Reactivity of Brönsted acid ionic liquids as dual solvent and catalyst for Fischer esterifications

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Abstract−Several water-stable ionic liquids with different acidity and affinity were synthesized and applied as both solvents and acid catalysts for Fischer esterification of ethanol reacting with four aliphatic carboxylic acids (acetic acid, n-hexanoic acid, lauric acid, and stearic acid). Among the studied ionic liquids, [(n-bu-SO$_3$H) MIM][HSO$_4$] (3-butyl-1-(butyl-4-sulfonyl) imidazolium sulfate) and [(n-bu-SO$_3$H) MIM][p-TSO] (3-butyl-1-(butyl-4-sulfonyl) imidazolium toluenesulfonate) show higher reactivity for the production of ethyl esters. The catalytic activities of these ionic liquids are strongly dependent on the acidity of their anions and cations, as well as their hydrophilicity and affinity with the reactants. Water refluxing through the condenser may be another important reason for obtaining high conversion of esterification, indicating a water-sequester process is still needed in order to obtain a higher yield of ester in the ionic liquid catalyzed esterification system. Kinetics studies show the conversions of the acids increase with reaction temperature and time, and reach equilibrium within about two hours. The apparent activation energies are 39.1±2.0, 49.7± 2.5, 51.4±2.5 and 59.3±3.0 kJ·mol^{-1} for the formation of ethyl acetate, ethyl n-hexanoate, ethyl laurate and ethyl stearate, respectively.

Key words: Brönsted Acid Catalyst, Ionic Liquid, Fischer Esterification, Reaction Kinetics, Water Content

INTRODUCTION

Carboxylic acid esters are important intermediates for synthesis of dopes, adhesives, plasticizers, flavors, and pharmaceuticals. They are typically produced by Fischer esterification of carboxylic acids and alcohols [1-3]. The Fischer esterification reactions are usually catalyzed by bio-enzymes or acids including inorganic liquid acids (such as hydrochloric acid and sulfuric acid) and solid acids [2,4,5]. As we know, inorganic acids can cause equipment corrosion and bring serious environmental pollution. Solid acids have the disadvantages of less active sites, requiring extended reaction time, having low thermal stability and rapid deactivation from coking. Bio-enzymes are generally expensive for commercial use and difficult to recycle without activity loss. As an alternative, Brönsted acidic ionic liquid (IL) is becoming a popular choice of both solvent and catalyst for the Fischer esterifications and the other acid-catalyzed reactions [6-9]. This is because the Brönsted acidic ionic liquids have many unique properties including tunable acidity from different acid functional groups, low melting point, negligible vapor pressure, good solubility for most organic and inorganic compounds, and high thermal stability.

Deng's group reported the esterification of carboxylic acids with alcohols in acidic chloroaluminate ionic liquids [10]. Zhu et al. [11] used 1-methylimidazolium tetrafluoroborate as a catalyst for the esterification of carboxylic acids with alcohols and obtained a good yield and an easy post-separation process. However, these ionic liquids contain halogen atoms, which are poisonous when decomposed under certain reaction conditions [12]. As an improvement, some

greener ionic liquids that are free of halogen and relatively hydrolysis-stable have been synthesized by incorporating quaternary phosphonium cations and octyl sulfonate anion [13-16]. The emergence of the Brönsted acidic ionic liquids that bear an alkyl sulfonic acid group in an imidazole or triphenylphosphine cation [17-19] makes it possible to synthesize an ionic liquid having the acidity as high as that of sulfuric acid. In recent years, some new types of Brönsted acidic ionic liquids including pyridinium [20-22], alkyl ammonium [23-26] and alkyl pyrolidonium [27] derivatives have also been applied to catalyze the Fischer esterification reactions, and exhibited good catalytic performance, which are summarized in Table 1.

Although many kinds of ionic liquids have been used to catalyze the Fischer esterification reactions, it is still unknown which ionic liquid has the highest reactivity for these reactions. More importantly, the reaction mechanism and process parameters affecting the catalytic activity of ionic liquids are not well understood. The object of this research is to differentiate the reactivity of different ionic liquids for esterification reactions, and to elucidate the reaction mechanism and process parameter affecting the catalyst activity. For this purpose, five ionic liquids with different acidities and hydrophilicities are prepared for the esterification of aliphatic acids with ethanol. The effects of acidity and solubility (hydrophilicity) of ionic liquid, the length of carbon chains of carboxylic acids, and the water content in the reaction system on the yield of esters will be discussed. In addition, the apparent kinetic parameters will be estimated based on a simplified second-order reaction kinetic model.
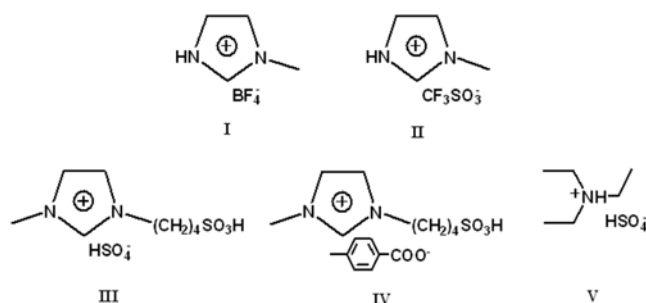
EXPERIMENTAL

