Physicochemical properties of betaine monohydrate-carboxylic acid mixtures

I Zahrina\textsuperscript{1,2}, M Nasikin\textsuperscript{1} and K Mulia\textsuperscript{1}\textsuperscript{*}
\textsuperscript{1}Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Depok 16424, Indonesia
\textsuperscript{2}Department of Chemical Engineering, Faculty of Engineering, University of Riau, Pekanbaru 28293, Indonesia

*E-mail: kmulia@che.ui.ac.id

Abstract. Green solvents are widely used to minimize environmental problems associated with the use of volatile organic solvents in many industries. DES are new green solvents in recent. The physicochemical properties of DES can be varied by properly combining of salts with different hydrogen bond donors. The objective of this work is to investigate the effect of varying molar ratios on the physicochemical properties of betaine monohydrate-carboxylic acid (i.e., propionic or acetic acid) mixtures. Properties of mixtures were measured at 40°C. The viscosity, polarity scale (E\textsubscript{NR}), density, pH, and water content tend to decrease with the decrease in a molar ratio of betaine monohydrate to acid. Conversely, the ionic conductivity was increased. The physicochemical properties of these mixtures depend on the hydrogen bonding interactions between betaine, water and acid molecules. Betaine monohydrate-carboxylic acid mixtures have wide range of polarity, low viscosity, high ionic conductivity, and density higher than 1 g⋅cm\textsuperscript{-3} that make them fit for numerous various applications. Additionally, due to these mixtures have acidic pH, it should be properly selected of metal type to minimize corrosion problems in industrial application.

1. Introduction
Deep eutectic solvents (DES) are new green solvents that have attractive physicochemical properties, such as non-toxic, non-volatility, non-flammability, thermal stability, non-flammability, high conductivity, and good solubilizing capacity [1]. DES are formed by mixing a quaternary ammonium salt (such as choline chloride, betaine) with hydrogen bond donor (HBD) compound, such as an alcohol, organic acid, sugar or amino acid [2]. DES were applied in catalysis, CO\textsubscript{2} removal, and metal ion adsorption, and extraction of organic and inorganic compounds [3-7].

The physicochemical properties of DES depend on the molar ratio of salt to HBD, and type of HBD. For instance, the density of choline chloride-fructose based DES, and choline chloride-glucose based DES tend to decrease with increase in concentration of salt in the mixture (in the range of choline chloride to sugar molar ratio of 1:1 to 2.5:1). At the same temperature and molar ratio of salt to sugar, the densities of choline chloride-fructose based DES are higher than choline chloride-glucose based DES [8,9]. Zahrina, et al. [10] reported that the mixture of betaine monohydrate and organic acid (propionic or acetic acid) form eutectic at a mole ratio of 1:2. The thermodynamic study revealed that interactions between betaine monohydrate and propionic acid mixture were greater than between betaine monohydrate and acetic acid mixture at eutectic. In addition, the interactions between betaine monohydrate and acid at the eutectic composition were higher than those at the hyper-eutectic.

The use of choline chloride-alcohol based DES as the solvents for extraction process shown that the extraction efficiency increase with the addition of alcohol concentration in the mixture [7,11]. The reasons for this phenomenon were probably related to physicochemical property of DES (viscosity,
surface tension, and basicity) and the interactions of hydrogen bonding between DES and solutes. The effect of diffusion and mass transfer improved with the increase in the polyol ratio in mixture due to the viscosity and surface tension decrease. However, a further decrease in the ratio of choline chloride can reduce the interactions between solutes and chloride anion [11].

The physicochemical properties of mixture of betaine monohydrate and carboxylic acid (propionic or acetic acid) at eutectic and hyper-eutectic should be studied in order to be utilized for several possible industrial applications. In this work, the effect of varying mole ratios on physicochemical properties, and the relationship between physicochemical properties and interaction between molecules in betaine monohydrate-carboxylic acid mixtures were investigated.

2. Materials and Methods

2.1. Materials
The synthesis grade of propionic acid and acetic acid (glacial) were purchased from Merck. Betaine monohydrate and nile red (dye) were purchased from Sigma Aldrich.

2.2. Preparation of betaine monohydrate-carboxylic acid mixtures
The betaine monohydrate and carboxylic acid (propionic or acetic acid) was mixed at different molar ratios. The mixture was placed in a bottle with a screw-cap and stirring bar. The mixture was heated in a hotplate stirrer (IKA C-MAG HS7) at 50±1°C with agitation of 150 rpm for 90 min.

