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Liquid-Liquid Extraction of Naphthenic Acid Using Thiocyanate Based Ionic Liquids

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Abstract

In this work the de-acidification of dodecane was investigated using [DBU] based ionic liquid with thiocyanate [SCN] anion. The liquid-liquid equilibrium data for ternary mixture of {dodecane + naphthenic acid + [DBU-Hex][SCN]} were experimentally determined at a constant temperature and pressure. The ternary diagram shows that all the tie lines have a positive slope at all concentration of naphthenic acid, thus indicating that the ionic liquid is enough for the de-acidification of dodecane. The liquid-liquid equilibrium data was correlated using non-random two liquid (NRTL) model. An extremely good fit was obtained for all the tie lines using the NRTL model.

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Keywords: Naphthenic acid; Ionic liquids (ILs); Liquid-liquid equilibrium (LLE), Non-Random Two Liquid (NRTL)

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1. Introduction

Naphthenic acid present in heavy crude oil is one of the major causes of corrosion in heavy crude oil refineries. Crude oil is considered as acidic if the total acid number (TAN) is greater than 0.5 mg KOH/g [1]. Naphthenic acid corrosion is more dominant in vacuum column of a refinery as well it can cause corrosion in the storage tanks and transport units. On the other hand it can also cause operational difficulties such as foaming and deactivation of the catalyst as well [2, 3]. The structure of these naphthenic acids is quite complicated and a wide variety of structure lies in this definition. Naphthenic acid is generally represented by the general formula $C_nH_{2n+z}O_2$, whereas n represents the carbon number and z indicates the hydrogen deficiency as a result of chain formation. The value of z could be zero or negative [4]. On the other hand naphthenic acid is a valuable by product that can be used in various industries such as paint, tire, fuel and wood industry [4]. Numerous methods have been studied by researchers in order to extract and recover naphthenic acid from crude oil such as neutralization, adsorption, thermal decomposition, catalytic decarboxylation, esterification and liquid-liquid extraction using organic solvents [5],[6-9],[10, 11]. However, all these methods have certain shortcomings that limit their viability at industrial scale as well they have negative impacts towards environment. The restrictive factors in the current methods demands for a simple, environmental friendly and industrially viable process for the extraction of naphthenic acid.

Due to the increase of awareness on environmental issues among petroleum and chemical industry, the use of ionic liquids (ILs) as a potential solvent for separation of aromatic and non-aromatic compounds has been an explosion of interest in various industries [12]. ILs are simply composed of heterocyclic organic cations and various anions. The physiochemical properties of ILs depend mostly on the cations and anions of respective ILs. The alkyl chain in the cation or symmetry of the shape may affect density, viscosity and surface tension while anion may affect thermal stability and miscibility [13]. The main advantage of ILs from polar and non-polar organic solvents is that it has an extremely low vapor pressure and wide range temperature for liquid phase. Due to unique properties of ILs, it is regarded as the green solvent for a lot of extraction processes [14, 15].

Although different ILs are used for extraction of naphthenic acid, most of them are applicable only in the case of very low total acid number (< 0.5 TAN). Moreover, most of them are using large amount of volatile organic solvents and the regeneration procedure of ILs and naphthenic acid is quite complicated [16-18][19]. In a few recent studies although they are using a high total acid number but all these experiments are performed at lab scale only and there is no liquid-liquid equilibrium data available for all these ionic liquids [20-22]. In one of the recent method the liquid-liquid equilibrium data is developed for [$C_n$mim][Phe] based ionic liquids as well as the equilibrium data had been correlated using different thermodynamic models as well [23]. This study also aims to develop the liquid-liquid equilibrium data for [DBU] based thiocyanate ionic liquid as well as correlation of the equilibrium data will be performed as well using non-random two liquid model.

2. EXPERIMENTAL SECTION

2.1 Materials

All the chemicals were purchased from Acros Organics and no further purification was carried out. The chemicals used in this study are sodium thiocyanate (98%), 1-bromohexane (98%), dichloromethane (HPLC grade) and Diazobicyclo[5.4.0]undece-7-ene (98%). Dodecane (99.0%) and benzoic acid (99.5 %) were purchased from Merk (Malaysia).

2.1. Synthesis of Halide Salts

The synthesis of halide salt was done according to the synthesis scheme given in Figure 1. To a 5 g solution of 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) in acetonitrile(35 mL), 6.5 g of 1-bromohexane was added into a round bottom flask and stirred at 50 °C for 48 h. The reaction mixture was cooled using ice bath and the acetonitrile was removed in a rotary evaporator. Cyclohexane was used to washed away white solid (chloride salt) obtained. After this the halide salt was dried under vacuum at 70 °C for 24 h.