1. Materials

N-methyl imidazole and 1,4-butane sulfonate were purchased

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Table 1. Fischer esterification reactions catalyzed by ionic liquids from the literature

Ref.	Type of IL	Mole ratio of acid : alcohol : IL	Reaction temperature (K)	Reaction time (h)	Conversion (%)	Selectivity (%)	Recycle times	Phase separation
[27]	[NMP]CH₃SO₃[c]	0.1 : 0.1 : 0.025 (mmol)	r.t.- 373	1-10	84-96	100	6	Yes
[23]	Quaternary ammonium salts with single substitution of alkane sulfonic acid	(1-1.3) : (1-2.5) : 1	r.t.-383	1.5-3	88.2-95.2	98.8-99.8	6	Yes
[24]	Sulfonic acid substitution imidazolium salt[a]	15 : 45 : 10 (mmol)	363, 393	2.5-4	57-99	51-100[b]	2	Not mentioned
[25]	Triethylammonium satls	(10-24) mmol : (20-24) mmol : (1-3) g	363, 393	4	56-99	-	3	Yes
[26]	Alkylammonium salts	20 mmol : 24 mmol : 1 g	363	4	18-94	-	-	Yes
[17,19]	[(n-bu-SO₃H)BIM]CF₃SO₃ and [Ph₃(n-pr-SO₃H)P][p-TSO][c]	17.5 : 17.5 : 4 (mmol) 0.38 : 0.38 : 1.9 (mmol)	295-448	45 min, 48 h	82, 96	-	4-5	Yes
[20]	N-propanesulfonic acid pyridinium	1 : (1-3) : 1	351-388	2-12	69.7-96.0	-	4	Yes
[22]	Pyridinium salts	(10, 12) mmol : (10, 12) mmol : (0.5, 1) g	363	4	68-87	98-100	2	Yes
[39]	Imidazolium and pyridinium sulfonic salts	1 : (1, 1.5) : 0.1	288-298	3-4	7.6-98.4 (yield)	-	3	Yes

[a]Esterification of olefins with alcohols or carboxylic acids

[b]Selectivity of main esterification products

[c]Abbreviations: [NMP]CH₃SO₃: N-methyl-2-pyrrolidonium methylsulfonate; [(n-bu-SO₃H)BIM]CF₃SO₃; 3-butyl-1-(butyl-4-sulfonyl) imidazolium trifluoromethane sulfonate; [Ph₃(n-pr-SO₃H)P][p-TSO]: triphenyl (propyl-3-sulphonyl) phosphonium toluenesulfonate

Fig. 1. Structures of the five ionic liquids catalysts to be investigated.

from Acros Organics (USA). 1,3-propane sulfonate was purchased from TCI Chemical Co. (Japan). All the other reactants and solvents were analytic reagent grade and used as received unless otherwise stated.

1-Butyl-imidazolium tetrafluoroborate ([BHIM]BF₄) (Catalyst I, Fig. 1) and 1-butyl-imidazolium trifluoromethanesulfonate ([BHIM] CF₃SO₃) (Catalyst II, Fig. 1) were provided by Hangzhou Chemer Chemical CO. LTD. The purity of these two ionic liquids is higher than 99%, which was confirmed by analysis data from FT-IR (Bruker Equinox 55, KBr) and NMR (Bruker Advance 500, CDCl₃, TMS). The other three ionic liquids [(n-bu-SO₃H)MIM][HSO₄] (Catalyst III, Fig. 1), [(n-bu-SO₃H)MIM][p-TSO] (Catalyst IV, Fig. 1) and [(CH₃CH₂)₃NH][HSO₄] (Catalyst V, Fig. 1) were synthesized according to our previous work [28,29] and literatures [17,30]. The resid-

ual water contents of all the five ionic liquids were determined by Karl Fischer Titrator (ZKF-1) to be less than 2%.

The physical and chemical properties of the five catalysts to be investigated are summarized in Table 2.

2. Fischer Esterification Reaction Experiments

The Fischer esterification reaction was carried out in a 25 ml three-neck flask equipped with magnetic agitation, a reflux condenser and a thermometer. The outlet of the reflux condenser was connected to a dry nitrogen gas at a constant pressure, and the reaction temperature was controlled by placing the flask in an oil bath at controlled temperatures.

