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AIP Conf. Proc. 1891, 020118 (2017)

<https://doi.org/10.1063/1.5005451>



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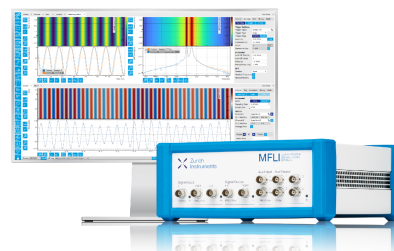
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Effect of Hydrophobic Ionic Liquids on Petroleum Asphaltene Dispersion and Determination using UV-visible Spectroscopy

Zeeshan Rashid^{1, a)}, Cecilia Devi Wilfredand^{2, b)} Thanabalan Murugesan^{1, c)}

¹*Department of Chemical Engineering Universiti Teknologi Petronas, Seri Iskandar, 32610, Tronoh, Perak, Malaysia*

²*Department of Fundamental and Applied Sciences, Universiti Teknologi Petronas, Seri Iskandar, 32610, Tronoh, Perak, Malaysia*

^{a)} *Corresponding author: Zeeshanrashid1@yahoo.co.uk*

^{b)} *cecili@utp.edu.my*

^{c)} *murugesan@utp.edu.my*

Abstract. Asphaltene aggregation and flocculation is one of the main problems faced by upstream industry. The aim of this research activity is to explore the effect of synthesized imidazolium and pyridinium based ionic liquids on the prevention of asphaltene aggregation problem in crude oil. In this research, number of hydrophobic and hydrophilic ionic liquids were tested. The investigations were performed for evaluating; the dispersion yield, effect of temperature, effect of stirring time and effect of solvent to flocculant ratio. Analysis were done using UV-visible Spectroscopy. The results depicted that the investigated hydrophobic ionic liquids have the tendency to abate asphaltene aggregation and can be considered as deflocculants.

INTRODUCTION

Arterial blockage due to the flocculation of petroleum asphaltenes in both upstream and downstream of oil industry is one of the vicious issues. Asphaltenes and resin which are the components of crude oil remain in colloidal form but asphaltenes precipitates once crude oil become thermodynamically unstable [1]. This instability can be due to the change in pressure, temperature and composition. Asphaltenes make aggregates upon precipitation hence cause dramatic decline in oil production. This led to various studies by several researchers in order to understand the chemistry of asphaltenes. It is reported that asphaltenes extracted from petroleum are strong H-bond receivers and weak H-bond givers. Some researchers suggested that aromatic π - π and dipole interaction were responsible for asphaltenes self-association [2].

p-dodecylbenzenesulfonic acid have been investigated for dispersing of asphaltene. However, they do irreversible electrophilic addition reaction with asphaltene that results in polymerization and deposition of asphaltene. Yet, acids may serve as good dispersant if their alkyl chain length is sufficiently large enough to give steric stabilization around the asphaltene. The inhibition of aggregation of asphaltenes in heavy oil can be abated by using ionic liquids (ILs). Organic salts, ILs, may become strong H-bond donor and can act as asphaltene stabilizer. Dispersing properties of ionic liquids along with low vapor pressure and melting point, non-flammability and solvating properties make them suitable candidate for treating asphaltic oil.

Previously, the ILs used for treating asphaltic oil were tetra chloride aluminate based and bromide based [3, 4]. In addition, phosphate based ILs were used to extract value-able components from the direct coal liquefied residue (DCLR) [5-8]. However, most of these ILs were solid at room temperature and they were operated at higher pressure, temperature and require longer reaction time. Moreover, very less work has been done to utilize ionic liquids for

asphaltene precipitation problem. In this paper synthesis and characterization of pyridinium and imidazolium ILs were performed. The dispersion properties of pyridinium and imidazolium ionic liquids on asphaltenes were investigated.

EXPERIMENTAL

Chemicals

1-Methyl imidazole, 1-bromobutane, 1-butylpyridinium chloride ([BPy][Cl]), 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][NTf₂]), 1-butyl-3-methyl-imidazolium tetrafluoroborate ([BMIM][BF₄]), 1-butyl-3-methyl-imidazolium bromide ([BMIM][Br]), 1-hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ([HMIM][NTf₂]) and lithium bis(trifluoromethylsulfonyl)imide (LiTf₂N) were provided from Merck company. Ethyl acetate, n-heptane silver nitrate and toluene were purchased from Sigma Aldrich. De-ionized water was used in synthesizing hydrophobic ionic liquids. All chemicals and solvents were used without further purification. The asphaltenes were extracted from Ratawi crude oil. The Chemical composition of asphaltenes were (%): C, 80.580; H, 7.551; N, 5.830; S, 8.762.

Instruments

Fourier Transform Infrared (FT-IR) spectra having the range of 4K-0.4K cm⁻¹ were run on a Bruker, Tensor 27 platinum ATR-FTIR spectrometer. The solution electronic results were documented on a PerkinElmer Lambda 35 UV-visible spectrophotometer using 1 cm quartz cells. The spectra were recorded on the wavelength of 346 nm, and the scan were conducted at a medium speed using a 20 nm slit width. Glass transition temperature determination was conducted using PerkinElmer Thermogravimetric analyzer (TGA) at a heating rate of 10 °C/min under nitrogen gas. The H-MNR spectra of the ILs were obtained on a Bruker 400 MHz spectrometer in deuterated methanol d-MeOH.

