

Synthesis of terpinyl acetate using octadecylamine ethoxylate ionic liquids as catalysts

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Abstract Terpinyl acetate, an important natural flavor, can be synthesized by esterification of α -pinene with acetic acid under acidic conditions. In this work, seven acidic ionic liquids were first synthesized, using octadecylamine ethoxylates (AC 1810, AC 1815, AC 1820, and AC 1830) as the cations, and characterized by FT-IR, ^1H NMR, and ^{13}C NMR spectroscopy. The ionic liquids were then used as catalysts in the synthesis of terpinyl acetate. The effect of preparation conditions on catalyst performance was examined. It was found that the acidic ionic liquid 1-(3-sulfonic acid)propyl-3-poly(ethylene glycol) octadecylamine polyoxyethylene ether tetrafluoroborate ($[\text{PAC1815}]^+[\text{BF}_4]^-$) was an excellent catalyst for synthesis of terpinyl acetate. The effects of the conditions used for preparation of terpinyl acetate were examined in detail, and the optimum preparation conditions were obtained. Under the optimum conditions, the yield of terpinyl acetate reached 35.70 %. When the catalyst was reused for the 5th time, the yield of terpinyl acetate was still 32.00 %. The results showed that effective separation and recycling of catalyst could contribute to developing a new strategy for synthesis of terpinyl acetate.

Keywords α -Pinene · Acidic ionic liquid · Esterification · Terpinyl acetate · Octadecylamine ethoxylates

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Introduction

α -Pinene accounts for 58–65 % of turpentine, a mixture extracted from pine terpene products. α -Pinene can be used as raw material to produce a variety of compounds by use of acid catalysts. One example is terpinyl acetate [1], an important naturally occurring compound widely used in chemical products and spices. In recent years it has been synthesized by direct esterification of α -pinene with acetic acid. In the esterification process, the selectivity of the catalyst is critical. Solid heteropoly acid [2], solid acid [3, 4], and zeolite [5] have all been used as catalysts in the reaction. However, these catalysts have many disadvantages, for example low catalytic activity and selectivity, long reaction time, and short lifetime, which greatly limit further development of the process. When seeking a new catalyst with high catalytic activity, selectivity and reusability are crucial for promoting development of the process.

Because ionic liquids can be used to design “environment-friendly” solvents and catalysts, they are widely used in many esterifications [6–15]. As catalysts they overcome the shortcomings of conventional catalysts and can be simply and easily separated from the products under mild conditions. Imidazole-based ionic liquids have usually been used as catalysts in esterification [16–20]. It has not been discovered whether ionic liquids with fatty amine ethoxylates as cations can be used as catalysts for esterification. Fatty amine ethoxylates when dissolved in alkali, water, or another neutral medium are non-ionic, whereas in acidic media they are cationic. Because of their excellent diffusion properties, they can greatly improve reaction rate and conversion rate as catalysts [21]. In the work discussed in this paper, seven acidic polyether ionic liquids were prepared and used in the esterification of α -pinene. By studying the reaction conditions, for example the nature and amount of the ionic liquid used, the ratio of reactants, and reaction temperature, the optimum reaction conditions were determined. The reusability of the catalyst was also investigated.

Experimental

Materials and instruments

All materials (α -pinene, acetic acid, deionized water, anhydrous magnesium sulfate, octadecylamine polyoxyethylene (AC 1812, AC 1815, AC 1820, AC 1830), 1, 3-propanesulfonic acid lactone (1,3-PS), sulfuric acid, phosphoric acid, *p*-toluenesulfonic acid (PTSA), tetrafluoroborate) were purchased from Aldrich. All were directly used after drying without further purification.

FT-IR spectra in the range 4,000–400 cm^{-1} were recorded with a Nicolet-510P (American Nicolet Instrument Corporation). NMR spectra of the ionic liquids were recorded with a 500 MHz Bruker spectrometer in DMSO or CDCl_3 and calibrated with tetramethylsilane (TMS) as internal reference. Gas chromatography–mass spectrometry (Agilent 6890 N/5973 N) was used for analysis of the composition of

the product. Separations were achieved on a 50 m × 0.25 mm × 0.25 μm HP-5 column. The column temperature was increased from 80 to 240 °C at 4 °/min.

