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Mechanistic studies of enhanced oil recovery by imidazolium-based ionic liquids as novel surfactants

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ABSTRACT

Ionic liquids are recently considered as an alternation to surfactants for their application in enhanced oil recovery (EOR) because of their promising surface-active properties. In the present study, the ability of a series of synthesized ionic liquids (C_8mimBF_4, $C_{10}mimBF_4$ and $C_{12}mimBF_4$) to reduce interfacial tension (IFT) and change the wettability of oil-wet rock have been investigated. Results demonstrated that all three synthesized ionic liquids enhanced interfacial properties and rock-wetting characteristics. The ionic liquids were able to significantly reduce IFT and remained stable at high temperature and saline conditions. Addition of organic alkali also showed a synergistic effect on IFT reduction between crude oil and ionic liquid solution. FTIR and zeta potential measurements were conducted to establish the mechanism of wettability alteration of oil-wet rock. Emulsification tests confirmed the capability of the ionic liquids to emulsify the trapped oil, which is an important mechanism of chemical EOR. The loss of ionic liquids by adsorption on rock surface was studied, and the adsorption data were analyzed by Langmuir and Freundlich models. Microemulsion study showed Winsor type III behavior with ultra-low IFT, which is beneficial for EOR application. Sand pack flooding experiments were conducted to study the EOR efficiency using the synthesized ionic liquids and around 32.28% additional recovery was observed after the conventional water flooding with injection of ionic liquid, polymer and alkali slugs.

Introduction

With the ever-growing global energy demand majority of oil producing companies are focusing on maximizing the recovery factor. Increasing demand and declining reserve are the major challenges faced by the companies in order to produce the remaining oil from the matured oil field. With the declining reserve discoveries, it is believed that enhanced oil recovery (EOR) technologies will play an active role in future to meet the energy demand.

After primary and secondary oil recovery significant fraction of original oil in place (OOIP) still remain trapped in the reservoir as residual oil [1]. The trapping of the non-wetting oil phase in the pores of the rocks is due to the capillary forces which exist in the form of interfacial tension (IFT). Enhanced oil recovery techniques are developed as a promising method aiming to reduce residual oil saturation [2]. Among the various EOR techniques, chemical flooding is one of the most successful techniques that has been used worldwide for decades because it is capable of reducing oil/water IFT and controlling mobility ratio [3]. Chemical flooding method adopted also has various disadvantages such as high toxicity, high cost and inability to perform in harsh environments [4]. Additionally, insoluble residues left by a surfactant or other chemical formulations can damage the oil reservoirs developing environmental impacts [5]. This lead to the research of chemical systems that are environmentally acceptable and can be used in EOR.

Ionic liquid has gained attention as a potential alternative to the conventional surfactant as they are environmentally friendly, non-toxic, non-corrosive [6], has a negligible vapor pressure, high thermal stability [7] and are recyclable. Ionic liquids are organic salts having a melting point below 100 °C and they are often found as a liquid up to a moderate temperature [8]. Ionic liquids are composed of organic cations such as imidazolium, ammonium or pyridinium cation and inorganic anions such as halide, $[AlCl_4]^-$, $[BF_4]^-$, or $[PF_6]^-$ and properties of the ionic liquid can be altered by tailoring cation and anion combinations [9]. Ionic liquids have exhibited a vital role in numerous fields such as organic and inorganic synthesis [10], extraction and separation [11], catalysis,

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electrochemistry, biomass conversion, desulphurization, scale removal, crude oil dissolution, and oil/water IFT reduction [12,13].

In the last few years, various research focusing on ionic liquid's application in the oil and gas industry has emerged. Studies have confirmed that ionic liquid possesses surface activity identical to surfactant and are able to form micelles in aqueous solutions [14,15]. Ionic liquids also exhibit good interfacial behavior thus lowering the IFT to a notable value [16]. Lowering of oil/water IFT and wettability alteration due to adsorption is considered as an important factor for recovery mechanisms in EOR [17]. Bowers et al. [18] reported that the aggregation behavior of ionic liquids with 1-alkyl-3-methylimidazolium salts in aqueous solution which depicts a short chain cationic surfactant and form aggregates above critical micellar concentration (CMC). Nandwani et al. [19] reported the advantage of ionic liquid (C_{16}mimBr) over traditional cationic surfactant (CTAB) in recovering more entrapped oil by lowering IFT of water/oil system and their ability to tolerate and function efficiently in harsh conditions of temperature and salinity. They also investigated ionic liquid reusability, where the effluent from a surfactant flooding process was reused in the CEOR process of another sand packed column to evaluate the depletion in efficiency of the chemical slug in recovering oil. Manshad et al. [16] investigated wettability alteration and IFT reduction by screening four ionic liquids, namely [C_{12}mim][Cl], [C_{18}mim][Cl], [C_8Py][Cl] and [C_{18}Py][Cl] and core flooding revealed 13% increase in oil recovery. To extend the application of ionic liquids, research for new and better ionic liquids aiming towards overcoming limitation of the existing families of ionic liquid is in progress.

