
Effect of 1-Butyl-3-Methylimidazolium Hexafluorophosphate [BMImPF₆] on the Precipitation of Insoluble Organic Solid Residues from Organic Solvents

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Abstract: Insoluble organic solid residues in crude oil can cause staining, lathering, corrosion and contamination of the end product. Hence, removing these insoluble solids from the process stream is pertinent. In this research, samples of insoluble organic solid residues were taken from a single phase bottom hole crude oil, Qua Iboe Light Mobile Nigeria, unlimited. 1-butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF₆] was synthesized, and its effect on the precipitation of insoluble organic solid residues from methanol, ethanol and iso-amyl alcohol was investigated. Results of weight % of insoluble organic solids retrieved from methanol, ethanol and iso-amyl alcohol were 80.1 ± 0.2%, 74 ± 0.3%, 73.3 ± 0.2%, respectively. Comparatively, weights % of insoluble organic solids precipitated with methanol was higher (0.8010 g, 80.1%) than ethanol (0.7400 g, 74%) and iso-amyl alcohol (0.7330 g, 73.3%). This result corroborates the fact that insoluble organic solids are better precipitated from more polar organic solvents. Weights % of insoluble organic solids precipitated from methanol + [BMImPF₆], ethanol + [BMImPF₆] and iso-amyl alcohol + [BMImPF₆] were 80.4 ± 0.1%, 76 ± 0.2% and 75 ± 0.2% respectively. This result implies that organic solvent + [BMImPF₆] combinations yielded greater organic insoluble solid precipitates than those obtained with molecular organic solvents.

Keywords: Organic Solvents, Ionic Liquid, Organic Solids

1. Introduction

Ionic liquids (ILs) are salts that remain liquid below 100°C [1, 2]. Ionic liquids possess fascinating properties such as low melting point, high thermal stability (which makes them more resistant to changes in their chemical or physical structure). Ionic liquids are called universal solvents [3] and described as designer solvents, hence are used as green solvents in different industrial practices [4]. The physiochemical properties of an IL can be tuned for specific applications [5, 6]. A survey of the literature shows a plethora of industrial applications of ionic liquids. Application of ionic liquids in catalysis, as acid, base, organocatalysts and as soluble supports for catalysts have been reported [7]. Ionic liquids as components of liquid/liquid extraction systems, suitable for isolation of

both organic compounds and inorganic ions were investigated [8]. Recoveries of iron (Fe) and manganese (Mn) using solvent extraction and stripping with ionic liquids have been reported [9].

Keaveney and others developed a framework for predicting the effect of an ionic liquid solvent on the outcome of organic processes [10]. The applications of ILs reveal new perspectives in electrocatalysis and other branches of applied electrochemistry [11–13]. Trioctylmethylammonium bis(2-ethylhexyl) phosphate [TOMA][D₂EHP]; trioctylmethylammonium benzoate [TOMA][BA]; trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate [P_{6,6,6,14}][D₂EHP]; and trihexyltetradecylphosphonium benzoate [P_{6,6,6,14}][BA] were synthesized and used in the extraction of molybdenum(VI) (Mo) from aqueous solutions [14].

Ionic liquids (ILs) have proved to be adequate media for CO₂

dissolution, activation, and stabilization of radical and ionic electrochemical active species in aqueous solutions [15]. The Impact of ionic liquid 1-(4-fluorobenzyl)-3-(4-phenoxybutyl)imidazole-3-ium bromide [FPIM]Br on the electrodeposition of Nickel (Ni) and Cobalt (Co) from an aqueous sulfate bath has been reported by Omar and others [16]. Ionic liquids have been used as effective solvents to synthesize aerogels [17]. Application of ionic liquids to energy storage and conversion materials and devices has also been reported [18].

This study describes the synthesis of ionic liquid: 1-butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF₆], and the study of its effect on the precipitation of insoluble organic solid residues from organic solvents.

2. Materials and Methods

2.1. Materials

Ethanol, Methanol and Iso-amyl alcohol were purchased from Aeser and Aldrich and used without further purification. 1-butyl-3-methylimidazolium hexafluorophosphate [BMImPF₆] was synthesized and characterized.