Synthesis of ionic liquids

A known amount of AC 18n was placed in a flask with stirrer, thermometer, Allihn-type condenser, and constant-pressure spherical dropping funnel. The flask was placed in a water-bath with an electrically operated agitator. 1,3-Propanesulfonic acid lactone was dissolved in ethyl acetate and the solution was added dropwise to an equimolar amount of AC 18n at 55 °C, and reaction was performed at 55 °C for 2 h. After reaction, ethyl acetate was removed under vacuum, and the red-brown liquid 1-(3-sulfo)propyl-3-polyoxyethylene octadecylamine vinyl ether (PAC 18n) was obtained. The PAC 18n was dissolved in water and an equimolar amount of acid (sulfuric acid, phosphoric acid, *p*-toluenesulfonic acid, or tetrafluoroborate) was slowly added dropwise to the PAC18n at 90 °C. Reaction was performed at 90 °C for 2 h. After removal of the water under vacuum 1-(3-sulfo)propyl-3-octadecylamine polyoxyethylene salts ([PAC 18n]⁺[R]⁻) were obtained as brown viscous liquids. The synthetic process is shown in Fig. 1.

The ionic liquids synthesized in this study were all liquids. They were characterized to determine their structures. The results were as follows.

[PAC 1820]⁺[PTSA]⁻: FT-IR spectra (KBr liquid film, cm⁻¹): 3,396 (–OH stretching), 2,920 (saturated C–H stretching), 1,459 (C–H bending), 1,353 (N–CH₂, C–H deformation), 1,235 (S=O stretching), 1,112 (C–O–C stretching), 728 (–(–CH₂)₃– in-plane rocking), 593 (S–O stretching). ¹H NMR spectrum (solvent D₂O, 500 MHz): δ 7.54–7.05 (4H, CH × 4), δ 5.21–5.15 (1H, OH), δ 4.65–3.24 (84H, CH₂–O and NCH₂), δ 2.96–2.17 (4H, CH₂ × 2), δ 1.89–1.85 (6H, CH₂ × 3), δ 1.40 (3H, CH₃), δ 1.17–1.00 (34H, CH₂ × 17), δ 0.77–0.76 (6H, CH₂ × 3). ¹³C NMR spectra (solvent D₂O, 500 MHz): δ 165.50, δ 129.13, δ 125.47, δ 71.70, δ 69.56, δ 64.23, δ 63.77, δ 60.30, δ

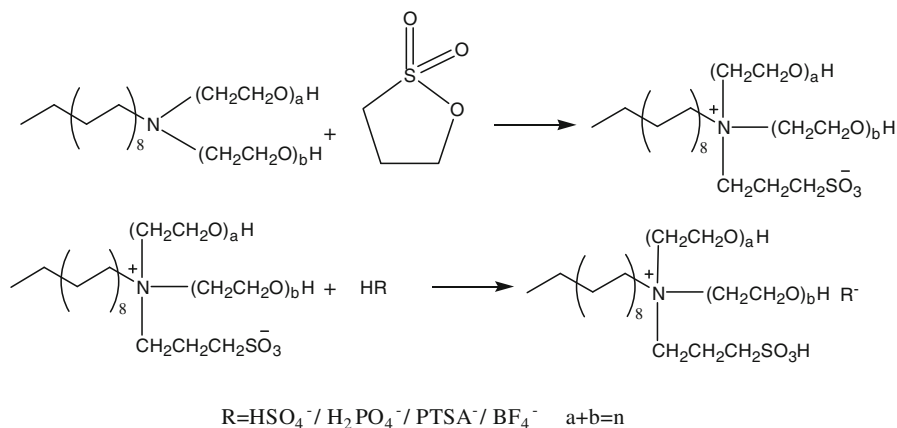


Fig. 1 Synthesis of the ionic liquids [PAC 18n]⁺[R]⁻

47.85, δ 47.29, δ 31.90, δ 29.84, δ 29.73, δ 29.07, δ 27.08, δ 25.93, δ 22.61, δ 21.55, δ 20.56, δ 17.74, δ 13.92.

