



# Naphthenic acid extraction and speciation from Doba crude oil using carbonate-based ionic liquids



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## HIGHLIGHTS

- Carbonate-based ionic liquids can be used to remove naphthenic acids from crude oil.
- The reaction mechanism involves the formation of an ionic liquid-naphthenic acid complex.
- The complex can be reacted with carbonic acid to reform the ionic liquid.
- Recycling of the ionic liquid has been demonstrated.

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## ABSTRACT

A number of tetraalkylammonium methylcarbonate and hydrogencarbonate based ionic liquids are shown to be capable of reacting with the naphthenic acids contained in Doba crude oil via a neutralisation reaction. Spectral studies show that the ionic liquids neutralisation mechanism involves the formation of an ionic liquid-naphthenate complex, liberating methanol and carbon dioxide. Extraction of the neutralised complex into a separate methanol phase and subsequent regeneration using aqueous carbonic acid results in ~70% of the ionic liquid being recovered for recycle. Isolation of the naphthenic acids shows that these make up to 0.85 wt% of the crude oil. Speciation of the naphthenic acids shows a mixture of monocyclic, through to tetracyclic structures with carbon numbers in the range C<sub>12</sub>–C<sub>40</sub>.

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## 1. Introduction

As conventional oil reserves are declining, the extraction and treatment of high acid crude oil is becoming increasingly important. One of the most important characteristics of high acid crude oil is the presence of naphthenic acids which are responsible for corrosion in transport through pipelines, distillation units and heat exchangers [1,2]. As a consequence crude oils with high naphthenic acid content are often marketed at a lower market price. The total acid number (TAN) of which naphthenic acids are a major part is a measurement of acidity that is determined by the amount of potassium hydroxide in milligrams that is needed to neutralize the acids in one gram of oil. Crude oils of high TAN content are deemed to be those with TAN greater than 1.0 mg KOH g<sup>-1</sup> of crude oil which can be handled by specialist refineries, whilst

almost all refineries can handle TAN levels of ≤0.3 mg KOH g<sup>-1</sup> crude oil [3].

A number of unsuccessful techniques have been applied to solve mitigate naphthenic acids including solvent extraction [4], adsorption [5] and thermal decomposition [6]. Other problematic techniques to remove naphthenic acids involve neutralisation and extraction using either alkaline earth metals [7] or organic bases [8,9].

In recent years, numerous catalytic methods have been developed to overcome the disadvantages of the conventional processes. Esterification using metal carboxylates [10] and oxides [11] or decarboxylation using zeolites [12] have been successful although high operating temperatures (300–400 °C) are still required. Hydrotreating using transition metal oxides supported on alumina have also been successful but require a supply of hydrogen gas for the reaction [13]. Supported palladium and platinum catalysts have proved to be the most active metals in the liquid or gas phase destruction of naphthenic acids via decarboxylation [14] and decarbonylation [15]. For example, supported platinum and

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platinum–rhenium metals can effectively decarboxylate a series of fatty acids at low temperatures even in the absence of hydrogen [16]. Moreover, the same titania based-metal catalysts have shown significant sulphur resistance for fine chemical synthesis [17]. Despite the high activity and chemical stability it is unlikely that platinum group metal based catalysts will be cost effective and issues such as catalyst fouling could hinder a large scale bulk operation.

The use of ionic liquid (IL) technology has emerged as an alternative route for the removal of naphthenic acids. A range of triflate, thiocyanate and octylsulfate imidazolium ionic liquids were successful in the extraction of aliphatic and aromatic acids from dodecane [18]. Functionalised ionic liquids, such as those with basic anions, have also been employed as reagents to neutralise and extract naphthenic acids from hydrocarbons. Recently, we described the use of amino-acid ionic liquids for naphthenic acid sequestering from crude oil and distillate fractions [19]. Whilst these ionic liquids were shown to be efficient in the removal of the NA from crude oils, the high cost of these materials led us to explore lower cost alternatives. In this regard, the synthesis of methylcarbonate ([MeCO<sub>3</sub>]<sup>−</sup>) or hydrogencarbonate ([HCO<sub>3</sub>]<sup>−</sup>) based ionic liquids have been examined and tested in the extraction of naphthenic acids from crude oil. They are significantly cheaper than amino-acid based ionic liquid systems and can be formed via a green halide-free synthesis [20–22]. Herein, we describe the synthesis, physical characteristics and application of these materials for the neutralisation and extraction of naphthenic acids from crude oil. We also examine the speciation of the acids extracted and the nature of the leaching of the crude oil into the extraction phase.

