) + heptane (3)			
1-2	1581.0	66983	0.006
1-3	5262.3	14960	
2-3	3448.0	600.52	

Equation 1: selectivity Equation 2: solute distribution ratio

$$S = \frac{x_2^I \cdot x_3^I}{x_2^II \cdot x_3^II} \quad \beta = \frac{x_2^I}{x_2^II}$$

Components:
(1) ionic liquid
(2) thiophene/benzothiophene
(3) heptane

Phases:
(I) phase rich in hydrocarbon
(II) phase rich in ionic liquid

Fig. 5. Plots of the selectivity (a) and solute distribution ratio (b) as a function of the mole fraction of solute in the hydrocarbon-rich phase for the ternary systems: (●) {[BMMOR][TCM] (1) + thiophene (2) + heptane (3)}; (○) {[BMMOR][TCM] (1) + benzothiophene (2) + heptane (3)}; (●) {[HMMOR][TCM] (1) + thiophene (2) + heptane (3)}; (○) {[HMMOR][TCM] (1) + benzothiophene (2) + heptane (3)}; (●) {[BMPYR][TCM] (1) + thiophene (2) + heptane (3)} at $T = 298.15$ K [2]

The oxidative-extractive desulfurization of model fuels has been studied using tricyanometanide-based ionic liquid. Model liquid fuel was prepared by dissolving benzothiophene in octane (500 ppm of sulfur). Oxidation in this process was achieved by adding hydrogen peroxide and acetic acid to the mixture.

$$\text{Extraction efficiency (\%)} = \frac{S_{BE} - S_{AE}}{S_{BE}} \cdot 100\%$$

where S_{BE} and S_{AE} refer to the total concentration of sulfur in the model oil before and after extraction.

Fig. 6. The effect of extraction time (a) and the amount of oxidant (b) on sulfur removal. As extractant used:

[BMMOR][TCM]:
(●) at $T = 308.2$ K, (○) at $T = 318.2$ K;
[BMPYR][TCM]:
(●) at $T = 308.2$ K, (○) at $T = 318.2$ K;

References

- [1] J. M. Prausnitz, R. N. Lichtenthaler, E. Gomes de Azevedo, *Molecular Thermodynamics of Fluid Phase Equilibria*, Third Edition, (1999) Prentice Hall International Series in the Physical and Chemical Engineering Sciences
- [2] U. Domańska, E. V. Lukoshko, M. Królikowski, *J. Chem. Thermodyn.* 61 (2013) 126–131.

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