[PAC 1820]⁺[H₂PO₄]⁻: FT-IR spectra (KBr liquid film, cm⁻¹): 3,389 (–OH stretching), 2,920 (saturated C–H stretching), 1,460 (C–H bending), 1,353 (N–CH₂, C–H deformation), 1,249 (S=O and P=O stretching), 1,108 (C–O–C stretching), 543 (S–O and P–O stretching). ¹H NMR spectrum (solvent D₂O, 500 MHz): δ 5.21 (1H, OH), δ 4.65–3.09 (84H, CH₂–O and NCH₂), δ 2.77–2.69 (4H, CH₂ × 2), δ 1.90–1.80 (6H, CH₂ × 3), δ 1.56 (3H, CH₃), δ 1.17–1.11 (34H, CH₂ × 17), δ 0.73–0.71 (6H, CH₂ × 3). ¹³C NMR spectra (solvent D₂O, 500 MHz): δ 130.04, δ 129.37, δ 71.68, δ 64.18, δ 63.79, δ 60.27, δ 60.06, δ 58.42, δ 54.01, δ 52.71, δ 47.90, δ 47.22, δ 32.53, δ 31.86, δ 29.80, δ 29.35, δ 26.96, δ 26.29, δ 25.96, δ 23.01, δ 22.56, δ 17.66, δ 13.87.

[PAC 1820]⁺[HSO₄]⁻: FT-IR spectra (KBr liquid film, cm⁻¹): 3,473 (–OH stretching), 2,919 (saturated C–H stretching), 1,460 (C–H bending), 1,353 (N–CH₂, C–H deformation), 1,247 (S=O stretching), 1,110 (C–O–C stretching), 727 (–(CH₂)₃–in-plane rocking), 585 (S–O stretching). ¹H NMR spectrum (solvent D₂O, 500 MHz): δ 5.21–5.15 (1H, OH), δ 4.65–3.10 (84H, CH₂–O and NCH₂), δ 2.79–2.70 (4H, CH₂ × 2), δ 1.93–1.80 (6H, CH₂ × 3), δ 1.57 (3H, CH₃), δ 1.18–1.11 (34H, CH₂ × 17), δ 0.73–0.71 (6H, CH₂ × 3). ¹³C NMR spectra (solvent D₂O, 500 MHz): δ 165.30, δ 130.14, δ 71.85, δ 69.80, δ 67.37, δ 66.70, δ 64.45, δ 64.03, δ 60.58, δ 60.26, δ 58.70, δ 58.45, δ 54.36, δ 53.10, δ 48.14, δ 47.86, δ 47.51, δ 32.59, δ 31.94, δ 29.82, δ 29.39, δ 27.18, δ 26.49, δ 24.64, δ 23.08, δ 22.60, δ 21.60, δ 17.80, δ 13.91.

[PAC 1820]⁺[BF₄]⁻: FT-IR spectra (KBr liquid film, cm⁻¹): 3,455 (–OH stretching), 2,920 (saturated C–H stretching), 1,458 (C–H bending), 1,353 (N–CH₂, C–H deformation), 1,248 (B–F stretching), 1,110 (C–O–C stretching). ¹H NMR spectrum (solvent D₂O, 500 MHz): δ 4.64–3.10 (84H, CH₂–O and NCH₂), δ 2.77–2.70 (4H, CH₂ × 2), δ 1.97–1.87 (6H, CH₂ × 3), δ 1.57 (3H, CH₃), δ 1.20–1.14 (34H, CH₂ × 17), δ 0.73–0.70 (6H, CH₂ × 3). ¹³C NMR spectra (solvent D₂O, 500 MHz): δ 71.71, δ 64.20, δ 63.82, δ 60.33, δ 58.43, δ 52.75, δ 47.87, δ 47.30, δ 31.90, δ 29.83, δ 29.39, δ 22.59.