Besides ionic liquids, sulfuric acid was also used in the esterification for comparison. In a typical esterification reaction entry, a 10 mmol of catalyst (ionic liquid or H₂SO₄) was first added into the glass reactor, then heated to the reaction temperature and that lasted 2 hrs to further remove the water. 20 mmol of the carboxylic acid (or 10 mmol of stearic acid) and 40 mmol of ethanol were added to initiate the reaction and that lasted another 6 hrs. When a reaction was finished, the reactor was cooled to room temperature and the reaction solution settled into two layers. A sample was taken from the top layer for analysis of esters and carboxylic acids by gas chromatography (HP5890, 25 m×0.32 mm capillary column of HP-FFAP, FID detector) based on the standard method [31]. The remaining mixture was extracted with diethyl ether for 4 times to recycle the ionic liquid. For the kinetics experiment, the amount of catalyst and reactants increased while the mole ratio was fixed. Samples were taken during the reaction experiments and analyzed by using the same method as described above.
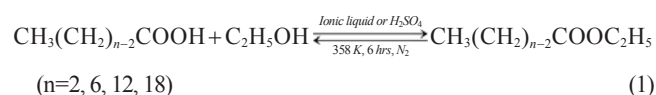
Table 2. Physical and chemical properties of the five ionic liquids catalysts to be investigated

Ionic liquid	[BHIM]BF$_4$	[BHIM]CF$_3$SO$_3$	[(n-bu-SO$_3$H)MIM][HSO$_4$]	[(n-bu-SO$_3$H)MIM][p-TSO]	[(CH$_3$CH$_2$)$_3$NH][HSO$_4$]
Code	I	II	III	IV	V
H-NMR (Bruker advance DMX-500 spectrometer at 500 MHz)	-	-	(500MHz, DMSO-d$_6$, TMS): δ9.16 (s, 1H), 7.78 (s,1H), 7.71 (s, 1H), 6.28 (s, 2H), 4.19 (t, 2H, J=7.0 Hz), 3.86 (s, 3H), 2.57 (t, 2H, J=7.7 Hz), 1.89 (m, 2H), 1.56 (m, 2H)	(500 MHz, D$_2$O, TMS): δ8.46 (s, 1H), 7.49 (d, 2H, J=8.0 Hz), 7.26 (s, 1H), 7.21 (s, 1H), 7.16 (d, 2H, J=8.0 Hz), 4.70 (s, 1H), 4.01 (t, 2H, J=7.0 Hz), 3.67 (s, 3H), 2.74 (t, 2H, J=7.7 Hz), 2.19 (s, 3H), 1.78 (m, 2H), 1.54 (m, 2H)	(500 MHZ, CD$_3$OD, TMS): δ1.24 (t, J=7 Hz, 9H, CH$_3$), 3.13 (q, J=7 Hz, CH$_2$), 5.18 (s, NH)
FT-IR (Nicolet NEXUS 670 F7-IR)	-	-	3,416 cm^{-1} (O-H), 3,157 cm^{-1} (unsaturated C-H), 2,960 cm^{-1} (saturated C-H), 1,655 cm^{-1} (S=O), 1,576 cm^{-1} (C=N), 1,459 cm^{-1} (C=C), 1,171 cm^{-1} (C-N), 1,040 cm^{-1} (C-C)	3,399 cm^{-1} (O-H), 3,153 cm^{-1} (unsaturated C-H), 2,956 cm^{-1} (saturated C-H), 1,719 cm^{-1} (S=O), 1,574 cm^{-1} (C=N), 1,458 cm^{-1}, (C=C at imidazole ring), 1,235 cm^{-1} (C=C at benzene ring), 1,187 cm^{-1} (C-N), 1,034, 1,009 cm^{-1} (C-C)	-
ESI-MS of positive-ion (m/z) agilent 1100 series LC/MSD trap SL	-	-	219.0, 437.0	219.0, 437.0	-
Acidity	Weak Lewis acid	Weak lewis acid	Strong Brönsted acid with two acidic groups	Strong Brönsted acid with one acidic group	Middle strong Brönsted acid with one acidic group
Water content	<0.5%	<0.5%	<2%	<2%	<2%
Water miscibility	Not miscible	Not miscible	Miscible	Miscible	Miscible
Other properties	-	-	About 80% of total yield	About 80% of total yield	(1) m.p. 364-365 K (literatures 364 K[30], 356-358 K[26]) (2) yield: 83%

