



Investigation of synthesis of some ionic liquids from nitrogen compounds and fatty acids of waste oils

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ABSTRACT

In order to reduce the environmental pollution and the dependence on fossil fuel resource which is depleting, the utilization of waste vegetable oils (WO) for preparation of valuable products are of concern. Four ionic liquids triethyl ammonium carboxylate ([TEA][WO]), octyl ammonium carboxylate ([Oca][WO]), trialkyl methyl ammonium carboxylate ([Aliquat][WO]) and n-octyl methyl imidazolium carboxylate ([OMIM][WO]) were synthesized from four different nitrogen compounds and fatty acids of waste vegetable oils. The influence of some parameters such as solvent, reaction temperature, reaction time and molar ratio of acid and nitrogen compound (NC) on ionic liquid synthesis yields was investigated. The results show that the structure of nitrogen compounds effects on the synthesis performance and governs the parameters of processes. This is due to the nitrogen compounds as starting materials control not only their activity in reaction with fatty acids but also the solubility and the melting points of corresponding ionic liquids. Certain suitable conditions were chosen for each ionic liquid.

1. Introduction

The amount of waste vegetable oil generated in each country is significant and varies depending on the use of vegetable oils. Managing waste vegetable oils is a major challenge due to of potential soil and water pollution. Every year, hundreds millions of tons of waste vegetable oil are collected and utilized for various purposes worldwide. It is estimated that about 0.7 – 1 million tons of waste vegetable oil are collected in Europe annually, with around 200 thousand tons generated in the UK, of which about

80 thousand tons are collected for the production of biodiesel. Restaurants, hotels, and fast-food chains in the US generate approximately 10 million tons of waste vegetable oil annually [1]. According to Chhetri et al. [2], approximately 135 thousand tons of waste vegetable oil are generated in Canada annually, while Turkey produces over 350 thousand tons. According to the Food and Agriculture Organization (FAO), China accounts for about 80 million tons of waste vegetable oil. In Vietnam, If all the discharged vegetable oil is collected, its amounts are counted to 200 thousand tons/year.

In addition to harming human health, discharging directly waste vegetable oil into the environment also causes water sources, soil, and air pollution. Meanwhile, composition of waste vegetable oil is similar to that of vegetable oil and is highly suitable for using as a feedstock for production of biofuel and additives for vegetable-based lubricants.

Ionic liquids are a group of substances with many unique physicochemical properties that are applied in various fields [3-6]. Some ionic liquids showed high efficiency as lubricants and lubricating additives and [7-9]. However, most of used ionic liquids composed of tetraborate, hexafluorophosphate, diethyl phosphate... anions which are high cost and environmental pollution. Fatty acids based ionic liquids are high compatibility with lubricants deriving from vegetable oils and can be used as additives for vegetable oil based lubricants. In this study, aiming to reduce costs and create ionic liquids capable of compatible with vegetable oil-based lubricants, four vegetable fatty acid based-ionic liquids triethyl ammonium carboxylate, octyl ammonium carboxylate, trialkyl methyl ammonium carboxylate and n-octyl methyl imidazolium carboxylate were synthesized under different parameters to find the optimal conditions. To find the influence of NC structure on the IL synthesis yield and properties, the selected nitrogen compounds containing different number of alkyl groups with different long carbon chains.

2. Experimental

Materials

Triethyl amine, HCl, ethyl acetate, octylamine, aliquat, 1-methyl imidazolium and 1-Chlorooctane were supplied by Merck company; KOH and ethanol was purchased from Guangdong Guanghua, China, RCOOK (salt of fatty acids of waste vegetable oils) separated from waste cooking vegetable oils in our laboratory as briefly described following: mixture of waste vegetable oil and solution of 5M KOH in ethanol was stirred at 70°C in one hour. Ethanol was evaporated and RCOOK was filtered and rinsed with water.