2.3. Determination of physicochemical properties of mixtures
The viscosity and density of betaine monohydrate-carboxylic acid mixtures were measured at 40°C by triplicate runs. The viscosity was performed according to the procedure in ASTM D445 using a viscometer type U-tube reverse (Cannon-Fenske) in a water-bath with controlled temperature. The density was measured using a calibrated density bottle [IP Method 733].

The procedure in polarity scale (ENR) is following the previous work [2]. Polarity scale measurements were carried out using a Spectroquant Pharo 300 model spectrophotometer. The pH of each mixture was measured by EcoTest pH2. The water content in mixtures was measured by titration method using MKS-1s Karl-Fischer moisture meter.

2.4. NMR analysis
The NMR spectra of NOESY (1H-1H-nuclear overhauser enhancement spectroscopy correlation) and COSY (spectroscopy correlation) of betaine monohydrate-acid mixtures were recorded with a JEOL JNMECA 500 NMR spectrometer using D2O as solvent.

3. Results and discussion
The polarity and viscosity are important properties for solvent which corresponding with their solubilizing ability for solutes [12]. As can be seen in Figure 1a, the polarity scale (ENR) of betaine monohydrate-propionic acid mixture is higher than betaine monohydrate-acetic acid mixture at the same molar ratio. Methanol has the polarity scale in the range of betaine monohydrate-propionic acid mixtures. The betaine monohydrate-acetic acid mixtures have higher polarity scale than water, and lower than methanol. The betaine monohydrate-acetic acid mixture inferred has higher hydrogen bonding ability and thus lower polarity scale (or higher polarity) than the betaine monohydrate-propionic acid mixture. Generally, the polarity of DES rises from the hydrogen bonding ability of the involved hydrogen bond donor. While upon the salt interact with the hydrogen bond donor, partially offset by a loss of hydrogen-donor ability due to some of the hydrogen bond donor groups interact with the ions [13]. In this work, if the molar ratio of salt to acid decrease thus the hydrogen bonding ability also increased and thus leading to increase in the polarity (or decrease in polarity scale). Similar result also reported by Abbot et al. [14] that the polarity scale E30(30) (using Reichardt’s dye) of choline chloride-glycerol DES decrease with an increase in glycerol concentration.
The viscosity of betaine monohydrate-carboxylic acid mixtures in the range of 6.4–73 cSt at a temperature of 40°C (Figure 1b). The low viscosity value makes these mixtures fit for numerous various applications including as the solvents for the extraction processes. The viscosities of betaine monohydrate-propionic acid mixtures were higher than betaine monohydrate-acetic acid mixtures. However, viscosity of the mixture tends to similar with decrease in the mole ratio of salt to acid. The high viscosity of DES is often attributed to the presence of an extensive hydrogen bond network between salt and hydrogen bond donor which causing the lack of free volume within the DES [14]. The betaine monohydrate-propionic acid mixture has greater stability than betaine monohydrate-acetic acid mixture at the eutectic composition [10]. Therefore, the betaine monohydrate-propionic acid mixture has higher viscosity if compared with the betaine monohydrate-acetic acid mixture at a molar ratio of 1:2. At a molar ratio of 1:3, the excess Gibbs free energy ($G^\circ$) of betaine monohydrate-acid mixtures was higher than those at a molar ratio of 1:2 [10]. The presence fewer interactions between components in addition of acid concentration in the mixture, and it cause the viscosity decrease. The NMR spectra of betaine monohydrate-propionic acid mixtures are depicted in Figures 2 and 3.

In the NOESY spectra of betaine monohydrate-propionic acid mixtures, the interactions between methyl group proton of betaine monohydrate and both of the protons of the methyl and methylene groups of propionic acid were present. Also, there are intra-molecular interactions in the acid molecules. However, the interactions between betaine monohydrate and propionic acid are similar at the molar ratios of 1:2 and 1:3 (Figures 2a and 3a). In the COSY spectra of betaine monohydrate-propionic acid mixture at a molar ratio of 1:2 (Figure 2b) revealed that the proton of methyl group interact with $H_2O$ of the betaine monohydrate molecule. However, this interaction is loss at a molar ratio of 1:3 (Figure 3b). The water content in the mixtures tends to significantly decrease with the increase in acid concentration in the mixture (Figure 4), and the hydrogen bonding interactions can be
formed between hydroxyl group of water and carbonyl group of acid. The carbonyl group of betaine monohydrate can also interact with the hydroxyl group of acid. In addition, the carbonyl group of acid can also interact with hydroxyl group of acid if the acid concentration increases. Therefore, the hydrogen bonding interactions between salt and acid also tend to decrease and lead to decrease in the viscosity of mixtures.