[PAC 1810]⁺[BF₄]⁻: FT-IR spectra (KBr liquid film, cm⁻¹): 3,470 (–OH stretching), 2,918 (saturated C–H stretching), 1,461 (C–H bending), 1,355 (N–CH₂, C–H deformation), 1,250 (B–F stretching), 1,108 (C–O–C stretching). ¹H NMR spectrum (solvent D₂O, 500 MHz): δ 4.60–3.12 (44H, CH₂–O and NCH₂), δ 2.75–2.66 (4H, CH₂ × 2), δ 1.95–1.84 (6H, CH₂ × 3), δ 1.56 (3H, CH₃), δ 1.17–1.12 (34H, CH₂ × 17), δ 0.72–0.70 (6H, CH₂ × 3). ¹³C NMR spectra (solvent D₂O, 500 MHz): δ 72.09, δ 70.07, δ 69.89, δ 69.69, δ 64.43, δ 64.03, δ 60.62, δ 58.71, δ 55.58, δ 54.26, δ 53.11, δ 48.18, δ 47.51, δ 31.98, δ 29.95, δ 29.81, δ 29.45, δ 29.18, δ 26.48, δ 26.19, δ 23.28, δ 22.66, δ 21.82, δ 17.97, δ 13.93.

[PAC 1815]⁺[BF₄]⁻: FT-IR spectra (KBr liquid film, cm⁻¹): 3,455 (–OH stretching), 2,920 (saturated C–H stretching), 1,459 (C–H bending), 1,353 (N–CH₂, C–H deformation), 1,247 (S=O stretching), 1,109 (C–O–C stretching), 1,060 (B–F stretching), 727 (–(CH₂)₃–in-plane rocking), 543 (S–O stretching). ¹H NMR spectrum (solvent D₂O, 500 MHz): δ 5.19 (1H, OH), δ 4.64–3.07 (64H, CH₂–O and NCH₂), δ 2.78–2.71 (4H, CH₂ × 2), δ 1.98–1.74 (6H, CH₂ × 3), δ 1.55 (3H, CH₃), δ 1.09 (34H, CH₂ × 17), δ 0.72–0.69 (6H, CH₂ × 3). ¹³C NMR spectra (solvent D₂O, 500 MHz): δ 71.90, δ 68.67, δ 64.24, δ 63.85, δ 60.39, δ 58.45, δ 58.19, δ

52.83, δ 47.90, δ 47.34, δ 31.92, δ 29.86, δ 29.71, δ 29.40, δ 29.09, δ 26.93, δ 26.34, δ 26.03, δ 23.06, δ 22.60, δ 21.62, δ 17.79, δ 13.87.

[PAC 1830]⁺[BF₄]⁻: FT-IR spectra (KBr liquid film, cm⁻¹): 3,465 (–OH stretching), 2,915 (saturated C–H stretching), 1,456 (C–H bending), 1,357 (N–CH₂, C–H deformation), 1,251 (B–F stretching), 1,106 (C–O–C stretching). ¹H NMR spectrum (solvent D₂O, 500 MHz): δ 4.63–3.12 (124H, CH₂–O and NCH₂), δ 2.78–2.69 (4H, CH₂ × 2), δ 1.95–1.84 (6H, CH₂ × 3), δ 1.59 (3H, CH₃), δ 1.24–1.12 (34H, CH₂ × 17), δ 0.71–0.68 (6H, CH₂ × 3). ¹³C NMR spectra (solvent D₂O, 500 MHz): δ 71.75, δ 69.62, δ 64.26, δ 63.88, δ 60.53, δ 60.35, δ 58.50, δ 54.33, δ 52.84, δ 47.90, δ 47.32, δ 31.92, δ 29.82, δ 29.05, δ 26.09, δ 22.62, δ 21.59, δ 17.73, δ 13.95.

The structures of the ionic liquids were confirmed by the results given above.

Determination of the acid value of the ionic liquids

Ionic liquid solutions of different concentration (0.005, 0.010, 0.015, 0.020, and 0.025 mol/L) were prepared. The ionic liquid solution (10 ml) was placed in a 100 ml tapered bottle and two drops of phenolphthalein indicator solution were added. The solution was then titrated with 0.10 mol/L aqueous potassium hydroxide standard solution until the indicator turned pink. Blank experiments were performed by the same method.

