



Application of new amphiphilic ionic liquid based on ethoxylated octadecylammonium tosylate as demulsifier and petroleum crude oil spill dispersant



Ayman M. Atta^{a,b,*}, Hamad A. Al-Lohedan^a, Mahmood M.S. Abdullah^a, Shymaa M. ElSaeed^b

^a Surfactants Research chair, Department of Chemistry, College of Science, King Saud University, PO Box 2455, Riyadh 11451, Saudi Arabia

^b Petroleum Application Department, Egyptian Petroleum Research Institute, Cairo 11727, Egypt

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ABSTRACT

This work reports the synthesis and application of amphiphilic ionic liquid (IL) in the petroleum field. The ionic liquid was synthesized by etherification of octadecylamine with tetraethylene glycol followed by quaternization with *p*-toluene sulfonic acid. The chemical structure was confirmed by NMR spectroscopy. The surface activity, aggregation, adsorption, and the solubility of the ethoxylated octadecylammonium tosylate were investigated. The interfacial parameters between IL aqueous solution and crude oil emulsions were determined from interfacial tension measurement. The results showed the dependence of interfacial tension on the concentration, crude oil emulsion composition and chemical structure of the prepared amphiphiles. The mechanism of aggregation and adsorption ethoxylated octadecylammonium tosylate was proposed and confirmed at different interfaces. The demulsification and oil spill dispersion efficiencies were investigated at different amphiphile concentrations. The performance of amphiphilic ILs revealed that their demulsification efficiency reached 100% and the settling time required for efficient separation decreased with increment of water contents of crude oil emulsions. Moreover, the prepared amphiphilic ILs achieved oil spill dispersion efficiency more than 80% at surfactant oil ratio (1:25).

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Introduction

Recently, the sustainable technologies became the first priority in the petroleum and chemicals industry [1]. Ionic liquids (IL) attracted great attentions as sustainable materials due to their low volatility (low vapor pressure), thermal stability, low toxicity, high surface activity due to the presence of cations and anions species in the same molecules, and high performance as catalysts, and desulfurization solvents in the petroleum fields [2–5]. ILs are ionic molecules that contain both organic cations and inorganic or organic anions. The difference between inorganic salts and ionic liquids is based on the size of cations and anions when compared with sodium or halides. Commonly, the derivatives organic cations were imidazolium, pyridinium, pyrrolidinium, ammonium,

phosphonium and sulfonium. The organic anions were alkylsulfate, alkylsulfonate, *p*-toluenesulfonate (tosylate) and trifluoroacetate. The inorganic anions were halides, tetrachloroaluminate, hexafluorophosphate, tetrafluoroborate and bis(trifluoromethylsulfonyl) imide as examples. The properties of ILs depend on choosing the correct cations and anion for a specific synthesis. There are several petroleum processes used different oil-field chemicals such as emulsifiers, demulsifiers, inhibitors, dispersants and scavengers to modify the crude oils and their products specifications [6–9]. These chemicals are based on amphiphiles or polymeric surfactants mixtures having different hydrophile lipophile balances [10]. They have several advantages over organic surfactants used in petroleum oilfield chemicals due to their excellent rheology, better solubility in oils and solvents, anticorrosion and recyclability [11,12]. The demulsifiers were selected in the petroleum field after some preliminary screening based on bottle test. There are some proposed mechanisms such as mass-transfer velocity and the coalescence mechanisms used to correlate the surfactants efficiencies as demulsifiers and as oil spill dispersants with their hydrophilic–lipophilic balance (HLB)

* Corresponding author at: King Saud University, Department of Chemistry, College of Science, PO Box 2455, Riyadh 11451, Saudi Arabia.

Tel.: +00966 561557975; fax: +00966 0114675998.

E-mail address: aatta@ksu.edu.sa (A.M. Atta).

value and the size of hydrophilic groups of polymeric surfactants [13–16]. Moreover, it was reported that the solubility and high ability of demulsifiers to reach the interfaces affected their demulsification performances. ILs have greater tendency to reduce the interfacial tension between polar and nonpolar solvents and to reduce the water surface tension even at high salt contents or higher temperature [17]. In this respect, ILs achieved good results as demulsifier for petroleum crude oil emulsions, as asphaltene dispersants, paraffin deposition inhibitors, and as enhanced oil recovery [18,19].

It is very important to select the best method to synthesis ILs by choice the suitable hydrophobic cations and anions to use as oil-field chemicals. It was previously reported that, ILs as monomers, polymerizable monomers, oligomers and polymers were prepared using amines, phosphanes or sulfonates [20–22]. Usually, the tertiaryalkyl amines were quaternized with alkylhalides, alkyl or aryl sulfonates followed by anion exchange reactions. It is better to complete this reaction without solvent; however, microwave was used as source of energy to complete these reactions [23–25]. Moreover, the ability of ILs to adsorb at interfaces without aggregations to reduce the interfacial tension between interfaces and their ability to emulsify, dehydrate the crude oil emulsion or disperse crude oils are the main principles to design ILs. To achieve these goals, tertiary amine based on etherified octadecyl amine was quaternized with *p*-toluene sulfonic acid to produce ethoxylated octadecylammonium tosylate as hydrophobic IL. The reaction was carried out without solvent. The surface and interfacial activities of the prepared IL were measured to confirm the dispersion and demulsification mechanisms of IL as dehydrating agents and oil spill dispersant for crude oil emulsions and spills.