Influence of solvents on ionic liquid synthesis

Synthesis of [TEA][WO]

- Synthesis of triethylammonium chloride

30.3 g (0.3 mol) 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 into the flask for 2 h. During the addition, the suspension's temperature was kept below 0–5 °C. Once added, the temperature was increased to 50 °C and the suspension was stirred for 2 h at this temperature. The reaction mixture was evaporated for removing any water and unreacted HCl to get a white waxy product.

- Synthesis of [TEA][WO] using RCOOK (from fatty acids waste vegetable oils) and triethyl ammonium chloride

Water solvent: 7.4 g of RCOOK (~0.0231 mol) (from waste vegetable oil) was dispersed in 17 mL of water in a 250 mL flask by stirring for 2 h at room temperature to obtain a homogeneous mixture. Then 2.4373 g of $C_2H_5)_3NHCl$ (0.0177 mol) was added to the RCOOK mixture. The reaction mixture was stirred for 7 h at 55°C. The mixture was then transferred to a 250 mL extraction funnel. The organic phase (upper) was separated and washed six times, each time with 20 mL of distilled water to remove sodium chloride and unreacted RCOOK.

Ethanol solvent: 7.4g of RCOOK (~0.0231 mol) (from waste vegetable oil) was dissolved in 70 mL of ethanol in a 250 mL flask by stirring for 2 h at room temperature to obtain a homogeneous mixture. 2.4373 g $C_2H_5)_3NHCl$ (0.0177 mol) was added to the RCOOK mixture. The reaction mixture was stirred 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 containing 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.

Synthesis of octyl ammonium carboxylate [Oca][WO] from fatty acid of waste vegetable oil

- Synthesis of octyl ammonium chloride

38.7 g of (0.3 mol) octyl 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. 34g of 36-38% HCl solution was slowly dropped for 2 h. During the addition, suspension's temperature was kept below 0–5 °C. Once added, the temperature was increased to 70 °C and the suspension was stirred for 2 at this temperature. The reaction mixture was concentrated to remove excess water and nreacted HCl to get white waxy product.

- Synthesis of [Oca][WO] using RCOOK (from fatty acids of waste vegetable oils) and octyl ammonium chloride

This step was performed in water or in ethanol solvent using the similar methods to that of [TEA][WO].

Synthesis of [Aliquat][WO]

The ionic liquid [Aliquat][WO] was synthesized from Aliquat (a mixture of trioctylmethyl ammonium chloride and tridecylmethyl ammonium chloride) and the potassium salt of fatty acid of waste vegetable oil using the similar methods to that of [TEA][WO].

Synthesis of [OMIM][WO]

Ionic liquid [OMIM][WO] is synthesized from octyl methyl imidazolium chloride ($[C_{12}H_{25}N_2]Cl$, [OMIM]Cl) and the potassium salt of fatty acids from waste vegetable oils.

Synthesis of [OMIM]Cl

0.5 mol of methyl imidazole was added to a 2-neck flask equipped with a stirrer and a reflux condenser, then was heated to 75°C. 0.5 mol of 1-chlorooctane $C_8H_{17}Cl$ was added dropwise to the flask over 1 h. The mixture was continued stirred and heated at 75°C for 100 h, resulting in a light red and viscous solution. 50 mL of ethyl acetate was used to extract and remove any unreacted substances in the solution (procedure: the reaction mixture and ethyl acetate are added to a separatory funnel, shaken, and then allowed to phase separation, followed by separation of the lower IL layer). The purification was repeated 3 times to remove almost all unreacted methyl imidazole and $C_8H_{17}Cl$. The bottom layer was heated to 80°C under reduced atmosphere until the mass of the solution remains unchanged to completely evaporate the ethyl acetate and obtain [OMIM]Cl. Obtained ionic liquid is weighed to evaluate the reaction yield.

Synthesis of IL [OMIM][WO] from [OMIM]Cl

This step was performed in water or in ethanol solvent using the similar way to that of [TEA][WO]

Influence of reaction temperature, time and molar ratio of acid to nitrogen compound

Experiments for synthesis of ionic liquid [TEA][WO] were conducted at temperatures of 30°C, 40°C, 50°C, and 60°C, while the ionic liquids [Oca][WO], [Aliquat][WO], and [OMIM][WO] were synthesized at temperatures ranging from 55°C to 95°C.