RESULTS AND DISCUSSION

1. Esterification Catalyzed by Ionic Liquids

The ionic liquids used for esterification reactions in this paper can be divided into four types: (1) ionic liquids with only weak Lewis acidity and hydrophobic anions (catalysts I and II in Table 2); (2) Brönsted ionic liquid with dual acidic function groups and a hydrophilic anion (catalyst III in Table 2); (3) Brönsted ionic liquid with hydrophobic anion (catalyst IV); and (4) Brönsted ionic liquid with a hydrophilic and acidic anion (catalyst V). Four aliphatic carboxylic acids, i.e., acetic acid, n-hexanoic acid, lauric acid and stearic acid, were applied to react with ethanol using IL or sulfuric acid as catalyst, which can be expressed as:

$$CH_3(CH_2)_{n-2}COOH + C_2H_5OH \underset{358\,K,\,6\,hrs,\,N_2}{\overset{Ionic\ liquid\ or\ H_2SO_4}{\rightleftharpoons}} CH_3(CH_2)_{n-2}COOC_2H_5$$

$$(n=2, 6, 12, 18) \tag{1}$$

The experimental results of Fischer esterification for $CH_3(CH_2)_{n-2}$ COOH reacting with ethanol are summarized in Table 3. The conversion is based on the consumption of carboxylic acid.

It can be seen from Table 3 that catalysts III and IV have the same or even better reactivity than H$_2$SO$_4$ in catalyzing those esterification reactions, and catalyst V has the same or a bit lower reactivity

than H$_2$SO$_4$. While, catalysts I and II have the poorest reactivity with the conversion of acids less than 60%. The catalytic activity order obtained in this work can be explained by the acidity order of these ionic liquids because the Fischer esterification reaction is an acid-catalyzed reaction. Both catalysts III and IV have a sulfonic group, which gives the strongest acidity among these ionic liquids, while catalyst V has an HSO$_4^-$ anion ion, which has middle acidity, leading to relatively less reactivity. Catalysts I and II have only weak Lewis acidity, so they have the lowest catalytic reactivity. It should be noted here that organic amine salt is generally not viewed as a Brönsted acid even if it has H atom(s) connected to N, although only few studies believe otherwise [27,32].

Another factor influencing the catalytic activity is the water solubility or hydrophilicity of ionic liquids. This is because the Fischer esterification is a reversible reaction in which carboxylic acid and alcohols form water and water-immiscible ester. If only ester is the water-immiscible component in the reaction system, it is easy to understand that the water miscibility of ionic liquids will improve the catalytic activity, because the product ester phase will be separated from the water miscible reaction phase, and drive the esterification reaction to completion. As we can see from experimental entries 1-12 in Table 3, while water-miscible acetic acid/n-hexanoic acid were used as reactants, catalyst II had a higher reactivity than

Table 3. Results of Fischer esterification for $CH_3(CH_2)_{n-2}COOH$ reacts with ethanol catalyzed by ionic liquids or H_2SO_4

Entry	Catalyst	n	Conversion of acid (%)	Selectivity of ester (%)
1	[BMIM][BF$_4$]	2	56	98
2	[BMIM][CF$_3$SO$_3$]	2	60	99
3	[(n-bu-SO$_3$H)MIM][HSO$_4$]	2	91	100
4	[(n-bu-SO$_3$H) MIM][p-TSO]	2	88	98
5	([(CH$_3$CH$_2$)$_3$N][HSO$_4$]	2	85	98
6	H$_2$SO$_4$	2	85	97
7	[BMIM][BF$_4$]	6	20	99
8	[BMIM][CF$_3$SO$_3$]	6	44	97
9	[(n-bu-SO$_3$H)MIM][HSO$_4$]	6	100	100
10	[(n-bu-SO$_3$H) MIM][p-TSO]	6	91	98
11	([(CH$_3$CH$_2$)$_3$N][HSO$_4$]	6	80	99
12	H$_2$SO$_4$	6	79	97
13	[BMIM][BF$_4$]	12	22	99
14	[BMIM][CF$_3$SO$_3$]	12	32	100
15	[(n-bu-SO$_3$H)MIM][HSO$_4$]	12	91	99
16	[(n-bu-SO$_3$H) MIM][p-TSO]	12	95	98
17	[(CH$_3$CH$_2$)$_3$N][HSO$_4$]	12	73	97
18	H$_2$SO$_4$	12	89	100
19	[BMIM][BF$_4$]	18	46	98
20	[BMIM][CF$_3$SO$_3$]	18	20	99
21	[(n-bu-SO$_3$H)MIM][HSO$_4$]	18	97	98
22	[(n-bu-SO$_3$H) MIM][p-TSO]	18	97	100
23	([(CH$_3$CH$_2$)$_3$N][HSO$_4$]	18	73	97
24	H$_2$SO$_4$	18	95	98