In our earlier work [15], the surface activity of three synthesized ionic liquids namely, C_8mimBF_4, C_{10}mimBF_4 and C_{12}mimBF_4 were determined to understand the structure–property relationships for industrial applications. Characterization of the synthesized ionic liquid was done for structure confirmation and thermal stability. Surface activity of the ionic liquids was found to be improved with increasing alkyl chain length. The bulky heterocyclic ring form of imidazole acts as the cationic hydrophilic head of the imidazolium ionic liquids which gives the ionic liquid more hydrophilicity and hence increased interfacial activity. Surface adsorption parameters and the thermodynamic aspects of air-ionic liquid aqueous systems were also determined in our earlier. This work is an extension of the previous work and focuses on determining its effectiveness, in reducing surface tension, IFT and wettability alteration of oil-wet quartz surface for its potential application in EOR. Adsorption of synthesized ionic liquid on quartz surface was investigated and analyzed by fitting with Langmuir and Freundlich isotherm models. The phase behavior of the ionic liquid was also investigated. Finally, the synthesized ionic liquid slug was used for flooding to find its effectiveness in enhanced oil recovery.

Experimental

Materials required

1-Bromooctane (98%), 1-bromodecane (99.5%), 1-bromododecane (99.5%), 1-methylimidazole (99.5%), dichloromethane (99.5%) and sodium tetrafluoroborate (98.5%) were obtained from SRL chemicals for the synthesis of the ionic liquids. Ethyl acetate and acetone, which were used as a solvent for the synthesis route, were purchased from TCI chemicals. The brine of different concentrations was prepared using NaCl supplied by Sigma–Aldrich Co. LLC. To see the effect of alkali, organic alkali triethylamine (TEA) purchased from Sigma–Aldrich Co. LLC was used in IFT experiments. PHPA polymer from Sigma–Aldrich Co. LLC was used in sand pack flooding. The crude oil sample used was procured from ONGC (Ahmedabad, India). The oil has 29.21° API at 30 °C. Double distilled water was used to prepare the aqueous solutions.

Synthesis of ionic liquid

The reaction mechanism for the synthesis of the ionic liquid is presented in Fig. 1. As shown in Fig. 1, reactions between 1-methylimidazole and alkyl bromide (1-bromooctane for [C_8mimBF_4], 1-bromodecane for [C_{10}mimBF_4] and 1-bromododecane for [C_{12}mimBF_4]) in a ratio of 1:1 were carried out for 48 h under reflux condition at 70 °C. To eliminate unreacted materials, the reaction mixture was washed with ethyl acetate and then heated up to 70 °C to remove the rest solvents. A pale-yellow liquid was obtained, which was vacuum distilled and then vacuum dried at 80 °C. The product was further reacted with $NaBF_4$ in the presence of acetone for 10 h under 40 °C. Dichloromethane was then added to remove the residue. The final product was vacuum dried and traces of dichloromethane were eliminated [15,20].

Surface tension

The surface tension of synthesized ionic liquids was measured using Easy Dyne K20 Tensiometer (KRUSS Germany) at 30 °C with an accuracy of ±0.1 mN/m. The aqueous solutions of varying ionic liquid concentrations were prepared. The platinum ring used for

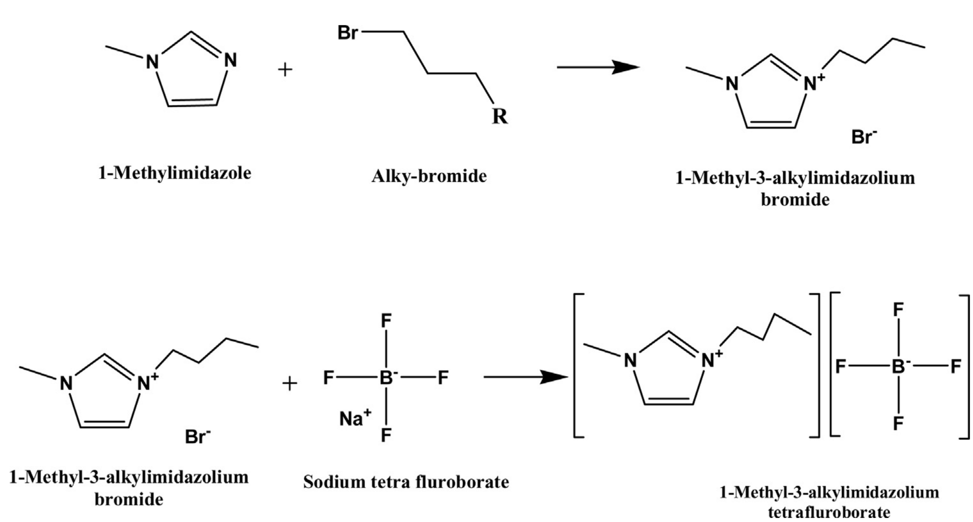

Fig. 1. Reaction scheme of ionic liquid synthesis.