All four ILs were synthesized over time periods ranging from 5.5 hours to 8 hours and with molar ratios of [RCOOH]:[NC] of 1.1; 1:2; 1:3; and 1:4.

Ionic liquid synthesis yield was determined by formula:

$$Y (\%) = \frac{m_{IL(eq)}}{m_{IL(ex)}} \times 100\%$$

Where: $m_{IL(eq)}$: weight of IL calculated from equation;

$m_{IL(ex)}$: weight of ionic liquid obtained from experiment.

Characterization

FT-IR of synthesized ionic liquids were measured by FT-IR Shimadzu, IRAffinity-1S. The samples were measured using the method of a KBr pellet.

3. Results and discussion

FTIR spectroscopy

The characteristic peaks of FT-IR spectra of synthesized ionic liquids [[TEA][WO], [Oca][WO], [Aliquat][WO], and [OMIM][WO] are summarized in Table 1.

Table 1. Some typical bands of FT-IR of synthesized ionic liquids.

Wave number (cm^{-1})	[TEA][WO]	[Oca][WO]	[Aliquat][WO]	[OMIM][WO]	Functional groups
3300-3500	-	-	-	x	-N-H in aromatic ring
3147	-	-	-	x	-C-H aromatic ring
2850-2925	x	x	x	x	-C-H in alkyl
1640-1690	x	x	x	x	-C=C-
1557-1562	x	x	x	x	-COO ⁻
1542		x			N-H in aliphatic ammonium
1375-1450	x	x	x	x	C-H in -CH ₃
1465-1471	x	x	x	x	C-H in -CH ₂
1170		x	x		C-N in aliphatic ammonium
716-721	x	x	x	x	-CH ₂ - long chain

The bands at wave numbers of 2850–2925 cm^{-1} are the aliphatic asymmetric and symmetric (C-H) stretching vibrations due to methyl groups. C=C and COO⁻ stretching vibrations are shown by wave numbers 1640–1690 cm^{-1} and 1557–1562 cm^{-1} . The band at wave numbers 716–721 cm^{-1} is due to the -CH₂- stretching vibration. The bands at wave numbers 1375–1450 cm^{-1} and 1465–1471 cm^{-1} are assigned to vibrations of C-H in -CH₃ and C-H in -CH₂ groups.

The bands at 1542 cm^{-1} come from N-H in aliphatic ammonium group of [Oca][WO]. The bands at 1170 cm^{-1} are assigned for C-N linkage in aliphatic ammonium of [Aliquat][WO] and [Oca][WO]. Broad bands in the range 3300–3500 cm^{-1} comes from the quaternary amine salt formation and the bands in the range 3157–3147 cm^{-1} come from C-H in imidazolium cyclic ([OMIM][WO]).

Influence of solvents

For synthesizing all four ionic liquids [TEA][WO], [Oca][WO], [Aliquat][WO], and [OMIM][WO], the rate determining step of the overall process is the general exchange reaction as follows:



(K[WO] is RCOOK salt of fatty acids of waste vegetable oils)

To increase the conversion, it is necessary to choose a solvent that neither dissolves KCl nor the ionic liquid. Additionally, solvent needs to be easily separated from ionic liquids, especially when the solvent dissolves the ionic liquid. Ethanol, which can dissolve the product ionic liquids but does not dissolve the co-product KCl (forming precipitate), was chosen as a solvent candidate for the reactions. In addition, water, which can dissolve the co-product KCl but less dissolve ionic liquid, was also chosen as an other solvent candidate. In both cases, ethyl acetate is used to purify the ionic liquids after phase separation. However, the solubility of the ionic liquids in different solvents depends on the nature of the nitrogen-containing compounds and fatty acids. Therefore, in this work, four ionic liquids [TEA][WO], [Oca][WO], [Aliquat][WO], and [OMIM][WO] were synthesized in both ethanol and water mediums to find the suitable solvent for each of them. The synthesis efficiency of the ionic liquids using different solvents is presented in Table 2.