Note: reaction temperature: 358 K, time: 6 h. mole ratio of acid : alcohol : catalyst=2 : 4 : 1 in cases n=2, 6, 12. Mole ration of acid : alcohol : catalyst=1 : 4 : 1 in case n=18

that of catalyst I because [CF$_3$SO$_3$]$^-$ functional group in catalyst I is more hydrophilic than [BF$_4$]$^-$ group in catalyst II. This finding is consistent with the results reported by other research groups [20, 26] as well as our former work [28]. However, when water-immiscible acid or alcohol is used as reactant, the hydrophobic group in the ionic liquids will contribute to the miscibility between reactants and catalyst, which may increase the reactivity of the catalyst. Therefore, when n-lauric acid or n-stearic acid is used as reactant in entries 13 to 24, the reactant acids become more and more hydrophobic and water-immiscible, the catalytic reactivity tends to be the reverse: [BHIM][CF$_3$SO$_3$] (catalyst II) turns to have lower reactivity than [BHIM][BF$_4$] (catalyst I) (entries 19 vs. 20), and [(n-bu-SO$_3$H)MIM] [p-TSO] (catalyst IV) has comparable or even higher reactivity than [(n-bu-SO$_3$H)MIM][HSO$_4$] (catalyst III) since [p-TSO]$^-$ is more hydrophobic than [HSO$_4$]$^-$ (entries 15 vs. 16, 21 vs. 22), although the latter is more acidic. This phenomenon was also observed in our previous research in which catalysts III and IV were applied to catalyze the hydrolysis of isoflavone glycosides [29].

The recycling performance of [(n-bu-SO$_3$H)MIM][HSO$_4$] catalyzing the esterification of n-hexanoic acid and ethanol was checked while the initiate mole ratio of acid/alcohol/ionic liquid was 2 : 4 : 1, and reaction temperature and time were 85 ^{o}C and 6 hr, respectively.

The ionic liquid was reused four times, with the yield of ethyl n-hexanoate decreasing slightly from 100% to 95.8%, showing good recycling performance of [(n-bu-SO$_3$H)MIM][HSO$_4$].

It can be also seen from Table 3 that carboxylic acid is smoothly transformed to ester with high selectivity in all cases, and no by-products such as olefins and ethers are detected, which is in good agreement with other reports [22,27].

2. Kinetics of Esterification Reactions Catalyzed by [(n-bu-SO$_3$H)MIM][HSO$_4$]

Kinetics studies of the esterification reactions of the four carboxylic acids and ethanol were performed at 338 K, 348 K, 358 K and 368 K using [(n-bu-SO$_3$H)MIM][HSO$_4$] ionic liquid as catalyst (Fig. 2). The amount of the catalyst and reactants increased to 50 mmol (IL): 100 mmol (acid, for n-stearic acid only 50 mmol was added): 200 mmol (alcohol) for convenience of sampling, while the other reaction conditions were kept the same as that in section 3.1. It can be seen from Fig. 2 that the conversions of the acids increase with reaction temperature and time, and reach to equilibrium within about two hours.

Fischer esterification is known as a second-order reversible reaction. Therefore, the consumption of carboxylic acid can be expressed by:

$$-\frac{d(\gamma_C \cdot c_C)}{dt} = k_f \cdot (\gamma_C c_C) \cdot (\gamma_A c_A) - k_b \cdot (\gamma_E c_E) \cdot (\gamma_W c_W)$$

$$= k_f \left[(\gamma_C c_C) \cdot (\gamma_A c_A) - \frac{1}{K} \cdot (\gamma_E c_E) \cdot (\gamma_W c_W) \right] \quad (2)$$

Where subscript C stands for carboxylic acid, A stands for alcohol, E stands for ester and W stands for water; c and γ are concentration and activity coefficients, respectively; k_f and k_b are formation and back-forth rate constants, respectively; K is equilibrium constant of the reaction, which equals to the ratio of k_f to k_b.