Esterification of α -pinene

Known amounts of α -pinene, acetic acid, and ionic liquid were placed in a reaction flask with an electronic stirrer. After reaction at a specific temperature for 10 h, 10 ml water was added in the mixture. The upper layer was collected and washed with water to pH 7. The product was dried over anhydrous magnesium sulfate then filtered to get obtain a clear organic solution. The solution was analyzed by GC. The lower ionic liquid catalyst was recovered after dehydration and reused. The mechanism of reaction [2] of α -pinene and acetic acid in the presence of a catalyst is shown in Fig. 2.

The products were analyzed by GC–mass spectrometry (Agilent 6890 N/5973 N). An HP-5 capillary column with a length of 50 m and an internal diameter of 0.25 mm was used. The injector and transfer line temperatures were 280 °C. The initial temperature of the column oven was maintained at 80 °C for 10 min then increased at 4 °/min to 240 °C which was maintained for 10 min. The carrier gas was N₂. The sample size was 0.1 μ L. The chromatogram obtained from the products of esterification of α -pinene is shown in Fig. 3. The identities of the products were determined by GC–MS. *R*_t (retention time): 12.42 min α -pinene; 12.89 min camphene; 15.36 min dolicymene; 15.63 min limonene; 17.85 min terpinolene; 21.78 min α -terpineol; 22.85 min fenchyl acetate; 25.29 min isobornyl acetate; 25.40 min bornyl acetate; 25.70 min 4-terpinenyl acetate; 27.79 min terpinyl acetate; 35.11 min terpinyl propionate.

