



Full Length Article

Performance and mechanism for extractive desulfurization of fuel oil using modified polyethylene glycol



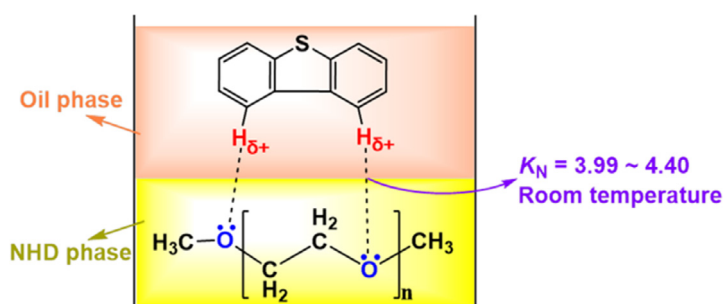
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GRAPHICAL ABSTRACT



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ABSTRACT

Polyethylene glycol (PEG) is not satisfactory for the removal performance of thiophenic sulfurs, e.g., low S -partition coefficient $K_N(S)$. The unsatisfactory K_N may be due to relatively low content of active O atom on PEG. Modification replacing $-OH$ group with $-OCH_3$ group can produce modified PEGs that have the higher active O-content. Polyethylene glycol dimethyl ether, which was commonly known as NHD, showed the higher K_N than PEG. Its K_N for dibenzothiophene (DBT) can reach as high as 3.99. The higher K_N was dominantly ascribed to the contribution of the active O atom: (1) H-bonding with DBT; (2) group similarity between C-O-C and C-S-C. Further, methoxy polyethylene glycol (mPEG) showed the best selectivity for DBT to toluene, compared with NHD and PEG. The best selectivity of mPEG may be attributed to its higher active O-content than PEG's and its stronger polarity than NHD's. Moreover, NHD and mPEG can be regenerated and recycled for several times without significantly decreasing the desulfurization performance.

1. Introduction

Thiophenic sulfurs in fuel oil, i.e., dibenzothiophene (DBT), benzothiophene (BT), thiophene (T), and their derivatives, are regarded as the main source of contamination [1]. For environmental protection,

desulfurization of fuel oil is increasingly important for petrochemical industry. Many regions have rigorous restriction to sulfur (S-) content in vehicle fuel. In China, S-content in gasoline and diesel has been limited to lower than $10 \mu\text{g}\cdot\text{g}^{-1}$ (ppm). For desulfurization technology, hydrosulfurization (HDS) is a conventional process in industry, but it

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encountered disadvantages, e.g., harsh condition (280–330 °C; 3–5 MPa) and low activity for polycyclic thiophenic sulfur like 4,6-dimethyldibenzothiophene (4,6-DMDBT) [1]. Hence, many efforts have been devoted to developing HDS with higher performance and milder condition [2–4]. Alternative technologies, such as extractive desulfurization (EDS) [5–7], adsorptive desulfurization (ADS) [8–11], oxidative desulfurization (ODS) [12–14], and their coupling technology [15,16], have attracted researchers for many years, because of the mild condition (ambient temperature and pressure) and higher activity for DBTs.

In other point of view, however, thiophenic sulfurs are also considered resources because they have high value. For example, DBT is a key pharmaceutical intermediate, and its derivatives are widely used in the field of dye, liquid crystal, and conductive material [17]. Thus, recovery of thiophenic sulfurs from oil is worth. From this point, HDS destroyed the valuable thiophenic sulfurs with desulfurization processing; whereas, EDS could protect them. In this work, we tried to find a highly efficient extractant for EDS and use it for the recovery of thiophenic sulfurs in the future.

For EDS, conventional solvents, e.g., N, N-dimethylformamide (DMF), N-methylpyrrolidone (NMP), and N-methylimidazole (MIM), can extract thiophenic sulfurs [18–20]. However, these solvents dissolve much in oil. This phenomenon resulted in a loss of extractant and secondary pollution of the oil. Thus, these solvents are not green for the EDS process. To obtain oil-insoluble extractant (Ex), researchers synthesized MIM- or NMP-based ionic liquid (IL). For example, [Bmim][AlCl₄], [Bmim][FeCl₄], NMP-SnCl₂, and NMP-FeCl₃ were very active for DBT [5,21–23]. Partition coefficient K_N (DBT) [$(\mu\text{g}_S/\text{g}_{\text{Ex}}^{-1})/(\mu\text{g}_S/\text{g}_{\text{Oil}}^{-1})$] of these ILs can be higher than 4.00 at room temperature. However, these ILs contained Lewis acid that was apt to produce HCl in the presence of moisture. Even more unfortunately, these ILs were not easy to be regenerated due to the strong complexation of the Lewis acid to thiophenic sulfur [24,25]. Therefore, ILs containing Lewis acid are not green either.

