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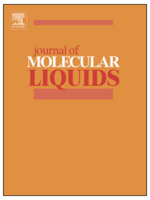

New experimental data on (solid + liquid) phase equilibria of *N*-hexyl-*N*-methylmorholinium bromide with glycols and sulfolane. The use of these binary systems in a sulfur extraction

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ABSTRACT

The main aim of this research is to investigate the use of [HMMOR][Br] and its binary mixtures in desulfurization processes. In this case, the (solid + liquid) phase equilibrium, SLE data of binary mixtures composed of *N*-hexyl-*N*-methyl-morphoilinium bromide, [HMMOR] [Br] and diethylene glycol, or triethylene glycol, or sulfolane have been determined and discussed. Dynamic method and differential scanning calorimetry were used to obtain the experimental points with satisfactory repeatability. The experimental data were correlated using NRTL and Wilson equations. Ionic liquid (IL) tested in this work was synthesized and the structure was confirmed by NMR spectra. Basic thermophysical characterization of pure IL including melting temperature, T_m and enthalpy of melting, $\Delta_m H$ were determined by DSC measurement. Based on the (solid + liquid) phase equilibrium measurements, the eutectic mixtures (EM) were chosen and their physicochemical properties such as density, ρ, and dynamic viscosity, η, were determined at temperature range $T = (293.15–353.15)$ K with increment 5 K. Based on SLE data, the binary system for use in extraction of sulfur compounds from model fuel was selected. The binary system in which the highest amount of sulfur compounds were extracted, further work was carried out on the extraction of sulfur compound in the presence of an oxidizing agent such as (hydrogen peroxide + acetic acid), isobutyl aldehyde (IBA) and (isobutyl aldehyde (IBA) + oxygen). Additionally, the multiple extraction using {[HMMOR][Br] + diethylene glycol} was carried out. In order to design the extraction processes, the basic thermodynamic properties such as phase equilibria measurements are essential. The presented work is a valuable supplement to the data from the subject matter.

1. Introduction

Desulfurization of diesel fuel has become an important industry subject due to the new legislative regulations to reduce sulfur content in the USA and Europe [1,2]. The emission of sulfur from petrol and diesel oils, which is linked to acid rain phenomena, plays a crucial role in pollution problems of cities in Europe and USA. Due to this situation, the European Union approved a new directive stating that the content of total sulfur in European gasoline and diesel fuels from 2010 onwards must be at a maximum concentration level of 10 ppm [2].

As oxidative desulfurization is conducted under very mild reaction conditions, much attention has recently been devoted to this process. In this contribution, the developments in selective removal of organosulfur compounds present in liquid fuels via oxidative desulfurization, including both chemical oxidation and biodesulfurization, are reviewed.

Liquid fuels contain a large variety of sulfur compounds (thiols, sulfides, disulfides and thiophenes), which generate SO_2 and airborne particulate emissions during combustion. Therefore, desulfurization of light oil is extremely important in the petroleum processing industry. Several processes have been proposed in the past to deal with the problem of removing these compounds from light oil. Among them, hydrodesulfurization (HDS) in the most common industrial process is that of treating the fuel under high temperatures and high pressures with hydrogen. The literature describing this technology is vast, amounting to thousands of patents and scientific and engineering papers [3–6]. Hydrodesulfurization is able to remove the refractory sulfur; however, for these compounds, the process is very expensive and it is performed under very high temperature and pressure conditions [3]. The main drawback of this process are the drastic conditions for its implementation and the fact that the HDS is limited in treating benzothiophenes (BTs) and dibenzothiophenes (DBTs), especially DBTs having alkyl substituents on their 4 and/or 6 positions [3–5].

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In recent years, special attention is paid to alternative technologies such as oxidative desulfurization with extraction using ionic liquids. Oxidative desulfurization (ODS) has been considered as a further new technology for desulfurization of light oil. This desulfurization process includes an oxidation in a first step; and liquid extraction at the end. It is evident that the greatest advantages of the ODS process are low reaction temperature and pressure, and that expensive hydrogen is not used in the process. Another feature of ODS is that the refractory S-containing compounds in ODS are easily converted by oxidation. Therefore, ODS has great potential to be a complementary process to traditional HDS for producing deeply desulfurized light oil. Sulfur-containing compounds are oxidized using a selective oxidant to form compounds that can be preferentially extracted from light oil due to their increased relative polarity. Such oxidants include peroxy organic acids, hydroperoxides, nitrogen oxides, peroxy salts and ozone, etc. which can donate oxygen atoms to the sulfur in mercaptans (thiols), sulfides, disulfides and thiophenes to form sulfoxides or sulfones. Oxidation is accomplished by contacting an oxidant with light oil under optimum conditions and continuing the reaction until the oxidized S-containing compounds are formed. Then the reaction is stopped before the oxidant attacks other, less reactive, light oil components, or the other components of the light oil cannot be oxidized under such conditions. Washing, extraction and chemical post-treatment can remove any unused oxidant that remains in the light oil. The oxidized compounds can be extracted from the light oil by contacting oxidized light oil with a nonmiscible solvent. This solvent is selective for the relatively polar oxidized *S*-containing compounds. The oxidized compounds and solvent are separated from the light oil by decantation. The light oil is water washed to recover any traces of dissolved extraction solvent and polished using other methods, such as by absorption using silica gel and alumina. The extraction solvent is separated from the mixture of solvent and oxidized compounds by a simple distillation for recycling. By following these steps, the highest amount of undesirable compounds is extracted from the fuel while doing the least amount of damage to the end product. In many cases, the process improves the fuel quality as well.

