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Influence of some parameters on synthesis processes of triethyl ammonium oleate and triethyl ammonium stearate

Bui Thi Le Thuy[1*], Nguyen Duc Chinh[2], Cong Ngoc Thang[3], Vu Van Toan[3], Vu Duy Thinh[3], Ta Thi Toan[3]

[1] *Key research group: Green Chemistry Process (HUMG-GCP), Ha Noi University of Mining and Geology, 18 Vien, Duc Thang yard, Bac Tu Liem district, Ha Noi.*
[2] *Petrovietnam exploration production Corporation, 26th Floor, Charm Vit Tower, 117 Tran Duy Hung St., Cau Giay Dist.,Hanoi, Vietnam*
[3] *Ha noi University of Mining and Geology, 18 Vien, Duc Thang yard, Bac Tu Liem district, Ha Noi.*
**Email: thuykhai2001@gmail.com*

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ABSTRACT

Two ionic liquids named triethyl ammonium oleate ([TEA][Oleate] and triethyl ammonium stearate ([TEA][Stearate]) were synthesized from triethyl amine and oleic/stearic acids in water and in ethanol solvents. The synthesized ionic liquids were characterized by FT-IR and NMR spectra to confirm their structure. The influence of some parameters such as structure of ionic liquid anion, solvent, reaction time, reaction temperature, and acid/amine molar ratio on the synthesis processes of triethyl ammonium oleate and triethyl ammonium stearate was investigated. Ethanol was found suitable as a solvent for these processes because it dissolves formed ionic liquids but does not dissolve co-product KCl. In order to shift the equilibrium to increase the ionic liquid yields, an access amount of acids was used. Stearate-based ionic liquid should be synthesized at higher a temperature and longer time than oleic-based ionic liquids.

1. Introduction

Usage of ionic liquids in different applications is increasingly because of their special physical and chemical properties. They are good compatible with many compounds, high polarity, negligible volatility, high thermal stability, high ionic conductivity, low melting point, and structural designability [1-3]. The physical and chemical properties of ILs can be tuned by changing the cation and anion comprising the ionic liquid. In addition, ILs are nonflammable, high thermal and electric conductivity. Therefore, ILs can be used in a variety of task-specific applications. [4-8]. They are considered as "designed" solvents or catalysts for variety of processes and reactions. However, their industrial usage has been limited because the high cost for producing them. Ionic liquids made from oleic acid and trialkyl amines or alkyl amines were prepared and used as solvent for selective extraction of bitumen from Alberta oil sands at room temperature [9]. Tetraalkylammonium oleate and linoleate based ionic liquids were reported as promising extractants for Mn(II), Fe(II), and Zn(II), Co(II), Ni(II) chlorides from aqueous solutions with excellent extraction (>99%) efficiencies [10,11]. Some ionic liquids were used as both lubricants and lubricating additives and showed high efficiency [12-14]. Most of investigated ionic liquids are based on tetraborate, hexafluorophosphate, diethyl phosphate… anions which are high cost and environmental pollution. Fatty acids based Ionic liquids are of interests because its high compatibility with lubricants deriving from vegetable oils. Fatty acid-based

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ionic liquids were used effective breaking of water in oil emulsions, corrosion Inhibitors for C-steel [15,16].

Ionic liquids made from triethyl amines and fatty acid are compatible with oil and proposed to be used as additives for lubricating oil but their synthesis has not fully investigated synthesizing.

In addition, the preparation of ionic liquids from fatty acids deriving from vegetable oils could reduce the environmental pollution and the dependence on fossil fuel resource which is depleting. Because oleic and stearic acids are the main components of fatty acids of vegetable oils, the synthesis procedure of triethyl ammonium oleate and triethyl ammonium stearate were used as reference for synthesizing ILs from fatty acids of vegetable oils.

In our previous work, these two ionic liquids were prepared by one step and three step methods [13]. The three-step method used acetone solvent gives higher yield and requires less time but consumes more chemicals and forms products with lower purity compared to one step method. In order to improve this method and to get higher ionic liquid yield the present work focuses on using other solvents instead of acetone and combining the 2th and 3th steps in one pot. In addition, the influence of some reaction parameters such as reaction temperature, reaction time and molar ratio of reactants on synthesis yields of ionic liquids triethyl ammonium oleate and triethyl ammonium stearate was investigated. The suitable conditions for synthesis each ionic liquid were proposed.