It can be seen from the results in Table 2 that when ethanol was used as solvent for synthesizing [TEA][WO] and [Oca][WO], ionic liquid yields relatively high, ranging from 82% to 84%. This is because KCl dissolves very little in ethanol and, therefore, the equilibrium shifts towards the formation of ionic liquids. The efficiency of synthesizing these two ionic liquids in water solvent doesn't higher than 84% due to their partial solubility in water.

Similarly to [TEA][WO] and [Oca][WO] ionic liquids, [OMIM][WO] partially dissolves in water then its

efficiency is lower when using water solvent compared to ethanol solvent.

Table 2. Synthesis efficiency of 4 ILs [TEA][WO], [Oca][WO], [Aliquat][WO], and [OMIM][WO] in different solvents (molar ratio [RCOOK]:[NC] = 1:3)

IL	Solvent	Tem. ($^{\circ}\text{C}$)	Time (h)	Efficiency (% kl)
[TEA]	Ethanol	50	6.5	84.86
[WO]	Water	50	6.5	40.9
[Oca]	Ethanol	78	7	82.69
[WO]	Water	80	7	40.0
[Aliquat]	Ethanol	78	7.5	64.7
[WO]	Water	85	7.5	78.1
[OMIM]	Ethanol	78	7	88.7
[WO]	Water	80	7	35.2

[Aliquat][WO] is not soluble in water, therefore, it can be synthesized in both aqueous medium and ethanol solvents. The efficiency of synthesizing [Aliquat][WO] in water (78.1%) is higher compared to [TEA][WO] and [Oca][WO] ionic liquids using the same medium. However, three long alkyl groups in starting material aliquat causes a steric hindrance during the reaction of aliquat and RCOOK. Therefore, the yields of synthesizing [Aliquat][WO] in ethanol solvents is also moderate and reaches 64.7%. However, since a significant amount of ethanol solvent need to be used, for cost reduction purposes, water solvent is more favor.

Therefore, ethanol solvent was used for synthesizing the ionic liquids [TEA][WO], [Oca][WO] and [OMIM][WO] while [Aliquat][WO] was synthesized in water solvent.

Influence of reaction temperature

Based on the survey experiments conducted and refence [10], the ionic liquid [TEA][WO] synthesis was carried out at temperatures of 30 $^{\circ}\text{C}$, 40 $^{\circ}\text{C}$, 50 $^{\circ}\text{C}$, and 60 $^{\circ}\text{C}$; and the synthesis of ionic liquids [Oca][WO], [Aliquat][WO], and [OMIM][WO] was conducted at temperatures ranging from 55 $^{\circ}\text{C}$ to 95 $^{\circ}\text{C}$. The results are depicted in Tables 3 and Figure 1a.

It can be observed from Table 3 that as the temperature increases from 30 $^{\circ}\text{C}$ to 50 $^{\circ}\text{C}$, the yield of ionic liquid rapidly increases from 65.1% to 86.3%. However, when the temperature is raised to 60 $^{\circ}\text{C}$, the efficiency significantly decreases, possibly due to the

evaporation of TEA (bp 89.28 °C), leading to a shift the equilibrium in the reverse direction.

Table 3 The influence of reaction temperature on the synthesis efficiency of IL [TEA][WO], (RCOOK):[TEA] = 1.3).

No	Time (h)	Temperature (°C)	Efficiency (%) [TEA][WO]
1	6.5	30	62.1
2	6.5	40	73.1
3	6.5	50	84.86
4	6.5	60	81.2

