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Liquid–liquid equilibrium (LLE) data for ternary mixtures of {[EMIM][$EtSO_4$] + thiophenebenzothiophene + n-hexadecane}and {[EMIM][$MeSO_3$] + thiophene/benzothiophene + n-hexadecane} at 298.15 K

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ABSTRACT

The tie-line composition for the ternary systems of [EMIM][$EtSO_4$](1) + thiophene(2)/benzothiophene(2) + n-hexadecane(3), and [EMIM][$MeSO_3$](1) + thiophene(2)/benzothiophene(2) + n-hexadecane(3) is experimentally determined at 298.15 K. This measured LLE data was compared and correlated with COSMO-RS model, NRTL and UNIQUAC models. The good fitness of experimental data with model values was calculated by RMSD and a good agreement was obtained. Besides, the extraction capability of [EMIM][$EtSO_4$] and [EMIM][$MeSO_3$] towards sulphur-containing compounds was also investigated with respect to distribution coefficient and selectivity. The consistency of tie-line data was ascertained by applying the Othmer–Tobias and Hand equations.

1. Introduction

Reduction of sulphur content in liquid fuels is very important for environmental protection. The removal of sulphur is generally done through hydrodesulphurization (HDS) process. As the European Union (EU) and Environmental Protection Agency (EPA) regulations require less than 10 ppm sulphur in liquid fuels, thus there is a demand for *a new process* for deep desulphurization. The conventional HDS process requires both high temperature and high pressure hydrogen gas. Moreover, HDS is not effective at removing aromatic sulphur such as thiophene (TS), benzothiophene (BT), dibenzothiophene (DBT) and its alkyl substituted derivatives [1,2]. Therefore, some alternative methods have been explored such as reactive distillation, several precipitation techniques, reactive alkylation, complexation, adsorption desulphurization, extractive desulphurization, oxidation desulphurization, biodesulphurization, photochemical desulphurization, and several ultrasonic treatment extractions, as well as solvent extraction. Among these methods, solvent extraction is a well-established process in the petroleum industry [3]. Solvent extraction can be carried out at or around ambient temperature and pressure, without the need for hydrogen gas, and does not change the chemical structure of liquid fuel components [4]. However, the extraction solvent must show high capacity, high solute distribution ratio, high selectivity and high performance index. In addition, the extraction solvent should also be sufficiently selective towards sulphur containing compounds without affecting octane number (due to iso-octane concentration in gasoline) of gasoline and cetane number (due to hexadecane concentration in diesel) of diesel fuels [2–4]. There are many organic solvents such as polyalkyleneglycol, polyalkyleneglycol ether, pyrrolidones, imidazolidiones, dimethyl sulfoxide and pyrimidinones that have been used for the removal of sulphur containing compounds from liquid fuels, but none of them shows a good performance in order to minimize the negative health impact and environmental pollutant emission (i.e. SO_X emissions into atmosphere)from liquid fuels.

Ionic liquids (ILs) have been recognized as green and designable solvents, which remain as liquid over a wide temperature range including room temperature. ILs are easy to synthesis, handle and they present several characteristic advantages over organic solvents. ILs have negligible vapor pressure, high chemical and thermal stability, non-flammability, higher density and less viscosity. These properties can make them environmentally friendly solvents for effective separation of aromatic sulphur-containing compounds from liquid fuels at 298.15 K without solvent loss into the atmosphere [5]. However, the use of ILs in large scale applications is limited due to their moisture sensitivity (chloroaluminate), formation of hydrolysis products in the presence of water at elevated temperature (Lewis and Bronsted-acidic ILs), low stability of anions (hexafluorophosphate), and cost (fluorinated

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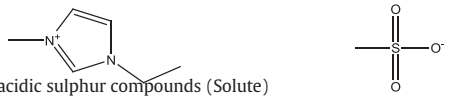
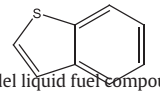
Table 1
List of chemicals used in this study.

S.No	Name	Structure	Acronym
		Ionic Liquids (Solvent)	
1	1-Ethyl-3-methylimidazolium ethylsulphate		[EMIM][$EtSO_4$]
2	1-Ethyl-3-methylimidazolium methylsulphonate		[EMIM][$MeSO_3$]
		Non-acidic sulphur compounds (Solute)	
3	Thiophene		TS
4	Benzothiophene		BT
		Model liquid fuel compounds (Carrier)	
5	n-Hexadecane (cetane)		HX

amides). To avoid these problems, alkyl sulfates, phosphates, bis (trifluoromethylsulfonyl) imide and acetate anion-based ILs is better for industrial purpose [6–9].