The second step of the oxidative desulfurization process is the removal of the oxidized compounds by contacting the distillate with a selective extraction solvent. A liquid–liquid extraction technique using water - soluble polar solvents, e.g. dimethylsulfoxide (DMSO), dimethylformamide (DMF) and acetonitrile is usually employed. The former two solvents have a high extractability for sulfones but have a high boiling point at 300 °C, which is close to the boiling point of the sulfones, and thus they may not be reused for further extraction based on recovery by distillation. In contrast, acetonitrile is used as an extraction solvent since it has a relatively low boiling point (82 °C) and is separated easily from the sulfones by distillation. When acetonitrile is contacted with light oil, a large number of aromatics is extracted simultaneously with the sulfones. The addition of water, however, suppresses the extractability of the sulfones. Therefore the solvents should be sufficiently polar to be selective for polar compounds in the process of extraction.

The best candidate as an oxidizing agent is hydrogen peroxide. This presents a high amount of active oxygen by mass unit (47%). It is a commercial product often used at an industrial level, and gives only water as a product [7]. A catalyst is required so that the hydrogen peroxide efficiently oxidizes the sulfur compounds [8–11]. Besides traditional volatile organic solvents, the use of ionic liquids to extract sulfur from gasoline and diesel has been the object of active research in recent times due to their interesting properties. Ionic liquids are salts (hence entirely composed of ions) with a low melting temperature (usually a threshold of 373.15 K is considered). Many ionic liquids are thermally and chemically stable, and they are in the liquid state over a wide range of temperatures. As a result of their ionic character, they have a practically negligible vapor pressure under common process operating conditions, thus being easily recoverable from molecular volatile compounds and avoiding losses to the atmosphere (with the subsequent polluting effects). Moreover, a judicious selection of their constituent ions can tune the properties of the ionic liquids to a considerable extent, thus allowing the 'design' of a specific ionic liquid to meet the requirements for a particular target [12–15].

The use of ionic liquids for the selective extraction of sulfur compounds from fuels was reported for the first time in 2001 by Wasserscheid and co-workers [16]. Since then, the desulfurization ability of many ionic liquids has been tested. The first studies focused on ionic liquids containing the $[PF_6]^-$ and $[BF_4]^-$ anions [17,18]. However, these ionic liquids are prone to hydrolyze even in the presence of humidity, generating dangerous hydrolysis products [19]. Thus, the use of other ionic liquids incorporating anions such as alkylsulfates, thiocyanate or bis(trifluoromethylsulfonyl)imide became more intense, also because of their lower viscosities [20–32]. Some works with acetate and dialkylphosphate ionic liquids were also published [33–39]. Regarding the selection of cations, a trend to use pyridinium cations acquired relevance in the last years, since Holbrey et al. [40] established the following ranking of ionic liquids for desulfurization depending on the cation core: alkylpyridinium ≥ pyridinium $\approx$ imidazolium $\approx$ pyrrolidinium. Recently, several studies with ionic liquids based on morpholinium and piperidinium cations have also been published [41–48].

One way to improve the solubility of the sulfur-containing compounds in the ionic liquid is to oxidize these components and then they can be more easily extracted. This is the basis of the oxidative desulfurization (ODS). The oxidizing systems used for ODS with ionic liquids are very varied. The main oxidant used is hydrogen peroxide, with only a few works using others, such as sodium hypochlorite, dioxygen, or ozone [49–51]. Additionally, numerous catalysts have been explored, ranging from traditional organic acids, such as acetic or formic acid, to polyoxometalates (POMs) [52–54], or metal—based solid compounds [55].

In the last years, our research group has provided an exhaustive research work on liquid–liquid equilibria of ternary systems composed of a hydrocarbon (aliphatic or aromatic), a sulfur-containing compound, and an ionic liquid [23,25,28,29,30,43]. Two basic thermodynamic parameters for the evaluation of the performance of extracting solvents were calculated from the liquid–liquid equilibrium data: the solute distribution ratio and the selectivity. Furthermore, a measurements of activity coefficients at infinite dilution [27,42,44–47] and liquid—liquid phase equilibria for binary mixtures of ILs with aliphatic hydrocarbons and thiophene as model sulfur compound were carried out [26,62]. It was shown that ionic liquids exhibit the high value of selectivity for of *n*-heptane/thiophene system, which creates hopes of using ionic liquids for separating sulfur compounds from fuel on the industrial scale.

In the available literature, the most reported types of deep eutectic solvents are based on mixtures of quaternary ammonium, or phosphonium-based salts with a variety of other chemical species that can serve as hydrogen bond donors (HBDs). Recently, the extractive desulfurization of liquid fuels was adopted using a group of ammonium-based deep eutectic solvents. [56–60] Salts were chosen from choline chloride, tetramethylammonium chloride and tetrabutylammonium chloride, while HBDs were chosen from glycerol, polyethylene glycol, ethylene glycol, propionic acid and imidazole. A high desulfurization efficiency was obtained using the DES made of tetrabutylammonium chloride or bromide with polyethylene glycol. This was mainly due to the hydrogen bond formed between PEG and benzothiophene as a representative sulfur compound in the fuel. Based on the literature data, the binary mixture of bromide—based salt with diethylene and triethylene glycols were chosen to determine the efficiency of the desulfurization process. In the literature data, the phase equilibria diagrams for this type of binary systems were not determined. Authors presented only the mole ratio of the reagents that form DES mixtures.

This work in a continuation of our latest work [62] on the possibility of using eutectic mixtures in desulfurization of fuel. In the first part of this research, the (solid + liquid) phase equilibria have been measured for binary systems consist of *N*-hexyl-*N*-methylmorpholinium bromide,