It can be seen from the Figure 1a that when the mole number of the reactants is fixed, the efficiency for synthesizing [OcA][WO] and [OMIM][WO] increases dramatically from 69.1% and 67.1% to 82.69% and 88.7% when the temperature rises from 55°C to 78°C. The synthesis efficiency of [OMIM][WO] increases more slowly when the temperature is increased to 85°C and 95°C. For [OcA][WO], when the temperature is further increased to 85°C, the efficiency decreases slightly, and it decreases significantly when temperature raised to 95°C. Compared to other ionic liquids, [Aliquat][WO] requires higher temperatures for implementation due to the presence of three octyl (decyl) groups and one methyl group in Aliquat, leading to higher viscosity and larger spatial hindrance compared to other reactants. Specifically, the maximum efficiency for synthesizing [Aliquat][WO] achieved at 85°C. Therefore, the suitable temperatures for synthesizing [TEA][WO] is 50°C, [Aliquat][WO] is 85°C, while [OcA][WO] and [OMIM][WO] are 78°C.

Influence of reaction time

The experiments of synthesis of the ionic liquids [TEA][WO] were conducted at 50°C, [OcA][WO] and [OMIM][WO] at 78°C, while [Aliquat][WO] was performed at 85°C, with the molar ratio [RCOOK] to [NC] of 1.3, and at various time intervals ranging from 5.5 h to 8 h.

The results presented in Figure 1b show that as the reaction time increases from 5.5 h to 6.5 h, the efficiency of [TEA][WO] significantly rises from 56.2% to 84.86%. However, when the reaction time is extended from 6.5 h to 8 h, the reaction efficiency increases only slightly from 84.86% to 85.7%. Similarly, the synthesis efficiency of [OcA][WO] and [OMIM][WO] also increases rapidly from 66.4% and

65.2% to 82.69% and 88.7%, respectively, when the reaction time is extended from 5.5 h to 7 h, after that the synthesis efficiency stabilizes. For [Aliquat][CO], a longer reaction time is required, with the highest efficiency achieved after 7.5 h.

Investigation of the reactant molar ratio

The synthesis of [TEA][WO] was carried out at 50°C, [Aliquat][WO] at 85°C, and [OcA][WO] and [OMIM][WO] at 78°C with reaction times ranging from 6.5 h to 7 h for [TEA][WO], [OcA][WO], and [OMIM][WO] and 7.5 h for [Aliquat][WO]. The reactions were conducted with different reactant molar ratios [RCOOH]:[NC] of 1.2, 1.3, and 1.4. The results are given in Figure 1c.

The results showed that efficiency of ionic liquids synthesis increased with increasing the molar ratio of [RCOOH] to [NC] from 1.1 to 1.3. The highest efficiency of ionic liquids synthesis was observed when the molar ratio of [RCOOH] to [NC] of 1.3, reached 84.86%, 8.69%, 78.1% và 88.7% for [TEA][WO], [OcA][WO], and [OMIM][WO], respectively. These results are consistent with those in previous investigations [10]. Increasing the molar ratio to 1.4 does not significantly enhance the efficiency. This can be explained by the necessity of using excess of one of the reactants to shift the equilibrium. Here, an excess of RCOOH was chosen due to its lower cost and more environmental safety. Thus, the optimal reactant molar ratio for the reaction [RCOOH]:[NC] of 1.3, satisfies one of the principles of green chemistry, minimizing environmental pollution.

Based on the above results, the optimal conditions for synthesizing the 4 ionic liquids [TEA][WO], [OcA][WO], [Aliquat][WO], and [OMIM][WO] are summarized in Table 4.

Table 4. Optimal conditions for synthesizing [TEA][WO], [OcA][WO], [Aliquat][WO], and [OMIM][WO].

Parameter	Optimal conditions			
	[TEA][WO]	[OcA][WO]	[Aliquat][WO]	[OMIM][WO]
Solvent	Ethanol	Ethanol	Water	Ethanol
T (°C)	55	78	85	78
Time (h)	6	7	8	7
[RCOOH]/[NC] (mol)	1.3	1.3	1.3	1.3