Experimental

Materials

All chemicals were analytical grade and produced from Sigma Aldrich Chemicals Co. Octadecylamine (ODA), *p*-toluene sulfonic acid monohydrate (PTSA; 99.5%), were used without further purification. Tetraethylene glycol (TEG), 2, 2-dichlorodiethyl ether(DCDE), and sodium hydroxide were used for etherification of ODA. Toluene, xylene, dioxan, ethylene glycol dimethylether and ethanol were used as solvents. Double distilled water (DDW) is used for different measurements. Sea water of Arabic Gulf was used to prepare synthetic crude oil emulsions and oil spill. Its salinity, current resistivity and conductivity are 39.99 g/L, 0.019 Ω and 2.2 mS/M, respectively. ARBREAK™ 8141 as commercial demulsifier produced by Baker Petrolite based on a high-molecular weight oxyalkylated phenolic resin was used to compare its results with the present work. It was generally used in dilute form in aromatic solvent or blended with chemicals of different generic structure to give synergistic formulas which may have greater efficiency.

Arabian heavy crude oil produced by Aramco, Saudi Arabia was used and its specifications are reported in previous work [26]. The asphaltene and water contents are 8.3 and 0.145 wt.%, respectively. The crude oil emulsions having different crude oil compositions were prepared according to previous reported method [26]. The crude oil/water ratios were 90/10, 70/30 and 50/50 used to prepare different crude oil emulsions. The crude oil and sea water mixtures were stirred using mechanical homogenizer at 9000 rpm for 30 min.

Synthesis procedure

ODA (0.05 mol; 13.47 g) was dissolved into 100 mL of xylene and mixed with 0.1 mol of TEG (18.6 g) in the presence of 0.1 mol

(14.3 g) of DCDE as linking agent and 0.2 mol (8 g) of NaOH. The mixture was heated under nitrogen atmosphere and refluxed for 5 h. The remained solid NaCl precipitate was filtered after removing of 50 mL of xylene solvent by evaporation under vacuum using rotary evaporator. The remained product was mixed with hot super saturated NaCl aqueous solution and extracted by mixing with isopropanol. The organic layer was removed and the etherified product of *N,N*-bis-hexaoxyethylene octadecylamine was separated as wax solid product and abbreviated as HEOD. The melting temperature and yield % of HEOD are 56 °C and 85%, respectively.

Equal mol amounts of HEOD and PTSA were mixed and stirred after heating at 185 °C for 24 h under nitrogen atmosphere. The reaction mixture was heated under reduced pressure of 10 mm.Hg for 24 h using rotary evaporator. The solid product of *N,N*-bis-hexaoxyethylene octadecylammonium tosylate (HEOD-TS) was obtained after cooling to room temperature. The melting temperature, and yield % of HEOD-TS were 83–85 °C and 99.3%, respectively.

Characterization

The chemical structure of HEOD and HEOD-TS were elucidated using ¹H and ¹³C NMR spectroscopy model a 400 MHz Bruker Avance DRX-400 spectrometer.

The surface and interfacial tension of HEOD and HEOD-TS solution were determined using drop shape analyzer model DSA-100(Krüß GmbH, Hamburg, Germany).

Krafft temperature (T_K) was determined from measuring the conductivity of HEOD and HEOD-TS aqueous solution at different temperatures using Fisher scientific AB30 conductivity meter.

Fluorescence optical microscopy (Olympus BX-41 fitted with DP70 digital camera) was used at an excitation wavelength of 280 nm to investigate the dispersion of crude oil droplets.

Images of dispersed oil droplet were recorded using Olympus BX51 polarized-light microscope equipped with a Linkam THMS 600 hot stage.

The relative solubility number (RSN) of HEOD and HEOD-TS was determined by titration their solutions (1 g in mL of dioxane 96 mL and toluene 4 mL) against water. The volume of water (mL) was determined as RSN.

Application of HEOD and HEOD-TS as oil spill dispersants [27]

Solutions of 50 g of either HEOD or HEOD-TS in 100 mL of ethanol were used to disperse oil spill. The evaluation process was carried out according reported method in previous work [27]. In brief, Arabian heavy crude oil (5 g) was added on the surface of 250 mL of sea water in 500 mL beaker. The oil spill was stirred with magnetic stirrer at 700 rpm to obtain vortex with depth of 1 cm. Different surfactants to oil ratios (SOR) ranged from 1:1 to 1:100 were added to crude oil mixture during 1 min. The stirring was stopped and 50 mL of the dispersed solution of crude oil in sea water was removed after 2 min. The dispersed crude oil in water (50 mL) was extracted with 50 mL of chloroform two times. The chloroform was evaporated using rotary evaporator to determine the weight of extracted crude oil. The oil spill dispersant efficiency (OSE) was calculated as [27]:

$$OSE = \frac{(\text{Wt. of extracted crude oil} \times 500)}{(\text{Wt. of crude oil})} \quad (1)$$

Application of HEOD and HEOD-TS as demulsifier [26]

The demulsification of crude oil emulsions using different concentrations of HEOD and HEOD-TS was carried out according

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