2. Experimental

Materials

Triethyl amine, ethyl acetate and hydro chloride were supplied by Merck company; Oleic acid, stearic acid, ethanol and potassium hydroxide was purchased from Guangdong Guanghua, China.

Experimental

Synthesis of ionic liquids

Triethyl ammonium oleate [TEA][Oletate] and triethyl ammonium stearate [TEA][Stearate] were synthesized by reactions [10]:

- Synthesis of triethylammonium chloride:

$(C_2H_5)_3N + HCl \rightarrow (C_2H_5)_3NHCl$ (1)

- Synthesis of [TEA][oleate] or [TEA][Stearate] from oleic acid or stearic acid and triethylammonium chloride

$RCOOH + KOH \rightarrow RCOOK + H_2O$ (2)

$RCOOK + (C_2H_5)_3NHCl \rightarrow [RCOO]^-[HN(C_2H_5)_3]^+ + KCl$ (3)

- Synthesis of triethyl ammonium chloride [14]

30.3 g (0.3 mol) of triethyl amine was added into a 3-neck flask immersed in an ice bath. The flask was connected to a reflux condenser, a dropping funnel and a thermometer. 34 g of 36-38% HCl solution was slowly dropped for 2 h. During the addition, suspension's temperature was kept around 0–5 °C. Once added, the temperature was increased to 50 °C and the suspension was stirred for 2h at this temperature. The reaction mixture was evaporated at reduced atmospheric to remove excess water and unreacted HCl to get white waxy product.

- Synthesis of triethyl ammonium oleate [TEA][Oleate]

In order to investigate the influence of solvent the synthesis was performed in two kinds of solvents (in water and in ethanol).

Water solvent: 6.5142 g of oleic acid (0.0231 mol) was added into a flask containing 80 mL of distilled water dissolving 1.7864 g of KOH (1.7864/56=0.0319 mol). The flask was connected to a refflux condenser and a thermometer and immersed in an oil bath. The mixture was stirred at 75°C for 3 h, then 2.4373 g of $(C_2H_5)_3NHCl$ (0.0177 mol) was added and continued to stir for 6h at 45°C. The mixture was then transferred to a 250 mL extraction funnel, it was allowed to stand and separated into 2 phases. The organic phase containing IL was separated and washed 2 times with 100 mL of warm water at 45°C to remove KCl and unreacted KOH, RCOOK. Then the liquid was dried to obtain a slightly yellow viscous ionic liquid.

Ethanol solvent: 6.5142 g of oleic acid (0.0231 mol) was added into a flask containing 80 mL of ethanol dissolving 1.37 g of KOH (0.0319 mol). The flask was connected to a reflux condenser and a thermometer and immersed in oil bath. The mixture was stirred at 75°C for 3h, then 2.4373 g $(C_2H_5)_3NHCl$ (0.0177 mol) was added and continued to stir for 6 h at 45°C. KCl precipitate formed was filtered and washed with ethanol. Ethanol was distilled off from the filtrate for recycling. The remained oily liquid includes IL and unreacted reactants. To purify, the oily liquid was dissolved in ethyl acetate, and the mixture was filtered to remove any unreacted reactants. Ethyl acetate was then evaporated to obtain pure IL.

- Synthesis of triethyl ammonium stearate [TEA][Stearate]

Similar to [TEA][Oleate], in order to investigate the influence of solvent the synthesis of [TEA][Stearate] was performed in two solvents (in water and in ethanol).

Water solvent: 6.6504 g of stearic acid (0.0231 mol) was added into a flask containing 80 mL of distilled water dissolving 1.7864g KOH (1.7864/56=0.0319 mol). The flask was connected to a reflux condenser and a thermometer and immersed in an oil bath. The mixture was stirred at 55°C for 3 h, then 2.4373 g of $C_2H_5)_3NHCl$ (0.0177 mol) was added and continued to stir for 7 h at 55°C. The mixture was then transferred to a 250 mL extraction funnel, it was allowed to stand and separated into 2 phases. The organic phase containing IL was separated and washed 2 times with 100 mL of warm water at 45°C to remove KCl, unreacted KOH and RCOOK. Then the liquid was dried to obtain a slightly yellow viscous ionic liquid.