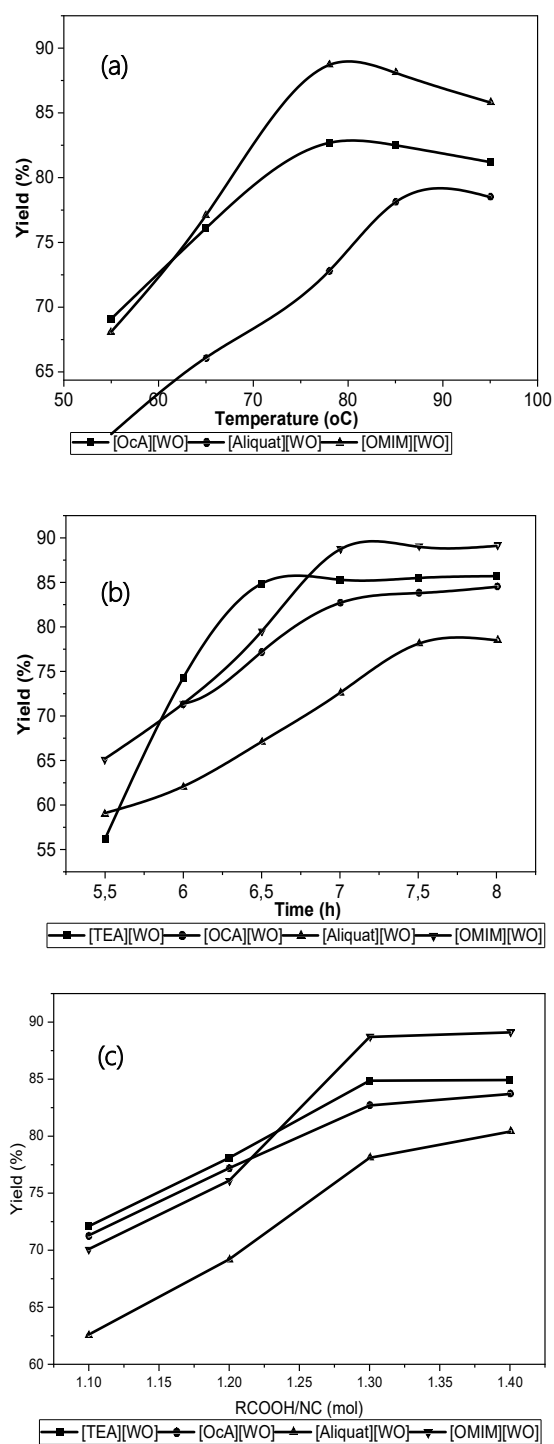


Figure 1. Synthesis efficiency of IL [OcA][WO], [Aliquat][WO], and [OMIM][WO] in different solvents; (a) Influence of reaction temperature (molar ratio RCOOK:[NC] = 1.3; reaction times [OcA][CO] and [OMIM][CO] are 7 hours, [Aliquat][CO] is 8 hours); (b) Influence of reaction time (molar ratio [RCOOK]:[NC] = 1.3; Reaction temperature for [TEA][WO] is 50°C, for [Aliquat][WO] is 85°C, and for [OcA][WO] and [OMIM][WO] is 78°C); (c) Influence of reactant molar ratio ([TEA][CO] at 55°C, [Aliquat][CO] at 90°C, and [OcA][CO] and [OMIM][CO] at 78°C).

Conclusion

The cationic structure of ionic liquids profoundly affects their reactivity and, therefore, controls the reaction conditions of synthesis of 4 ionic liquids [TEA][WO], [OcA][WO], [Aliquat][WO] and [OMIM][WO]. Based on obtained results [Aliquat][WO] should be synthesized in water medium while [TEA][WO], [OcA][WO] and [OMIM][WO] in ethanol solvent to give higher yields. [Aliquat][WO] needs longer time and higher reaction temperature while [TEA][WO] requires shorter time and lower reaction temperature than others. An excess amount of carboxylic acids should be used to shift the equilibrium and to increase the synthesis yield of ionic liquids. Bulky carbon chains in nitrogen-containing compounds increase steric hindrance, making the reaction more difficult and requiring to be carried out at higher temperatures for longer periods of time. Optimal conditions for synthesizing ionic liquids are presented in Table 4. In future works the possibility of using these ionic liquids as lubricant additives will be investigated.

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