

ABSTRACT

The prediction using COSMO-RS which majorly rely on hydrogen bonding mechanism, showed inconsistent results against experimental data. The present study using Raman spectroscopy has led to the same conclusion where π -electron density becomes a vital viewpoint in the process of screening potential ILs for desulfurization. The use of a new complementary method which estimates the aromaticity index (AI) for cation and double bond equivalent (DBE) for anion selection showed good agreement between the literature and experimental results. The AI and DBE methods were later used to select the appropriate combination of cation and anion of ILs for extractive desulfurization study.

From the 407 potential ILs selected based on COSMO-RS database, 25 ILs as suggested from the complementary method were synthesized for further evaluation. Out of the 25, some which are commercially available were purchased for validation purposes. The synthesized ILs were characterized accordingly by ^1H NMR, ^{13}C NMR, elemental analysis, and halide content including their water contents, densities and refractive indices. A single batch extraction at room temperature for extracting benzothiophene (BT) from model oil ($n\text{-C}_{12}$) was well studied to determine the optimum extracting conditions of stirring speed and extraction time. The effect of three important process variables (mass ratio, BT concentration and temperature) were also investigated using Response Surface Methodology (RSM). Using Composite Central Design (CCD), the mathematical model gave good fit with the experimental results ($R^2 > 0.86$) and this model suggested that for optimum desulfurization performance, the mass ratio (model oil/ILs) should be 0.92 at BT concentration and temperature of 2000 ppm and 30°C , respectively. Ternary diagram of individual hydrocarbon-IL-sulfur system was constructed to estimate the selectivity and capacity of the system as well as to study the miscibility between three different

types of hydrocarbons i.e. n -C₁₂, n -C₆ and p -xylene as solvent with BT (solute) and [bmim][TCM] (extractant).

Another screening method based on the relationships between physical properties i.e. density (ρ), refractive index (RI) plus molecular weight (M_w) and desulfurization performance by applying data mapping approach was proposed. The mapping of density against molecular weight explicitly identified four groups i.e. fluoro-based, cyano-based, phosphate-based and sulfate-based ILs which depicted a linear correlation towards desulfurization performance.

Five model fuels i.e. benzene/BT, p -xylene/BT, benzene/DBT, p -xylene/DBT and BT/DBT were investigated to further understand the extractive desulfurization before implementing on actual diesel fuel. Five ILs that showed high efficiency for removing BT from n -C₁₂ were selected namely [bmim][OSO₄], [bmim][DCA], [bmim][SCL], [bmim][BZT] and [bmim][TCM]. Among the five ILs, [bmim][TCM] gave the highest selectivity ratio of sulfur compounds (i.e. BT and DBT) in the presence of aromatic hydrocarbons (i.e. benzene and p -xylene), which indicates its potential as extractant for extractive desulfurization process. Only [bmim][OSO₄], [bmim][DCA] and [bmim][TCM] were used for desulfurization of commercial diesel fuel. By using GC-MS, the most extracted compounds were DBT and BT followed by benzene, toluene, p -xylene, n -C₆ and n -C₁₂. Based on the results of total sulfur concentration by Total Sulfur Analyzer (TSA), it is estimated that five cycle would be needed for [bmim][TCM] to achieve below than 50 ppm of total sulfur concentration.

The recyclability of ILs was also studied where physical (re-extraction using water and n -C₇) and electrochemical method were explored. Both depicted good results in regenerating spent ILs.