Strictly speaking, it is difficult to determine the intrinsic kinetic parameters for such reversible reactions because a new phase that is immiscible to reactants is generated during the reaction. Therefore, we only estimate the apparent parameters by assuming all the activity coefficients are kept constant during the reaction. Eq. (2) can therefore be rearranged as:

$$-\frac{dc_C}{dt} = k_f \cdot \left(\gamma_A \cdot c_C c_A - \frac{1}{K} \cdot \frac{\gamma_E \gamma_W}{\gamma_C} \cdot c_E c_W \right) \quad (3)$$

Normalizing Eq. (3) by dividing initial concentrations of reactants (c_{C0} and c_{A0}) at both sides:

$$-\frac{1}{c_{C0} \cdot c_{A0}} \frac{dc_C}{dt} = \frac{k_f}{c_{C0} \cdot c_{A0}} \left(\gamma_A \cdot c_C c_A - \frac{1}{K} \cdot \frac{\gamma_E \gamma_W}{\gamma_C} \cdot c_E c_W \right) \quad (4)$$

Letting, $X = 1 - (c_C/c_{C0})$, which stands for the conversion of carboxylic acid, the concentrations of other components can also be expressed by X as: $c_A = c_{A0} - c_{C0}X$; $c_E = c_W = c_{C0}X$. Eq. (4) can therefore be reformed as:

$$\frac{1}{c_{A0}} \frac{dX}{dt} = k_f \gamma_A (1-X) \left(1 - \frac{c_{C0}}{c_{A0}}X\right) - \frac{k_f}{K} \cdot \frac{\gamma_E \gamma_W}{\gamma_C} \cdot \frac{c_{C0}}{c_{A0}} X^2 \quad (5)$$

Rearranging:

$$\frac{dX}{dt} = k_f \gamma_A (1-X)(c_{A0} - c_{C0}X) - \frac{k_f \gamma_A}{K / \frac{\gamma_E \gamma_W}{\gamma_C \gamma_A}} \cdot c_{C0} X^2$$
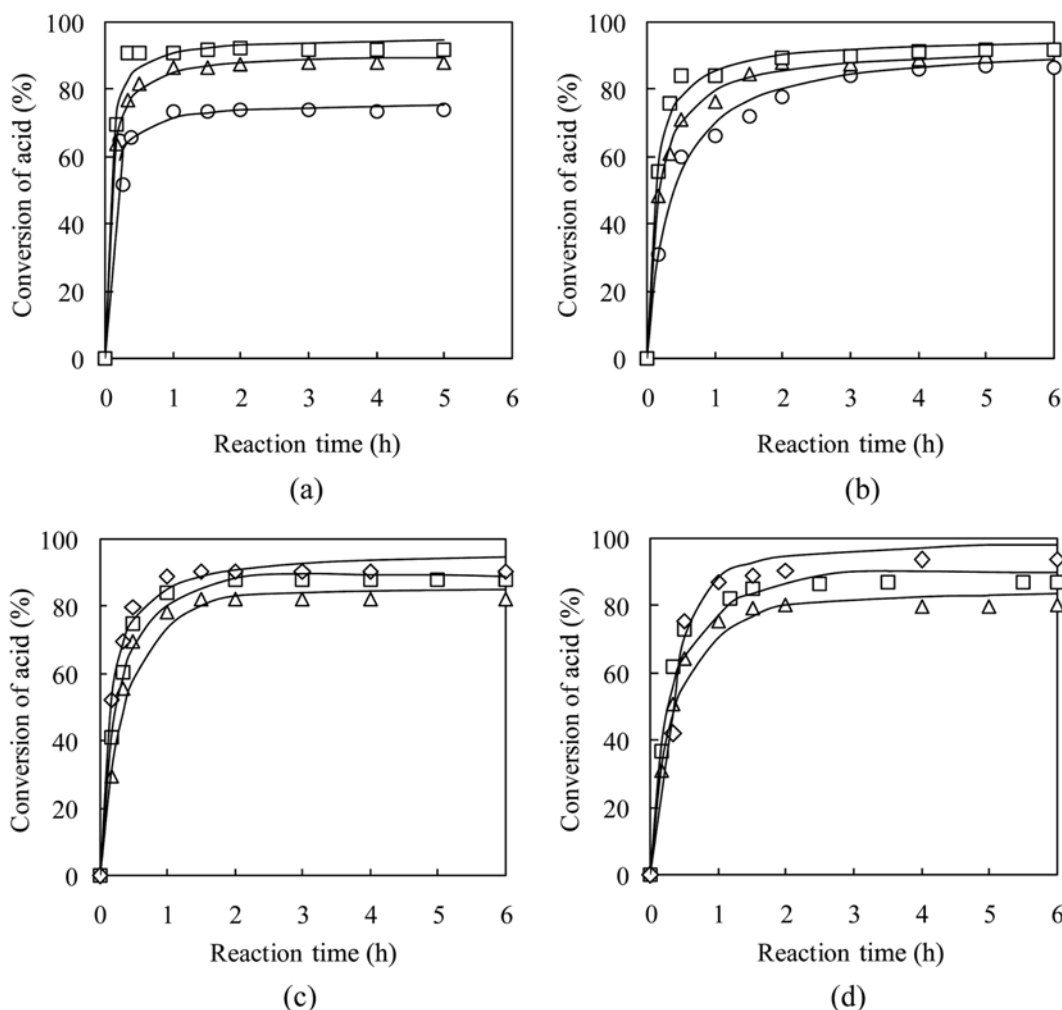
Fig. 2. Esterification conversion profile at different reaction temperature catalyzed by [(n-bu-SO₃H)MIM][HSO₄] (a) acetic acid+ethanol, (b) n-hexanoic acid+ethanol, (c) lauric acid+ethanol, (d) stearic acid+ethanol. ○ T=338 K, △ T=348 K, □ T=358 K, ◇ T=368 K, solid line is calculated from estimated kinetic parameters. Reaction conditions are the same as those in Table 2 except the ratio of catalyst and reactants increased to 100 mmol: 200 mol acid: 400 mol alcohol.