For more green EDS process, Lewis acid-free ILs were used, but their desulfurization performance significantly decreased. For example, K_N (DBT) of MIM/PA and [Bmim][SCN] was only 2.31 and 1.16 at room temperature, respectively [26,27]. Recently, polyethylene glycol (PEG) like PEG-400 was also used to desulfurize oil, but not very active for thiophenic sulfur either [28,29]. We measured the K_N of PEG-400 at 30 °C, and it was only 2.26 for DBT. For higher desulfurization performance, modification of PEG may be necessary. Before the modification, we tried to analyse the origin of desulfurization activity. For PEG, the activity might originate from either active O atom on ether group or active H atom on terminal –OH group, as depicted in Fig. 1. With increasing number-average molecular weight (M_n), the active O-content increases and accordingly the active H-content reduces. We selected several liquid PEGs with different M_n (600, 400 and 200), triethylene glycol (TEG), and ethylene glycol (EG) monomer as extractants for DBT. As shown in Figure S1 (Supplementary Material), S-removal of PEGs decreases in the order of PEG-600 > PEG-400 > PEG-200 > TEG > EG. The result indicates that the more the active O atom is, the higher the desulfurization activity shows.

For the modification, however, simply increasing the M_n to acquire more active O atom may be inappropriate because PEG with a larger M_n (greater than 700) become semisolid and even solid at room temperature. The solids without high specific surface area were usually confronted with low desulfurization performance. In Figure S1, the solid PEGs (PEG-1000 and PEG-2000) show much lower S-removal than the

liquid PEGs mentioned above. As a result, the modification should not only increase the active O-content of extractant, but also guarantee the fluidity thereof. However, the modification replacing the –OH group with –OCH₃ group may be a feasible way. The modified PEGs, such as polyethylene glycol dimethyl ether (NHD) or methoxy polyethylene glycol (mPEG) shown in Fig. 1, are richer in active O atom and Lewis acid-free. As listed in Table S1, further, the solubility of modified PEGs in *n*-octane is quite low (< 0.3 wt%), and that in toluene-containing oil is acceptable as well. Moreover, the modified PEG like NHD has been a commercial solvent for CO₂ absorption, and thus it is hardly limited in industry [30,31]. Hence, the modified PEGs were expected to become green and highly effective extractants for thiophenic sulfurs. The purpose of this work is to study the desulfurization feasibility of the modified PEGs and to explore their desulfurization mechanism.

2. Experimental

2.1. Chemical materials

DBT (98%), BT (97%), tetrahydrothiophene (THT, 99%), and methylcyclohexane (99%) were purchased from Aladdin Reagent, and 4,6-DMDBT (98%) was the product from Energy Chemical. NHD-250, mPEG-500, TEG (99.5%), T (99%), 1-octadecene (95%), and tetradecane (98%) were from Macklin Reagent, and NHD-500 was from Sigma Aldrich. PEGs (CP), EG (AR), *n*-octane (CP), naphthalene (AR), and cyclohexene (AR) were produced by Sinopharm Chemical, and toluene (AR) was from Tianjin Tianli Chemical. The M_n for each modified PEGs or other PEGs was given, e.g., NHD-500 ($M_n = 500$). All reagents were used as received without further purification.

2.2. Extractive desulfurization experiment

The model oil used in this work mainly consisted of *n*-octane and a thiophenic sulfur source (T, BT, DBT, and 4,6-DMDBT). The S-content of T, BT, and DBT was set as 1000 ppm, and that of 4,6-DMDBT was set as 940 ppm. To discuss the influence of aromatics on desulfurization performance, we prepared toluene-containing oil, in which the toluene content was set as 5, 10, 15, 20, and 25 wt%, respectively. Meanwhile, the S-content of T, BT, and DBT in toluene-containing oil was kept as 1000 ppm. To simulate the real system, we prepared the simulated real oil (SRO). The component of SRO-1, SRO-2, and SRO-3 was listed in Table 1, and the S-content in SRO was detected as 1125 ppm.

The typical extraction experiment was carried out in a batch vessel under ambient pressure. A certain amount of model oil (m_{Oil}) was put into a flask first, and then a specific amount of extractant (m_{Ex}) was added to the flask under vigorously stirring at the set temperature. After extraction, the oil samples were taken out for S-content analysis.

2.3. S-content and toluene content analysis and K_N determination

The S-content in model oil was determined by SN analyzer (KY-3000SN, Keyuan Electronic Instrument Ltd., Jiangsu, China) [32,33]. Analysis details were as follows: high purity Ar and O₂ as carrier gas and reaction gas; furnace temperature = 1000 °C; flow rate (Ar) = 240 ml/min, and flow rate (O₂) = 480 ml/min; injection volume = 4 μL . The toluene content was measured by high performance liquid chromatography (Shimadzu LC2030, equipped with UV-vis detector and a C-18 column). Analysis details were as follows:

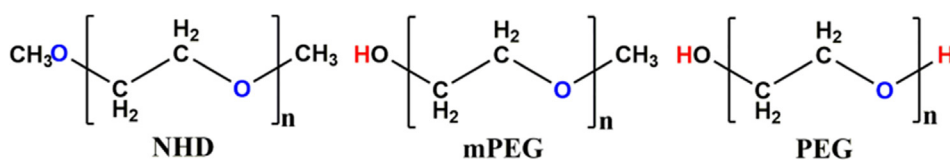


Fig. 1. Chemical structure of modified PEG and other PEG.

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