![Figure 2](image)

**Figure 2.** NOESY (a) and COSY (b) spectra of betaine monohydrate-propionic acid at a molar ratio of 1:2

![Figure 3](image)

**Figure 3.** NOESY (a) and COSY (b) spectra of betaine monohydrate-propionic acid at molar ratio of 1:3

The viscosity and conductivity of DES are strongly correlated with the ability of the involved molecules of the salt and hydrogen bond donor to move [15]. Therefore, the relationship between viscosity and ionic conductivity of NADES were analyzed using Walden plots. The ionic conductivities of the betaine monohydrate-acetic acid mixtures were higher than betaine monohydrate-propionic acid mixtures (Figure 5a). The ionic conductivity of betaine monohydrate-acetic acid mixtures tends to linearly increase with the addition in acid concentration. However, the ionic conductivity of betaine monohydrate-propionic acid mixture has slightly increase if mole ratio of salt to acid decrease. The ion mobility and conductivity are determined by not only the availability of suitable holes but also the type and strength of interactions between ion of salt and HBD [15]. Because the betaine monohydrate-propionic acid mixture has stronger interactions between components than betaine monohydrate-acetic acid mixture in the previous study [10], thus the betaine monohydrate-acetic acid mixture has higher ionicity and ability to move. According to the NMR spectroscopic results, the hydrogen bonding interactions between salt and acid decrease induce the ionic conductivity tend to increase with the decrease in molar ratio of salt to acid.
The betaine monohydrate-propionic acid mixtures present larger deviations from the ideal reference line (obtained for 0.01M KCl aqueous solution) than betaine monohydrate-acetic acid mixtures (Figure 5b). This indicates that the betaine monohydrate-propionic acid mixtures have lower ionicity, and thus their viscosity is higher than the betaine monohydrate-acetic acid mixtures. The lower ionicity was also obtained with decrease in a molar ratio of salt to acid whereas the viscosity of mixtures decreases.

![Figure 4](image)

**Figure 4.** Water content in betaine monohydrate-propionic acid mixtures (□) and betaine monohydrate-acetic acid mixtures (■)

![Figure 5](image)

**Figure 5.** Ionic conductivity (a), and Walden plots (b) of betaine monohydrate-propionic acid mixtures (□) and betaine monohydrate-acetic acid mixtures (■)

The densities of betaine monohydrate-propionic acid mixtures were lower than betaine monohydrate-acetic acid mixtures at the same molar ratio (Figure 6a). This result is indicating that the increase in chain length of acid induce the density decrease. Moreover, the density of these mixtures tends to decrease gradually as the acid concentration increases (or molar ratio of salt/acid decrease). Likewise, the density of DES from choline chloride-diacid mixture decreases with increasing chain length (oxalic acid > malonic acid > glutaric acid) at a molar ratio of salt to acid of 1:1 [16]. The molecular characteristics of the HBD and the mole ratio of salt to HBD have a large effect on the density of DES [9]. According to the hole theory (hard sphere model), the density of DES is affected by free volume [14]. The NMR spectroscopic result revealed that the hydrogen bonding interactions between salt and acid decrease with the decrease in mole ratio of salt to acid which the free volume can be increased in this mixtures and the density decrease. As presented in Figure 6b, the pH of betaine monohydrate-propionic acid mixtures was higher than the betaine monohydrate-acetic acid mixtures at the same molar ratio of salt to acid. Additionally, the decrease in mole ratio of salt to acid was gradually increase acidity of mixtures.
1.2 1.3 1.4 1.6 1.8

Density (40°C), g cm⁻³

1.00 1.04 1.08 1.12 1.16

Molar ratio of betaine monohydrate:acid

(a)

2.8 3.2 3.6 4.0 4.4 4.8

pH (40°C)

Molar ratio of betaine monohydrate:acid

(b)

Figure 6. Density (a) and pH (b) of betaine monohydrate-propionic acid mixtures (□) and betaine monohydrate-acetic acid mixtures (■)

4. Conclusions
The physicochemical properties of betaine monohydrate-carboxylic acid mixtures depend on molar ratio of salt to acid and type of acid. The hydrogen bonding interactions between components in the mixtures affect their physicochemical properties. The betaine monohydrate-carboxylic acid mixtures have wide range of polarity, low of viscosity, high ionic conductivity, and density higher than water. It makes these mixtures fit for numerous various applications including for the extraction processes. These mixtures have acidic pH (3-4.9), it should be properly selected of metal type to minimize corrosion problems in industrial application.

5. References
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