$$= k_f'(1-X)(c_{A0}-c_{C0}X) - \frac{k_f'}{K'}c_{C0}X^2$$

$$= k_f'c_{A0} - k_f'(c_{A0}+c_{C0})X + k_f'c_{C0}(1-1/K')X^2 \qquad (6)$$

Where $k_f'=k_f\gamma_A$, $K'=K/(\gamma_E\gamma_W/\gamma_C\gamma_A)$ are the apparent formation rate constant and apparent equilibrium constant, respectively. The two constants can then be simply estimated from Eq. (6) and the conversion data in Fig. 2 by Least-Square regression method. Values of the apparent activation energy were determined from the slope of ln k′ versus 1/T plots according to the Arrhenius equation, which are 39.1±2.0, 49.7±2.5, 51.4±2.5 and 59.3±3.0 kJ·mol⁻¹ for the formation of ethyl acetate, ethyl n-hexanoate, ethyl laurate and ethyl stearate, respectively. All the parameters are shown in Table 4. The maximum relative error between the predicted and experimental conversion of carboxylic acid was determined through, RE=max[abs $(X_{expt}-X_{calcd})/X_{expt}$]×100%, which is found to be around 5%.

It can be seen from Table 4 that the formation rate of the ester decreases with the increase of the carbon chain of aliphatic acid, while the other reaction conditions are kept the same. This phe-

nomenon is reasonable since the steric effect of the carbon chain on the reactivity of carboxyl group becomes stronger as the carbon chain becomes longer. Furthermore, the viscosity of carboxyl acid increases with the increase of the carbon chain, which slows down the reaction rate as the mass-transfer resistance becomes larger.

3. Effect of the Formed Water on Esterification

One may also notice from Fig. 2 that the conversion of acids at 6 hr and T=358 K is less than 92%, which is obviously lower than those in Table 3 (entries 3, 9, 15 and 21). However, the only difference between these two experiments is the proportional magnification of the amount of the catalyst and reactants in the kinetics experiment (data in Fig. 2). Since for both experiments a flask with a reflux condenser was used as reactor, the formed water during the reaction will reflux through the condenser and probably will be partly adhered on the inner-wall of the condenser, which will push the esterification reaction to the right side because part of the formed water is removed out from the reaction solution. For the experiment in section 3.1, the theoretical maximum amount of formed water is only 10 mmol. Such little amount of formed water is likely to evap-

Table 4. Calculated apparent kinetic parameters of esterification reactions catalyzed by [(n-bu-SO₃H)MIM][HSO₄]

Product	Temperature (K)	k_f' ($l \cdot mol^{-1} \cdot h^{-1}$)	K'	Apparent activation energy E ($kJ \cdot mol^{-1}$)
Ethyl acetate	338	0.13±0.01	1.66±0.09	39.1±2.0
	348	0.34±0.02	5.88±0.30	
	358	0.75±0.03	9.59±0.50	
Ethyl n-hexanoate	338	0.10±0.01	5.06±0.25	49.7±2.5
	348	0.34±0.02	7.15±0.36	
	358	0.95±0.05	9.56±0.50	
Ethyl laurate	348	0.38±0.02	3.28±0.16	51.4±2.5
	358	1.23±0.06	5.80±0.29	
	368	3.50±0.10	8.12±0.40	
Ethyl stearate	348	0.45±0.02	1.02±0.05	59.3±3.0
	358	1.84±0.09	1.90±0.10	
	368	5.83±0.10	4.87±0.25	

orate from the reaction liquid phase and hardly drop back. This might be an important reason that the conversion of esterification runs to very high (nearly 100%) in our results as well as in many reports [20,25-27] that used the same 'flask-reflux' reactor and small amount of reactants as ours. Contrarily, the amount of formed water in the kinetics experiment (Fig. 2) is larger and may drop more back to the reaction phase which inhibits the formation of the ester, leading to a lower final equilibrium conversion of the acids.