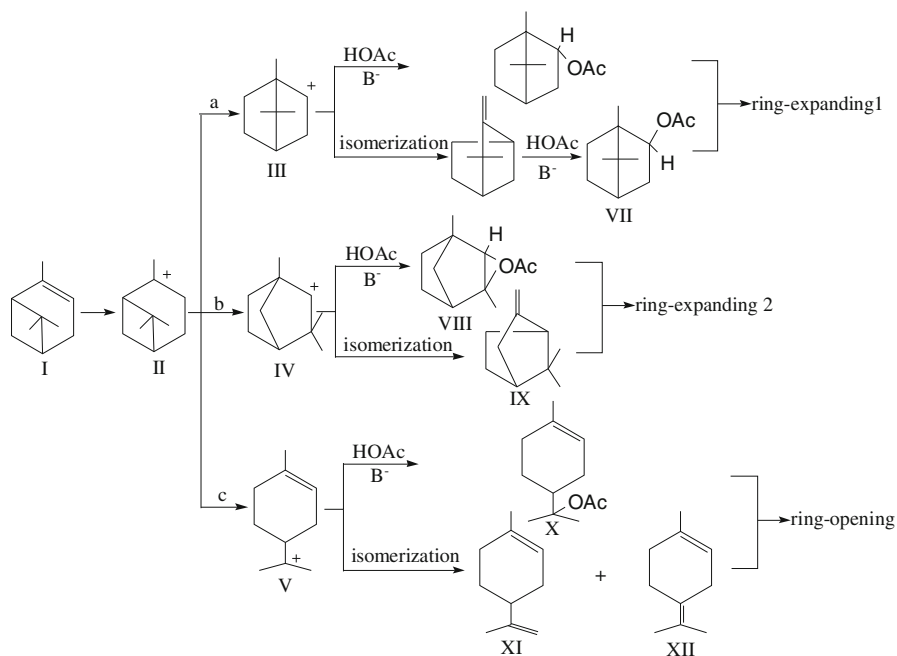


Fig. 2 Reaction of α -pinene with acetic acid

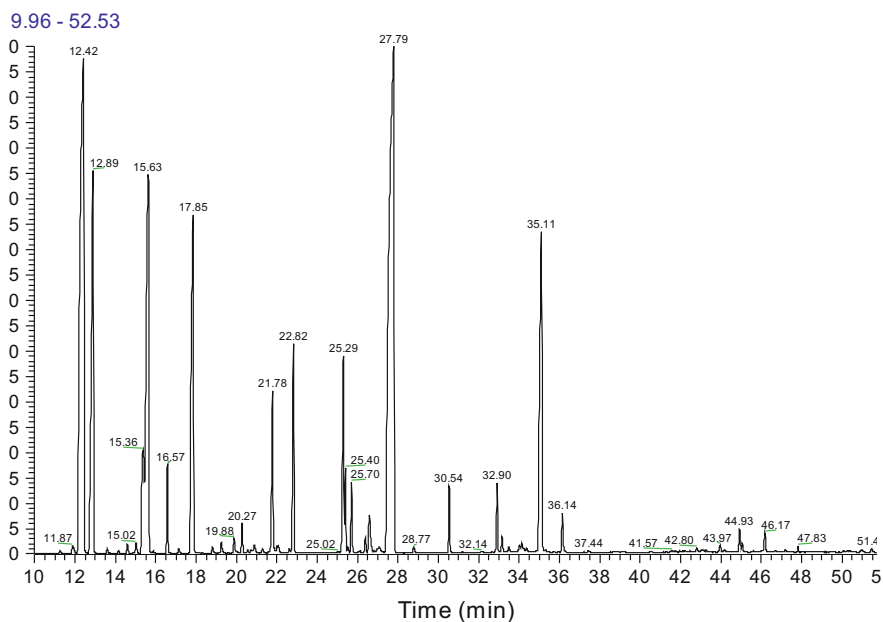


Fig. 3 Gas chromatogram obtained from the products of esterification of α -pinene

Results and discussion

The effect of the type of catalyst on the reaction can be seen in Table 1. With the same cation, the reaction was substantially affected by the anion species used. Table 1 shows that the yield of terpinyl acetate was highest when $[\text{PAC 1820}]^+[\text{BF}_4]^-$ was used as catalyst, and the yield was the lowest when $[\text{PAC 1820}]^+[\text{PTSA}]^-$ (PTSA: *p*-toluene sulfonic acid) was used. The acid values of the different ionic liquids are listed in Table 2. From this table it is apparent $[\text{PAC 1820}]^+[\text{BF}_4]^-$ had the maximum acid value whereas that of $[\text{PAC1820}]^+[\text{PTSA}]^-$ was lowest. It can, therefore, be concluded that the yield of terpinyl acetate was determined by the acid value of ionic liquids. In subsequent work we focused on studying the catalytic properties of $[\text{PAC 18n}]^+[\text{BF}_4]^-$.

From Table 3 it is apparent that the degree of polymerization (n) affected the yield of terpinyl acetate. With increasing n , the yield of terpinyl acetate first increased and then decreased. When n was 15, the yield of terpinyl acetate was maximum. This could be explained by its different acid value. As chain length increased, the acid content per unit mass decreased. Therefore as the n value increased, the amount of acid decreased (Table 4). When n was equal to 15, the acidic strength was quite suitable for this reaction. Therefore, $[\text{PAC 1815}]^+[\text{BF}_4]^-$ was used as the catalyst in the reaction.

Table 5 shows that the yield of terpinyl acetate increased with increasing reaction time. When reaction time was 10 h the reaction basically achieved balance, and the yield of terpinyl acetate reached its highest value of 35.70 %. When the reaction time exceeded 11 h, the yield began to decrease, indicating that long reaction times resulted in side effects and was of no benefit for generating terpinyl acetate. The appropriate time was, therefore, 10 h.

The effect of reaction temperature on esterification is also shown in Table 5. When the temperature was low, the rate of the reaction and the yield of terpinyl acetate were both low. As the temperature was increased, the reaction rate increased, and the yield of terpinyl acetate increased accordingly. When the temperature was too high, however, α -pinene tended to isomerize rather than esterify. The results showed the yield of terpinyl acetate first increased and then decreased with

Table 1 Effect of the type of catalyst on the reaction

Type of catalyst	Product components (%)					Yield of terpinyl acetate (%)
	α -Pinene	Camphene	Limonene	Terpinolene	Terpinyl acetate	
Blank	90.23	2.64	0.25	0.89	0.85	0.99
$[\text{PAC 1820}]^+[\text{PTSA}]^-$	48.90	16.61	10.70	5.42	13.23	15.49
$[\text{PAC 1820}]^+[\text{H}_2\text{PO}_4]^-$	47.76	9.47	9.39	4.75	17.22	20.02
$[\text{PAC 1820}]^+[\text{HSO}_4]^-$	24.63	8.01	20.78	13.69	15.39	17.90
$[\text{PAC 1820}]^+[\text{BF}_4]^-$	19.81	18.48	9.75	7.48	26.24	30.51