2.2. Methods

2.2.1. Synthesis of 1-butyl-3-methylimidazolium hexafluorophosphate [BMImPF₆]

1-butyl-3-methylimidazolium hexafluorophosphate [BMImPF₆] was synthesized according to method reported [1]. 81.89 g (1.0 mol) of 1-methylimidazole, 128.95 g (1.0 mol) of and 92.0 g (1.0 mol) of potassium hexafluorophosphate in a 500 mL three necked round bottom flask and refluxed at 80°C for 12 hours. 1-bromobutane and de-ionized water (100 mL) was added and a bi-phase was formed. The immiscible ionic liquid layer was separated from the water phase. The crude ionic liquid was washed with de-ionized water (50 mL) until the water phase stopped reacting with 0.001 M aqueous silver nitrate (AgNO₃). Diethyl ether (2 × 30 mL) was added to the ionic liquid and separated using a separating funnel. The ionic liquid was then dried in vacuum for 2 hours. This yielded 86% colourless liquid. The ionic liquid was characterized by ¹H, ¹³C, Nuclear Magnetic Resonance (NMR) spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy and Thermal Gravimetric Analysis (TGA).

2.2.2. Precipitation Procedure with Organic Solvents

30 mL of methanol was accurately transferred into a 250 mL conical flask containing 1 g of crude oil residue and stirred for 2 hours. The mixture was allowed to equilibrate for 48 hours and centrifuged with a Generic 3500 RPM Centrifuge at 3500 rpm per minute for 40 minutes to precipitate the insoluble organic solids. The methanol-solubles (asphaltene) were carefully filtered. Insoluble organic solids retrieved were further precipitated with (10 mL × 3) of methanol and filtered. The organic insolubles were dissolved with 150 mL n-hexane. Hexane was removed from the mixture through evaporation and the weights of the insolubles recorded. The same precipitation procedure was employed with 30 mL of methanol and iso-amyl alcohol respectively. The procedure was triplicated with each of the organic solvents.

2.2.3. Precipitation Procedure with Organic Solvents (Methanol, Ethanol and Iso-amyl Alcohol) with [BMImPF₆]

1.74 mL of synthesized [BMImPF₆] was transferred into a 250 mL conical flask containing 30 mL methanol and 1 g of crude oil residue. The mixture was agitated with an electronic shaker for 2 hours and allowed to equilibrate for 48 hours. The mixture was centrifuged with a Generic 3500 RPM Centrifuge at 3500 rpm per minute for 40 minutes and the insoluble organic solids precipitated. The methanol-[BMImPF₆] solubles were filtered carefully and stored in a desiccator. The insoluble organic solids were further precipitated with (3 × 10 mL) methanol. The insolubles were dissolved with 150 mL n-hexane. Hexane was removed from the mixture through evaporation and the weights of the insolubles recorded. The procedure was triplicated and the mean average weights % of the precipitates were recorded.

The same precipitation procedure was used with 30 mL of ethanol and iso-propanol respectively. The procedure was repeated three times for ethanol + [BMImPF₆] and iso-amyl alcohol + [BMImPF₆] and the mean average weights % of the precipitates were recorded.

3. Results and Discussion

Weights (%) of insoluble organic solids precipitated.

The weight (%) of organic insolubles recovered (asphaltene) by precipitation was calculated using the following formula and tabulated:

$$Wt = \frac{\text{Weight of dry insoluble organic solids}}{\text{Weight of organic solid sample}}$$

Table 1. Percentage weights of insolubles from methanol, ethanol, iso-amyl alcohol, methanol + [BMImPF₆], ethanol + [BMImPF₆] and iso-amyl alcohol + [BMImPF₆] solvents.

S/N	Solvent	Mean ± S.D of insoluble organic solids recovered (%)	Insoluble organic solids recovered (g)
1.	Methanol	80.1 ± 0.2	0.8010
2.	Ethanol	74.0 ± 0.3	0.7400
3.	Iso-amyl alcohol	73.3 ± 0.2	0.7330
4.	Methanol + [BMImPF ₆]	80.4 ± 0.1	0.8040
5.	Ethanol + [BMImPF ₆]	76.0 ± 0.2	0.7600
6.	Iso-amyl alcohol + [BMImPF ₆]	75.0 ± 0.2	0.7500

Precipitates of organic insolubles recovered from methanol, ethanol and iso-amyl alcohol are presented in Figures 1-3.