To verify this idea, we further conducted the esterification reaction of acetic acid with ethanol in (1) 10 ml sealed tube; (2) 10 ml sealed tube with 1 g dried 4A zeolite (pore size 0.38 nm, BET surface area 550 $m^2 \cdot g^{-1}$ and pore volume: 0.25 $cm^3 \cdot g^{-1}$); and (3) 25 ml flask with reflux condenser. Results are shown in Table 5.

It is well known that Fischer esterification is a reversible reaction. The removal of the formed water or ester from the reaction bulk will be favorable to the right-shift of the reaction, leading to a higher yield of ester. In most reports, ionic liquid is regarded as a kind of high-efficient acidic catalyst that can either combine (sequester) the water or isolate the ester to another phase so that the conversion of esterification runs to nearly 100% [10,20,23,25-27,32,33], in which a general 'flask-reflux' reactor was used. Whereas others do not believe the ionic liquids can sequester water or esters with enough efficiency, and they used other strategies such as membrane separation to isolate water in order to obtain higher esterification conversion [34,35]. Moreover, Forbes et al. considered the exist-

ence of some water might be necessary to enhance the catalytic activity of sulfonic acid based ionic liquid [18,19]. To sum up, so far the role of water and the water-sequestered effect of ionic liquid on ionic liquid catalyzed esterification seems ambiguous.

From our results in Table 5, however, one can clearly see that the existence of water in the reaction bulk obviously decreases the yield of acetate (entries 25 vs. 29 and 26 vs. 30), as the container is sealed so that the formed water cannot be easily evaporated. Whereas when zeolite 4A (a zeolite that is believed to only adsorb water from the above esterification system [36,37]) was used to adsorb the formed water, the yield of acetate slightly increased by ca 3%, compared to the corresponding reactions carried out in the general 'flask-reflux' reactors (entries 27 vs. 29 and 28 vs. 30). Based on our results, we therefore conclude that the removal of water from the ionic liquid-catalyzed esterification reaction system is necessary in order to obtain a higher yield of ester, although ionic liquid is generally viewed as a kind of water-sequester solvent and can be used to tailor the equilibrium conversion of esterification [38,39].

CONCLUSION

Five water-stable ionic liquids [BHIM]BF₄, [BHIM]CF₃SO₃, [(n-bu-SO₃H) MIM][HSO₄], [(n-bu-SO₃H) MIM][p-TSO] and [(Et)N₃H] HSO₄ were applied as both solvents and acid catalysts for Fischer esterification reactions of ethanol and four aliphatic carboxylic acids (acetic acid, n-hexanoic acid, lauric acid, and stearic acid).

Among the studied ionic liquids, [(n-bu-SO₃H) MIM][HSO₄] and [(n-bu-SO₃H) MIM][p-TSO] have higher reactivity for the production of ethyl esters. The catalytic activity of these ionic liquids is strongly dependent on the acidity of their anions and cations. The hydrophilicity of the ionic liquid and its affinity with the reactants affects a great deal of its catalytic reactivity: when lower-molecular water-miscible acids react with alcohol, the water miscibility of the ionic liquids will improve catalytic activity; in contrast, when water-immiscible long-carbon-chain acids or alcohol are used as reactant, the hydrophobic function group of the ionic liquid will improve its catalytic activity. Water refluxing through the condenser may be another important reason for obtaining high conversion of esterification, while esterification that occurs in a sealed container leads to a lower conversion, indicating a water sequester process is still needed

Table 5. Esterification of acetic acid with ethanol carried out in different reaction containers

Entry	Reaction container	Type of ionic liquid	Dehydrator	Yield of acetate (%)
25	10 ml sealed tube	III	-	84.5±2.1
26	10 ml sealed tube	V	-	82.3±2.1
27	10 ml sealed tube	III	1 g 4A zeolite	93.6±1.2
28	10 ml sealed tube	V	1 g 4A zeolite	91.1±1.3
29	25 ml refluxed flask	III	-	91.4±1.6
30	25 ml refluxed flask	V	-	88.7±1.1

Note: reaction temperature: 358 K, time: 6 h. mole ratio of acid : alcohol : IL=20 mmol : 40 mmol : 10 mmol

in order to obtain a higher yield of ester in the ionic liquid catalyzed esterification system. Kinetics studies of carboxylic acids reacting with ethanol at 338 K, 348 K, 358 K and 368 K show the conversions of the acids increase with reaction temperature and time, and reach equilibrium within about two hours. The apparent activation energies are calculated to be 39.1±2.0, 49.7±2.5, 51.4±2.5 and 59.3 ±3.0 kJ·mol^{-1} for the formation of ethyl acetate, ethyl hexanoate, ethyl laurate and ethyl stearate, respectively.

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