Synthesis of ionic liquids.

1-butyl-pyridinium bis(trifluoromethylsulfonyl)imide.

A solution of 1-butylpyridinium chloride and lithium bis(trifluoromethylsulfonyl)imide were made using deionized water. Lithium salt was used slightly in excess. These two solutions were mixed in three neck round bottom flask for 12 hours under nitrogen environment at room temperature. After which, the mixture made two distinct layers. The lower layer was the ionic liquid. The upper layer was discarded and IL was rinsed many times with cold water and checked the halid content using 0.1 M silver nitrate solution until no precipitation. The ionic liquid solution was rotavap and left in vacuum oven for 24 hours to remove solvent. The yielded ionic liquid was analysed by H-NMR: ¹H NMR (400 MHz, d-MeOH-d): δ 8.9276 [d, 2H (py)], 8.5764 [t, 1H (py)], 7.8729 [t, 2H (py)], 4.7227 [t, 2H, N-CH₂], 1.6831–1.7684 [m, 2H, CH₂], 1.4579–1.3699 [m, 2H, CH₂], 0.7765 [t, 3H, CH₃], ¹³C NMR (100 MHz, d-MeOH): δ 146.6750, 145.6056, 129.3686, 120.9827, 62.8797, 34.1199, 20.1253, 13.5362.

Asphaltenes extraction from crude oil.

Frist, Crude oil is dissolved in n-heptane in 1:40 by wt/vol and left over night for stirring at 60 °C under reflux. Vacuum filtration was done with 0.42micron nylon filter. The filtered material was dissolved in hot toluene to remove carbines from the asphaltenes. The solution was rotavap to remove toluene. After removing toluene, small amount of heptane was added to peel off the asphaltenes from the walls of rotavap flask. The sample was placed in vacuum dried for 4 hours to remove traces amount of solvents. At last, shiny black solid asphaltenes were obtained.

Preparation of standard solutions.

A 1K ppm asphaltene solution was made in toluene by adding 1 g of asphaltene into 1000mL of toluene. For making calibration curve, secondary solutions were made using 1000 ppm solution. The calibration curve shown in figure 1. The 800ppm asphaltene solution was titrated against heptane to determine the onset point of flocculation of

asphaltene. The number of solutions were made and left overnight then centrifuge at 3000 rpm for 30 mins. The determination was done with the help of UV-vis spectrometry.

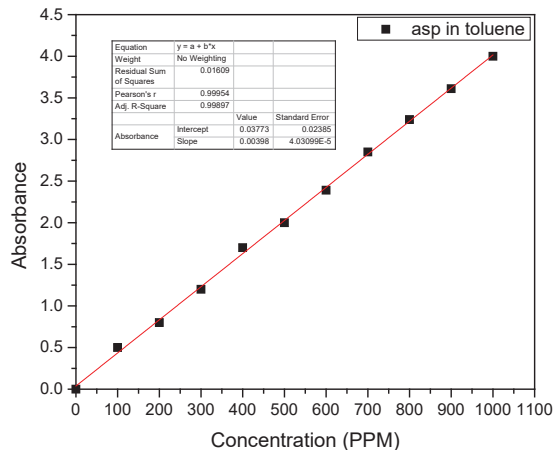


FIGURE 1. Calibration curve

Dispersion of asphaltene solutions with ionic liquids.

There is a liner relation between the absorbance of light and amount of asphaltene in toluene solution [9]. The calibration curve was established at a wavelength of 346 nm and then used to measure the asphaltene concentration in heptol solutions. The effect of the ILs for asphaltene deflocculation were studied systematically in this research. The asphaltenes dispersion was carried out by keeping the amount of ionic liquids constant and 5 mL of the asphaltenes solution was employed for each dispersion study. The samples were stirred for one hour at the temperature 323 K then filtered on the 0.22 μm Millipore filter after centrifugation. The weight of asphaltene in the filtrate was measured and compared with the initial weight.

RESULTS AND DISCUSSIONS

Ionic Liquids are being considered as green solvents and perhaps they may be used for treating asphaltene problem.

Effect of Ionic liquids on the flocculation onset.

Figure 2 reports the finding of the asphaltene precipitation onset using UV-visible method. The heptane/toluene (heptol) solutions displayed similar flocculation onset at about 1.63 (ratio of n-heptane and toluene by volume). We can say that ionic liquids do not alter the flocculation onset very significantly. Therefore, we kept the heptane/toluene ratio of 2 for rapid flocculation.