Figure 1. Insoluble organic solids for methanol.



Figure 2. Insoluble organic solids for ethanol.

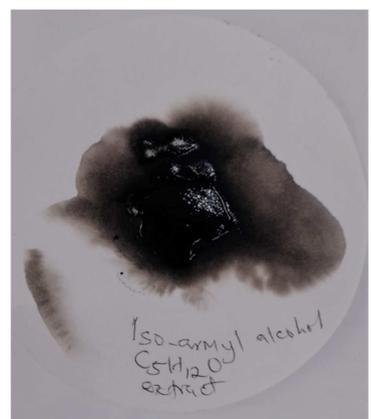


Figure 3. Insoluble organic solids for iso-amyl alcohol.

The Weight % of dried insoluble organic solids recovered after precipitation with methanol, ethanol and iso-amyl alcohol were $80.1 \pm 0.2\%$, $74 \pm 0.3\%$, $73.3 \pm 0.2\%$, respectively as presented in Figures 1-3. The weights of the dry insoluble organic solids in grams for methanol, ethanol and iso-amyl alcohol samples were 0.8010 g, 0.7400 g and 0.7330 g respectively. As shown, the amount of insoluble organic solids precipitated is in the order of methanol is greater than ethanol and iso-amyl alcohol. The result shows a decrease in the amount of precipitates with decrease in polarity (0.762, 0.654, 0.568) [19, 20] of the precipitating solvents. This result is similar to what was reported [20]. This result corroborates

the fact that organic solid-solvent interactions are weaker than the solvent-solvent interactions. Polarity is an important factor that contributes to solubility. The results indicate that solvent-solvent interactions get stronger with decreasing polarity of the alcohols, resulting in the precipitation of less organic insolubles. The organic solids with only carbon-carbon bonds are insoluble in polar solvents because, the organic solids form bonds through non polar van der waals interactions, but could not form significant attractive interactions with very polar molecules [21].

Figures 4-6 present the precipitates of organic insolubles recovered from mixtures of [BMImPF₆] in methanol, ethanol and iso-amyl alcohol respectively.



Figure 4. Insoluble organic solids for Methanol + [BMImPF₆].



Figure 5. Insoluble organic solids for ethanol + [BMImPF₆].

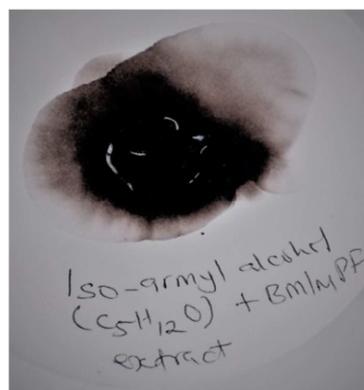


Figure 6. Insoluble organic solids for Iso-amyl alcohol + [BMImPF₆].

The Weight % of dried insoluble organic solids recovered after precipitation with methanol + [BMImPF₆], ethanol + [BMImPF₆] and iso-amyl alcohol + [BMImPF₆] were 80.4 ± 0.1%, 76 ± 0.2% and 75 ± 0.2% respectively. The weights (%) of the dry insoluble organic solids in grams for methanol in [BMImPF₆], ethanol in [BMImPF₆] and iso-amyl alcohol in [BMImPF₆] samples were 0.8040 g, 0.7600 g and 0.7500 g respectively. From the result, organic solvent-[BMImPF₆] combinations yielded greater organic precipitates than those obtained with molecular organic solvents as presented in Table 1.

4. Conclusion and Recommendation

From the results of the three organic solvents, methanol precipitated more organic insolubles than ethanol and iso-amyl alcohol. This could indicate that highly polar organic solvents are better precipitants of non polar insoluble organic solids. The results of the organic solvents in BMImPF₆ showed enhanced weights % of insoluble organic precipitates. The results of this study could be used in modelling the physical properties of insoluble organic solids in solution and their behaviour in petroleum refining processes.

The results could also help in curbing production, transportation and crude oil refining challenges.

This research was carried out at room temperature; hence, it recommends further precipitation studies of [BMImPF₆] in polar solvents at different temperatures.

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