In this study, the tie-line end composition for [EMIM][$EtSO_4$](1) + thiophene(2) + n-hexadecane(3), [EMIM][$EtSO_4$](1) + benzothiophene(2) + n-hexadecane(3), [EMIM][$MeSO_3$](1) + thiophene(2) + n-hexadecane(3) and [EMIM][$MeSO_3$](1) + benzothiophene(2) + n-hexadecane(3) systems is experimentally determined at 298.15 K. The ability and feasibility of [EMIM][$EtSO_4$] and [EMIM][$MeSO_3$] were analyzed with respect to the slope of tie-line in the phase diagram, distribution coefficient and selectivity values for deep desulphurization of liquid fuels. N-hexadecane (cetane number) was taken as a model for diesel compound. Meanwhile, thiophene and benzothiophene were used to represent non-acidic sulphur compounds (80%) in liquid fuels or diesel oil.

2. Experimental

2.1. Chemicals

Ionic liquids 1-ethyl-3-methylimidazolium ethylsulphate ([EMIM][$EtSO_4$]) and 1-ethyl-3-methylimidazolium methylsulphonate ([EMIM][$MeSO_3$]) with a nominal of purity ≥95% were purchased from Sigma-Aldrich, Germany. Thiophene and benzothiophene of purity >98% were supplied by Sigma-Aldrich, Germany. n-Hexadecane was obtained from Sigma-Aldrich with a quoted purity ≥99%. All chemicals were used without further purification. Molecular structure and physical properties of the substances are given in Tables 1 and 2.

2.2. Procedure and composition analysis

Feed mixtures of *n*-hexadecane and sulphur compounds (thiophene and benzothiophene) were prepared with the concentration of sulphur compound (thiophene or benzothiophene) ranging between 5 and 50 wt.%. After that, the IL [EMIM][$EtSO_4$] was added so that the feed to solvent mass ratio was 1:1. All weighing were done using Mettler Toledo weighing balance with an accuracy of $\pm 1\times10^{-4}g$. Screw-capped scintillation vials were used to hold the mixtures to ensure sufficient agitation was employed to achieve equilibrium. The vials were

Table 2
Physical properties of components used in this work.

Component Name	CAS no.	M.F	M.W g/mol	M.P K	B.P/F.P K	Assay %
[EMIM][$EtSO_4$]	342,573–75–5	$C_8H_{16}N_2O_4S$	236.29	263.15	356.15	≥99
[EMIM][$MeSO_3$]	145,022–45–3	$C_7H_{14}N_2O_3S$	206.26	–	559.15	≥95
Thiophene	110–54–3	C_4H_4S	84.14	235.15	357.15	≥99
Benzothiophene	95–15–8	C_8H_6S	134.20	303.95	494.15	≥98
n-Hexadecane	544–76–3	$C_{16}H_{34}$	226.44	293.15	560.15	≥99

Table 3
Experimental LLE data of the system Imidazolium based Ionic liquids (1) + sulphur-containing compounds (2) + n-Hexadecane (3) at 298.15 K (mole fraction).

Ionic Liquids	Sulphur-containing compounds	Ionic Liquid rich phase		n-Hexadecane rich phase	
		X_{21}	X_{31}	X_{22}	X_{32}
[EMIM][$EtSO_4$]	Thiophene	0.060	0.022	0.074	0.926
		0.111	0.021	0.134	0.866
		0.168	0.018	0.193	0.807
		0.207	0.012	0.250	0.750
		0.248	0.016	0.304	0.696
		0.305	0.007	0.356	0.644
		0.330	0.016	0.409	0.591
		0.370	0.006	0.455	0.545
		0.404	0.007	0.505	0.495
		0.424	0.010	0.555	0.445
[EMIM][$EtSO_4$]	Benzothiophene	0.049	0.011	0.050	0.950
		0.077	0.038	0.090	0.910
		0.120	0.009	0.139	0.861
		0.146	0.014	0.193	0.807
		0.176	0.009	0.244	0.756
		0.199	0.009	0.289	0.711
		0.213	0.004	0.336	0.664
		0.235	0.008	0.383	0.617
[EMIM][$MeSO_3$]	Thiophene	0.265	0.009	0.451	0.549
		0.266	0.007	0.492	0.508
		0.065	0.037	0.050	0.950
		0.123	0.021	0.102	0.898
		0.166	0.015	0.155	0.845
		0.226	0.011	0.207	0.793
		0.262	0.010	0.271	0.729
		0.308	0.011	0.312	0.688
		0.338	0.008	0.376	0.624
		0.358	0.006	0.432	0.568
		0.401	0.009	0.485	0.515
		0.425	0.019	0.531	0.469
[EMIM][$MeSO_3$]	Benzothiophene	0.055	0.039	0.030	0.970
		0.096	0.047	0.069	0.931
		0.120	0.015	0.102	0.898
		0.158	0.012	0.141	0.859
		0.190	0.013	0.190	0.810
		0.215	0.008	0.229	0.771
		0.248	0.015	0.277	0.723
		0.251	0.019	0.326	0.674
		0.267	0.014	0.378	0.622
		0.296	0.008	0.449	0.551