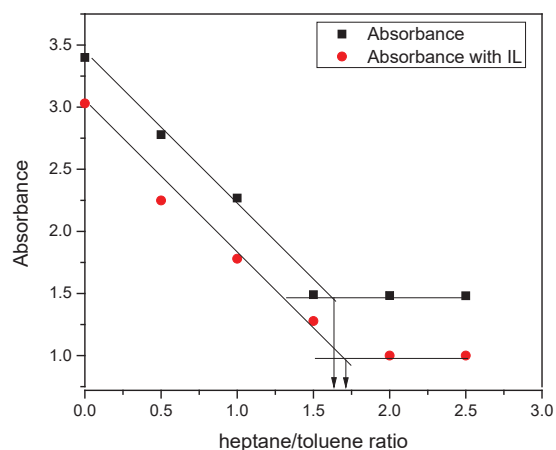


FIGURE 2. Effect of Ionic liquid on the onset of flocculation of asphaltenes

Effect of Ionic liquids as dispersants.

The ILs used were [BMIM][Br], [BMIM][BF₄], [BMIM][NTf₂] and [BPy][NTf₂]. The results were obtained by using UV-visible spectroscopy for the measurement of the concentration of asphaltene in solution. These results were compared with commercially available ionic liquid ([BMIM][Br]). Figure 3 illustrates the effect of ILs on the inhibition of asphaltene precipitation in heptane toluene solution. It can be observed that hydrophobic ionic liquids are more effective in dispersing asphaltene and dispersion increases with the increase in the degree of hydrophobicity, i.e [BMIM][BF₄] < [BMIM][NTf₂].

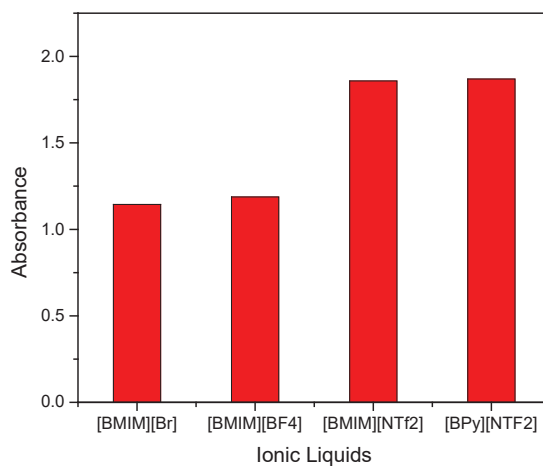


FIGURE 3. Effect of Ionic Liquids on asphaltenes dispersion.

Effect of amount of ionic liquid.

Dispersion of asphaltene is a function of amount of ionic liquid used as dispersant. Figure 4 illustrates that asphaltene dispersion increases with the rise of the amount of IL till the IL: asphaltene ratio of 2. There is no significant change of absorbance after this ratio which mean double the amount of IL is sufficient enough to inhibit the asphaltene precipitation.

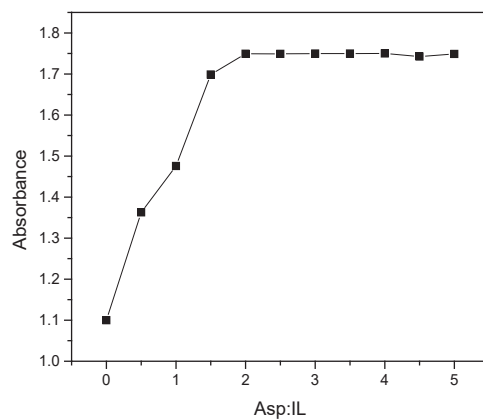


FIGURE 4. Effect of the amount of BMIM[Tf₂N] on asphaltene precipitation

Effect of Mixing Time.

Samples were mixed for number of periods of time, 1-10hrs, at 323 K and then centrifuged and filtered with the 0.2 μ m PTFE Millipore filter. The conc. of asphaltenes in the filtrate was measured and compared with the initial conc. Fig 5 illustrates the effect of stirring time on the amount of optimal mixing time is 5 hours.

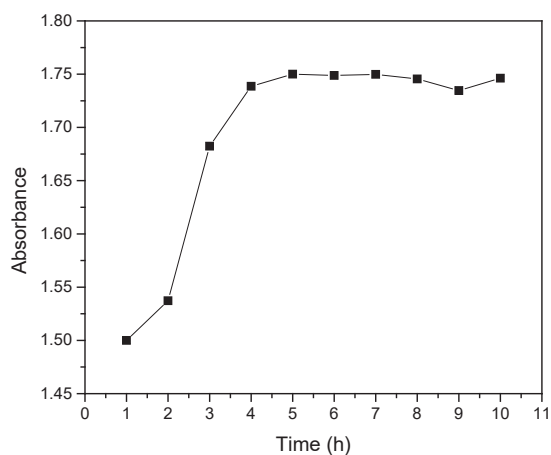


FIGURE 5. Effect of stirring time on asphaltene dispersion

CONCLUSION

In this research, hydrophobic ionic liquids were proposed to study the precipitation of inhibition of asphaltene in oil environment. The ILs with hydrophobic anions can be used to prevent asphaltene deposition. Finally, it should be mentioned that we observed and tested various parameters on the inhibition of asphaltene precipitation such as stirring time, amount of dispersant and effect of other ionic liquids.

ACKNOWLEDGMENT

Financial assistance from Universiti Teknologi PETRONAS is gratefully acknowledged.

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