Reaction conditions: $n(\alpha\text{-pinene}):n(\text{catalyst}):n(\text{acetic acid}) = 1:0.06:4$; α -pinene 0.05 mol, reaction temperature 30 °C, reaction time 10 h

Table 2 Effect of acid type on acid value

Concentration (mol/L)	Volume of KOH solution consumed ($V_1 - V_2$)			
	[PAC 1820] ⁺ [PTSA] ⁻	[PAC 1820] ⁺ [H ₂ PO ₄] ⁻	[PAC 1820] ⁺ [HSO ₄] ⁻	[PAC 1820] ⁺ [BF ₄] ⁻
0.005	0.90	0.95	1.05	1.45
0.010	1.80	1.90	2.10	2.80
0.015	2.72	2.80	3.16	4.12
0.020	3.61	3.70	4.22	5.50
0.025	4.50	4.65	5.20	6.40
Acid value (mg/g)	70.8	77.2	87.4	115.6

Table 3 Effect of degree of polymerization on the results of the reaction

Degree of polymerization	Product component (%)					Yield of terpinyl acetate (%)
	α -Pinene	Camphene	Limonene	Terpinolene	Terpinyl acetate	
10	16.77	20.72	10.33	9.30	28.45	33.11
15	7.13	17.23	16.55	13.99	30.70	35.70
20	19.81	18.48	11.62	10.89	26.24	30.51
30	25.81	15.81	12.51	6.66	25.07	29.20

Reaction conditions: $n(\alpha\text{-pinene}):n(\text{catalyst}):n(\text{acetic acid}) = 1:0.06:4$, α -pinene 0.05 mol, reaction temperature 30 °C, reaction time 10 h

Table 4 Effect of degree of polymerization on acid value

Concentration (mol/L)	Volume of KOH solution consumed ($V_1 - V_2$)			
	[PAC 1810] ⁺ [BF ₄] ⁻	[PAC 1815] ⁺ [BF ₄] ⁻	[PAC 1820] ⁺ [BF ₄] ⁻	[PAC 1830] ⁺ [BF ₄] ⁻
0.005	1.42	1.40	1.45	1.40
0.010	2.72	2.71	2.80	2.80
0.015	3.91	3.71	4.12	4.16
0.020	5.00	5.10	5.50	5.36
0.025	5.95	6.20	6.40	6.60
Acid value (mg/g)	159.3	132.2	115.6	87.1

increasing temperature. The terpinyl acetate content reached a maximum at 30 °C, which was, therefore, a suitable temperature.

When the amount of α -pinene was 0.05 mol, with increasing amount of acetic acid the yield of terpinyl acetate first increased and then decreased (Table 5). When the ratio $n(\alpha\text{-pinene})/n(\text{acetic acid})$ was 1:4, the yield of terpinyl acetate reached a maximum. As the amount of acetic acid was increased, mutual accessibility of acetic acid and α -pinene increased, so the yield of terpinyl acetate

Table 5 Effect of reaction conditions on the results of the reaction

<i>t</i> (h)	<i>T</i> (°C)	<i>n</i> (Acetic acid) (mol)	<i>n</i> (IL) (mmol)	Product components (%)					Yield of terpinyl acetate (%)
				α -Pinene	Camphene	Limonene	Terpinolene	Terpinyl acetate	
8	30	0.20	3.0	16.45	22.58	18.86	1.05	16.32	16.59
9	30	0.20	3.0	13.32	15.71	14.32	11.06	21.81	25.36
10	30	0.20	3.0	7.13	17.23	16.55	13.99	30.70	35.70
11	30	0.20	3.0	7.14	16.25	13.95	9.94	30.45	35.41
12	30	0.20	3.0	6.74	16.6	13.06	12.19	20.62	18.45
10	20	0.20	3.0	14.74	19.89	17.94	11.44	14.00	16.28
10	40	0.20	3.0	2.25	15.28	13.24	16.55	26.85	31.22
10	50	0.20	3.0	1.61	14.03	11.89	20.10	19.68	22.88
10	60	0.20	3.0	0.19	3.49	8.05	26.91	13.21	15.36
10	30	0.10	3.0	15.43	21.06	19.59	10.16	9.52	11.07
10	30	0.15	3.0	8.05	15.56	21.28	1.73	27.67	32.17
10	30	0.25	3.0	6.03	14.28	16.57	16.87	21.97	25.56
10	30	0.30	3.0	4.91	13.66	15.87	15.16	19.97	23.22
10	30	0.20	2.0	13.30	20.49	12.32	9.74	23.50	27.32
10	30	0.20	2.5	10.52	19.68	13.67	11.22	27.69	32.20
10	30	0.20	3.5	5.64	16.95	16.76	15.71	24.41	28.39
10	30	0.20	4.0	4.04	15.83	18.05	16.66	23.80	27.68