Ethanol solvent: 6.5142g stearic acid (0.0231 mol) was added into a flask containing 80ml ethanol dissolving 1.37 KOH (0.0319 mol). The flask was connected to a reflux condenser and a thermometer and immersed in an oil bath. The mixture was stirred at 75°C for 3h, then 2.4373 g $C_2H_5)_3NHCl$ (0.0177 mol) was added and continued to stir for 7 h at 55°C. KCl precipitate formed was filtered and washed with ethanol. Ethanol was distilled off from the filtrate for recycling. The remained oily liquid including IL and unreacted reactants. To purify, the oily liquid was dissolved in ethyl acetate, and the mixture was filtered to remove unreacted reactants. Ethyl acetate was then evaporated to obtain pure IL.

Influence of reaction temperature and reaction time, molar ratio of triethyl amine and RCOOK on IL synthesis

In this work, in order to investigate the influence of reaction temperature, reaction time and molar ratio of acid and amine on synthesis yield of ionic liquids [TEA][oleate] and [TEA][Sterate]; The reaction temperature, reaction time and TEA/RCOOH molar ratios was varied from 35°C to 65 °C, from 4 h to 8 h and from 1.1 to 1.4, respectively.

Ionic liquid synthesis yield was determined by formula:

$$Y\ (\%) = \frac{m_{IL\ (eq)}}{m_{IL\ (ex)}} x100\% \qquad (4)$$

where: $m_{IL(eq)}$: weight of IL calculated from equation; $m_{IL(ex)}$: weight of ionic liquid obtained from experiment.

Characterization

FI-IR and NMR spectra of synthesized ionic liquids were measured by FT-IR-1S Shimadzu and NMR Brucker Advance III 500 MHz in $CDCl_3$.

3. Results and discussion

Characterization of triethyl ammonium oleate [TEA][Oletate] and triethyl ammonium stearate [TEA][Stearate]

Structure of [TEA][Oleate] and [TEA][Stearate] are given in Fig, 1.

The prepared ionic liquids were characterized by FT-IR and NMR spectra. The presence of functional group amide is shown by a wide peak around 1200 cm^{-1}. The bands of wave numbers around 2922 cm^{-1} are the asymmetric and symmetric (C-H) stretching vibrations due to aliphatic methyl groups. C=C and C=O stretching is shown by wave numbers around 3010 cm^{-1} and 1710 cm^{-1}. The band at wave number 720 cm^{-1} is due to the C-N stretching vibration [17].

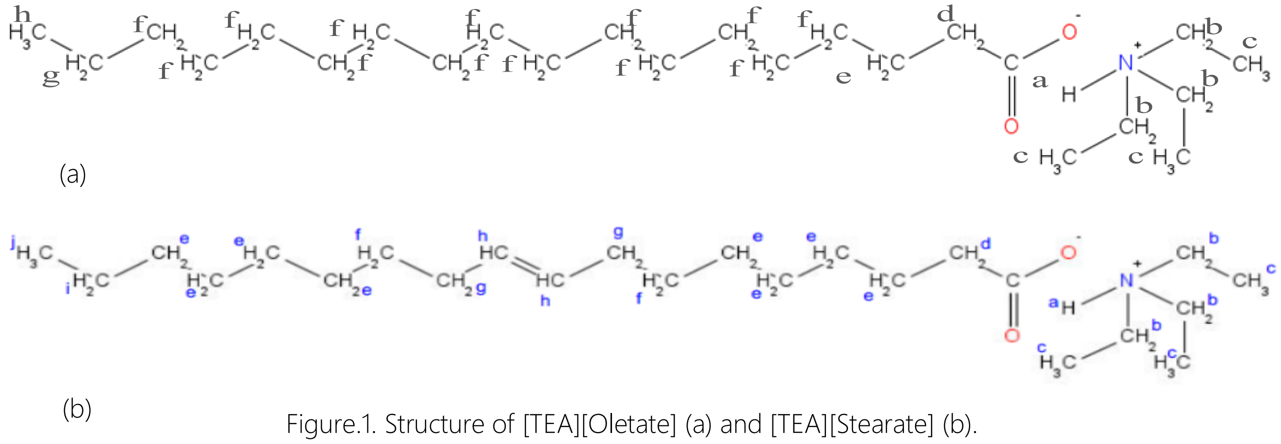

Figure.1. Structure of [TEA][Oletate] (a) and [TEA][Stearate] (b).