## 2. Experimental

### 2.1. Materials and methods

Doba crude oil was supplied by PETRONAS from the Chad oil-field of Central Africa. The purified naphthenic acids were purchased from Tokyo Chemical Industry (TCI) and had a Total Acid Number of 235.35 mg KOH g<sup>−1</sup>. Triethylamine (99%), tributylamine (99%) were supplied by Sigma–Aldrich and dimethylcarbonate (99%) was supplied by Alfa Aesar. Methanol (HPLC) grade was supplied by Sigma–Aldrich.

### 2.2. Synthesis of methylcarbonate and hydrogencarbonate ionic liquids

The preparation of trialkylmethylammonium methylcarbonate [N<sub>RRR1</sub>][MeCO<sub>3</sub>] (R = 2 or 4) was performed by reacting the corresponding trialkylamine (0.2 mol) with dimethyl carbonate (36.03 g, 0.4 mol) in 50 cm<sup>3</sup> of methanol in an autoclave at 6 bar and 393.15 K for 12 h. After the reaction the excess methanol was removed under reduced pressure. The resultant solution was washed with *n*-hexane (3 × 50 cm<sup>3</sup>) to remove excess dimethylcarbonate affording a light yellow liquid. The yield (calculated using NMR) was 78% for the [N<sub>4441</sub>]<sup>+</sup> based ionic liquid and 54% for the [N<sub>2221</sub>]<sup>+</sup> based ionic liquid. The ionic liquid was then further dried under high vacuum (1.0 × 10<sup>−3</sup> Pa) at 338.15 K for 24 h. The resultant ionic liquid crystallised upon standing at room temperature.

The [HCO<sub>3</sub>]<sup>−</sup> analogue was obtained via hydrolysis of [N<sub>RRR1</sub>][MeCO<sub>3</sub>] with water. The ionic liquid of choice (0.1 mol) was reacted with excess water (0.2 mol) at 363.15 K and left to mix for a minimum of 2 h. The side products of methanol and excess water were then removed under reduced pressure. The yellow liquid was further dried under high vacuum (1.0 × 10<sup>−3</sup> Pa) at 338.15 K for 24 h to produce a yellow solid at room temperature.

The NMR yield was 95% for the [N<sub>4441</sub>]<sup>+</sup> based ionic liquid and 97% for the [N<sub>2221</sub>]<sup>+</sup> based ionic liquid. The NMR data was collected using a Bruker Avance 300X spectrometer.

*Triethylmethylammonium methylcarbonate*, [N<sub>2221</sub>][MeCO<sub>3</sub>]: <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ/ppm = 0.78 (9H, *J* = 7.4 Hz, t, CH<sub>2</sub>–CH<sub>3</sub>); 2.8 (1H, *J* = 1.8 Hz, s, N–CH<sub>3</sub>); 2.94 (3H, s, H<sub>3</sub>C–OCO<sub>2</sub>); 3.08 (6H, *J* = 8.5 Hz, m, NCH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>). CHN Analysis (%): Calculated; C, 56.6; H, 10.9; N, 7.3; Found; C, 54.5; H, 11.3; N, 7.2. ESI–MS; +ve mode: 191.13 ([C<sub>9</sub>H<sub>21</sub>N]<sup>+</sup>); –ve mode: 75.05 ([C<sub>2</sub>H<sub>3</sub>O<sub>3</sub>]<sup>−</sup>).