IL, ionic liquid; $n(\alpha$ -pinene) = 0.05 mol

increased [21]. When the amount of acetic acid was excessive, however, the amount of catalyst per unit volume was too small for the esterification reaction. Therefore, $n(\alpha$ -pinene)/ n (acetic acid) should be controlled at approximately 1:4.

As is apparent from Table 5, as the amount of ionic liquid was increased, the yield of terpinyl acetate increased, indicating increasing the quantity of ionic liquid promoted this reaction. When $n(\alpha$ -pinene)/ n (ionic liquid) was 1:0.06, the yield of terpinyl acetate reached a maximum. If the amount of ionic liquid was increased beyond this, however, the amount of esterification product decreased. This might be because the initial increase of amount of acid ionic liquid per unit volume was beneficial to the reaction. When $n(\alpha$ -pinene)/ n (ionic liquid) exceeded 1:0.06, the viscosity and the mass transfer resistance of the system increased, contact of α -pinene and acetic acid decreased, and this finally resulted in a decrease of the yield of terpinyl acetate [22]. The viscosity of the reaction mixture was tested at 30 °C: $n(\alpha$ -pinene)/ n (ionic liquid) = 1:0.05, viscosity = 1.95 mPa S; $n(\alpha$ -pinene)/ n (ionic liquid) = 1:0.06, viscosity = 2.05 mPa S; $n(\alpha$ -pinene)/ n (ionic liquid) = 1:0.07, the viscosity = 2.25 mPa S. It is well known that with increasing viscosity mass transfer resistance is enhanced [23]. Taken together, the appropriate $n(\alpha$ -pinene)/ n (ionic liquid) ratio was 1:0.06.

When the catalyst was reused for the 5th time, the yield of terpinyl acetate was still 32.00 %, showing that effective separation and recycling of the catalyst could

Table 6 Results from re-use of the catalyst

Cycle	Product components (%)					Yield of terpinyl acetate (%)
	α -Pinene	Camphene	Limonene	Terpinolene	Terpinyl acetate	
1	7.09	17.20	16.59	14.02	30.73	35.73
2	8.13	15.85	19.37	12.74	30.05	34.94
3	7.68	14.97	21.23	11.86	29.65	34.48
4	7.73	13.53	24.51	10.28	28.93	33.64
5	9.34	11.76	26.21	9.46	27.52	32.00

Reaction conditions: $n(\alpha\text{-pinene}):n(\text{catalyst}):n(\text{acetic acid}) = 1:0.06:4$, $\alpha\text{-pinene}$ 0.05 mol, reaction temperature 30 °C, reaction time 10 h

be expected to contribute to the development of a new strategy for synthesis of terpinyl acetate (Table 6).

Conclusions

The ionic liquid 1-(3-sulfonic acid)propyl-3-poly(ethylene glycol)-yl octadecylamine polyoxyethylene ether tetrafluoroborate ($[\text{PAC} 1815]^+[\text{BF}_4]^-$) was synthesized and characterized. The ionic liquid had good catalytic activity in the esterification of α -pinene, and the catalyst could be reused. The optimum conditions obtained were $n(\alpha\text{-pinene}):n(\text{ionic liquid}):n(\text{acetic acid}) = 5:0.3:20$, $n(\alpha\text{-pinene}) = 0.05$ mol, reaction temperature 30 °C, and reaction time 10 h. A new method is therefore available for synthesis of terpinyl acetate.

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