^{1}H NMR δ(ppm) of [TEA][Oletate]:

0.880-0.912 (*t*, *J* = 5 Hz, 3H, CH_3^h); 1.301-1.241 (*t*, *J* = 5 Hz, 2H, CH_2^i); 1.32-1.87 (*m*, 2H, CH_2^f); 1.4 (*m*, 3H, CH_3^c) ;1.62-1.67 (*m* , 2H, CH_2^e); 2.010-2.076 (*s*, 2H CH_2^g); 2.776-2.96 (*s*, CH_2^d, 2H); 3.095-3.12 (m, 2H, CH_2^b); 5.30-5.36(m, 1H, CH^h) 9.48(m, 1H, NH^a).

^{1}H NMR δ(ppm) of [TEA][Stearate]:

0,86 (*t*, *J* = 5 Hz, 3H, CH_3^h); 1.20 (*t*, *J* = 5 Hz, 2H, CH_2^g); 1.27 (*m*, 2H, CH_2^f); 1.33 (*m*, 3H, CH_3^c); 1.52 (*m* , 2H, CH_2^e); 2.25 (*s*, 2H CH_2^d); 3.14 (*s*, CH_2^b, 2H); 9.12-9.62 (m, 1H, NH^a).

From the results of FT-IR and NMR spectra, two ionic liquids were successfuly synthesized.

Influence of factors on synthesis of [TEA][Oletate] and [TEA][Stearate]

Synthesis of ILs using different solvents

Two ionic liquids were formed by the exchange reactions (3), therefore, these reactions need to be conducted: i) in water which can dissolve the KCl co-product while the water-insoluble ionic liquid separates into a separate layer.; ii) in ethanol which can dissolve the ionic liquid products and does not dissolve the co-product KCl (forming precipitation). In both cases, ethyl acetate is used to purify the ionic liquids. The synthesis efficiency of ionic liquids using different solvents is presented in Table 1. Firstly, water was used as solvent in order to reduce the ost but the ionic liquid efficiency was rather low.

Table 1. IL synthesis efficiency in different solvents (molar ratio [RCOOH]/[TEA]= 1.3[*] (to shift the ; 6 h for [TEA][oleate] and 7 h for [TEA][Stearate])

Ionic liquids	Solvents	Yield (wt %)
[TEA][Oletate]	Water	42.5
	Ethanol	93.3
	Acetone	86.3 [9]
[TEA][Stearate]	Water	45.5
	Ethanol	90.5
	Acetone	83.5 [9]

[*] To shift the equilibrium toward ionic liquids, it is necessary to use an eccess amount of one of the reactants. Because the ionic liquid yield increased with the growth of [TEA]:[RCOOH] molar ratio up to 1.3 and then kept stable, therefore, that ratio of 1.3 was choosen.

The yields of [TEA][Oletate] and [TEA][Stearate] were 42.5% and 45.5% (Tab. 1). This can be due to the ionic liquids [TEA][Oletate] and [TEA][Stearate] are partially soluble in water which reduce the yield of obtained ionic liquids.

The equilibrium shifts toward reversed direction. When ethanol was used as solvent a fairly high ionic liquid yield were obtained. The yields of [TEA][Oletate] and [TEA][Stearate] were 93.5% and 90.3%

This can be explained that KCl does not dissolves in ethanol and equilibrium were shifted forward to creating ionic liquid. A quite large amount of ethanol was used but it can be recovered by distilled off. In our previous work, the 2th and 3th steps of IL synthesis process are performed in 2 pots and acetone was used as solvent for the 3th step [9]. However, two starting materials don't dissolve completely in acetone, therefore, the yield is lower than using ethanol solvent in this work. Therefore, the solvent ethanol was used during synthesis processes these ionic liquids.