*Triethylmethylammonium hydrogencarbonate*, [N<sub>2221</sub>][HCO<sub>3</sub>]: <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ/ppm = 0.78 (9H, *J* = 7.4 Hz, t, CH<sub>2</sub>–CH<sub>3</sub>); 2.8 (1H, *J* = 1.8 Hz, s, N–CH<sub>3</sub>); 3.06 (6H, *J* = 8.5 Hz, m, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, D<sub>2</sub>O); δ/ppm = 161.23 (OH–COO<sup>−</sup>). CHN Analysis (%): Calculated; C, 54.2; H, 10.7; N, 7.9; Found; C, 51.5; H, 12.3; N, 7.5. ESI–MS; +ve mode: 191.13 ([C<sub>9</sub>H<sub>21</sub>N]<sup>+</sup>); –ve mode: 61.05 ([CHO<sub>3</sub>]<sup>−</sup>).

*Tributylmethylammonium methylcarbonate*, [N<sub>4441</sub>][MeCO<sub>3</sub>]: <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ/ppm = 0.79 (9H, *J* = 7.4 Hz, t, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>); 1.18 (6H, *J* = 7.6 Hz, m, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>); 1.48 (8H, m, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>); 2.80 (1H, *J* = 1.8 Hz, s, N–CH<sub>3</sub>); 2.94 (3H, s, H<sub>3</sub>C–OCO<sub>2</sub>); 3.06 (6H, *J* = 8.5 Hz, m, NCH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>). CHN Analysis (%): Calculated; C, 65.5; H, 12.1; N, 5.1; Found; C, 62.5; H, 14.1; N, 5.2. ESI–MS; +ve mode: 200.24 ([C<sub>13</sub>H<sub>30</sub>N]<sup>+</sup>); –ve mode: 75.05 ([C<sub>2</sub>H<sub>3</sub>O<sub>3</sub>]<sup>−</sup>).

*Tributylmethylammonium hydrogencarbonate*, [N<sub>4441</sub>][HCO<sub>3</sub>]: <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ/ppm = 0.79 (9H, *J* = 7.4 Hz, t, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>); 1.18 (6H, *J* = 7.6 Hz, m, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>); 1.52 (8H, m, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>); 2.80 (1H, *J* = 1.8 Hz, s, N–CH<sub>3</sub>); 3.5 (6H, *J* = 8.5 Hz, m, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, D<sub>2</sub>O); δ/ppm = 161.23 (OH–COO<sup>−</sup>). CHN Analysis (%): Calculated; C, 65.5; H, 12.1; N, 5.1; Found; C, 63.5; H, 13.6; N, 5.4. ESI–MS; +ve mode: 200.24 ([C<sub>13</sub>H<sub>30</sub>N]<sup>+</sup>); –ve mode: 75.05 ([C<sub>2</sub>H<sub>3</sub>O<sub>3</sub>]<sup>−</sup>).

### 2.3. Properties of Doba crude oil

The physical properties of the crude oil are listed in Table 1 [23]. The boiling point distribution of the Doba crude oil and the treated Doba crude oil (Fig. 5) were determined using an Agilent Technologies 7890A GC system coupled with Agilent SimDis A.02.02 software.

### 2.4. Total acid number (TAN) measurement

The procedure for TAN determination was conducted using an automatic potentiometer with combined glass electrode (Metrohm Titrino Plus model 785) following the ASTM D664 method. A known mass of crude oil (~5.00 g) is placed into a 125 cm<sup>3</sup> beaker

**Table 1**  
Doba Blend physical properties (adapted from Ref. [23] and experimental values).

Properties	Test	Unit	Value
Density	ASTM D4052	kg m <sup>−3</sup>	925.0
API	ASTM D1298	°	21.01
Pour point	ASTM D5853	°C	−3
Flash point	ASTM D93	°C	77
TAN	ASTM D664	mg KOH g <sup>−1</sup>	3.81–3.85
Total sulphur	IP336	wt%	0.1
Total nitrogen	ASTM D4629	ppm	1961
Viscosity @ 15 °C	ASTM D445	mPa s	2690.15
Viscosity @ 50 °C	ASTM D445	mPa s	185.5
Asphaltene content	ASTM D3279	wt%	<0.7
Distillation	ASTM D86	°C	
IBP			173.6
FBP			715.4
Metal	ASTM D5078	ppm	
Nickel			11.2
Vanadium			3.6
Calcium			284.0

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