Influence of reaction temperature on IL synthesis performance

Preliminary investigations show that the synthesis of ionic liquid [TEA][oleate] can be performed at lower temperatures than [TEA][Stearate]. The experimental series using the same [RCOOH]/[TEA] molar ratio of 1:1.3; at different temperatures in 6 h with [TEA][Stearate] and in 7 h with [TEA][Stearate]. The results are given in Fig 2.

When the [RCOOH]/[TEA] molar ratio is fixed, the [TEA][Oleate] synthesis yield increases rapidly from 65.1% to about 93.3% with increasing the temperature from 35°C to 45°C and continues to increase more slowly to a temperature of 55°C. [TEA][Oleate] synthesis efficiency decreases when the temperature slightly increases from 55°C to 65°C. [TEA][Stearate] synthesis efficiency increases rapidly from 61.3% to 90.5% with increasing the temperature from 35°C to 55°C and when temperature continues to increase to a of 65°C the efficiency is constant.

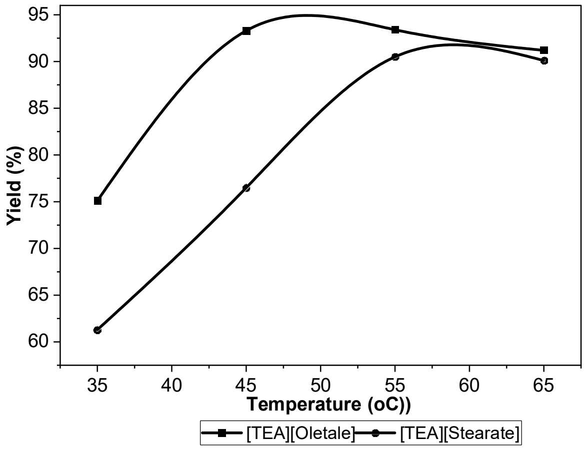

Figure 2. Influence of reaction temperature on the synthesis efficiency of [TEA][oleate] and [TEA][Stearate] (molar ratio [RCOOH]/[TEA]= 1.3; 6 h for [TEA][oleate] and 7 h for [TEA][Stearate]).

The reaction of sodium stearate with triethyl ammonium chloride requires a higher temperature than reaction of sodium oleate with triethyl ammonium chloride does because both stearate ionic liquid and sodium stearate have higher melting temperatures than [TEA][oletate] and sodium oleate, therefore, at the same temperature they have lower viscosity and mobility than corresponding compounds of oleic acid [11]. The suitable temperatures for synthesizing [TEA][oleate] and [TEA][Stearate] are 45°C and 55°C, respectively.

Influence of reaction time on IL synthesis performance

Synthesis of ionic liquids [TEA][Oletate] and [TEA][Stearate] were carried out at temperatures of 45 °C and 55 °C, respectively with the molar ratio of [RCOOH] to [TEA] is 1.3 and at different time intervals from 4 hours to 8 hours.

The results are presented in Fig. 3. The results showed that when increasing the reaction time from 4 hours to 6 hours, the [TEA][Oletate] yield rapidly increases from 66.1% to 93.3%. However, when increasing the reaction time from 6 to 8 hours, the reaction efficiency insignificantly increases from 93.3% to 93.9%. Similarly, the [TEA][Stearate] synthesis efficiency increased rapidly from 52.3% to 90.5% with increasing the time from 4 hours to 8 hours and then doesn't change with increasing the reaction time to 9 h.

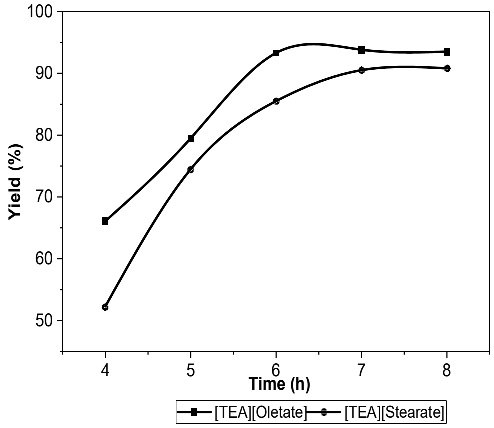

Figure 3. Influence of reaction time on the synthesis yield of [TEA][Oletate] and [TEA][Stearate] (with molar ratio [RCOOH]/[TEA]= 1.3; temperature 45 °C with [TEA][Oletate] and 55°C with [TEA][Stearate])

It can be seen that the reaction time for the synthesis of ionic liquid [TEA][Oletate] is lower than that of [TEA][Stearate]. This can be due to the presence of a double bond in oleic acid which results in the decrease in viscosity and mobility of the ionic liquid and, therefore, reaction time is reduced. Specifically, to obtain the same synthesis efficiency of over 90% [TEA][Oletate] needs 6 hours while [TEA][Stearate] needs more time, 7 hours.

This is explained that the higher the viscosity, the slower the reactants move, so that the collision between reaction centers on the substances is reduced. The time required to synthesize [TEA][Stearate] is 6 hours and [TEA][Stearate] is 7 hours.

Influence of [RCOOH]/[TEA] molar ratio on IL synthesis performance

TEA][oleate] was synthesized at 45°C in 6h and [TEA][Stearate] was conducted at 55°C in 7 h. Reactions were carried out with different [RCOOH]/[TEA] molar ratios of 1.1; 1.2; 1.3; 1.4. The results are presented in Fig. 4.

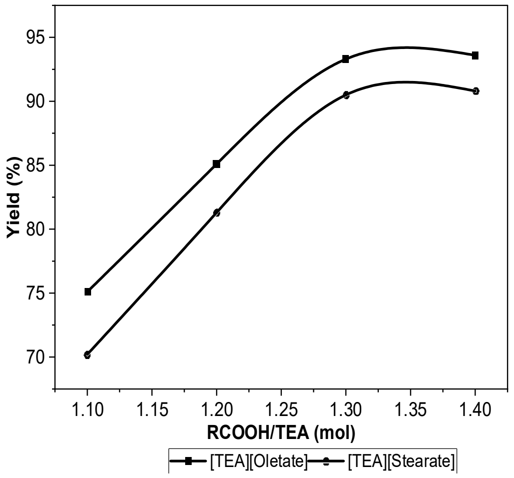

Figure 4. Influence of [RCOOH]/[TEA] molar ratio on IL synthesis performance

The obtained results show that at the molar ratio [RCOOH]/[TEA] of 1.3, the yields of [TEA][oleate] and [TEA][Stearate] reaches the high values of 93.3 % and of 90.5 %, respectively. When the [RCOOH]/[TEA] molar ratio increasing from 1.3 to 1.4, the performance does not increase significantly. This can be explained as to shift the equilibrium, it is necessary to use an excess amount of one of reactants. Here the excess amount of RCOOH was chosen because this component is cheaper and more environmentally safe. So the suitable [TEA]:[RCOOH] molar ratio of is 1.3.

Table 2. Optimal conditions for the synthesis of [TEA][oleate] and [TEA][Stearate]

No	Parameters	Ionic liquids	
		[TEA] [Oletate]	[TEA] [Stearate]
1	Solvent	Ethanol	Ethanol
2	Temperature (°C)	45	55
3	Time (h)	6	7
4	[RCOOH]/[TEA] ratio (mol)	1.3	1.3
	Yield (%)	93.3	90.5

From the above results, the optimal conditions for synthesizing the two ionic liquids [TEA][oleate] and [TEA][Stearate] can be summarized in Tab. 2.

4. Conclusion

In this research, two ionic liquids, [TEA][Oleate] and [TEA][Stearate], were prepared by 3 reactions in one pot, which can save time and cost. In addition, to shift the equilibrium toward ionic liquid products, two methods were used are using an excess amount of fatty acids (molar ratio [RCOOH]/[TEA]= 1.3) and using ethanol solvent that dissolves ionic liquid but does not dissolve co-product KCl. The suitable reaction time and temperature are 6h and 45 °C with [TEA][Oletate] and 6h and 45 °C with [TEA][Stearate]. These results can be used as a reference for the synthesis of other ionic liquids, especially for the synthesis of fatty acids of vegetable oil based-IL.

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