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Esterifications of Carboxylic Acids and Alcohols Catalyzed by $Al_2(SO_4)_3 \cdot 18H_2O$ under Solvent-Free Condition[1]

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Abstract—Esterifications of equimolar mixture of carboxylic acids and alcohols can be effectively catalyzed by $Al_2(SO_4)_3 \cdot 18H_2O$ under solvent-free condition. The esterification catalyzed by $Al_2(SO_4)_3 \cdot 18H_2O$ is a promising green method thanks to no need of organic solvent, no pollution, no causticity and ease to handle after reaction. This catalyst is of a low toxicity (usually it is used as purifying agent for drinking water), low-cost compound and is easily separated from the reaction mixture by simple filtration. Moreover, the catalyst can be recycled for the further esterification and the conversion does not evidently decrease.

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Esters are essential fine chemicals used widely in industry and agriculture production and daily life. They can be used as pharmaceuticals, flavors, polymerization monomers, plasticizers in rubber and plastic industry, emulsifiers in the food and cosmetic industry and solvent in chemistry industry due to a low toxicity [1–3]. Recently, long chain alkyl carboxylic acids esters were used as biosdiesel to substitute for decreasing fossil fuels [4, 5].

Traditional esterifications of carboxylic acids and alcohols are catalyzed by liquid strong acids, such as sulfuric, phosphoric or *p*-toluenesulfonic acids [6–9]. Although these homogeneous liquid Brønsted acids are highly efficient for esterifications, the reactions catalyzed by them have a lot of deficiencies: co-products, strong causticity to equipment, and a great deal of waste water in the process of dealing with product ester and so on. Therefore, chemists are always groping for an ideal esterification catalyst to substitute for strong liquid acid. Recently, it was continually reported that various kinds of novel solid acid catalysts were used to catalyze esterifications of carboxylic acids and alcohols, such as ion exchange resins [10, 11], mesoporous molecular sieves [12–14], solid superacids [15] and heteropolyacids (salts), lipase, sulfonic acids supported on molecular sieves, active carbon or polymers and so on [16–20]. Although these solid catalysts possess high activity and can be easily separated from reaction system, they have also a row of shortcomings: ion exchange-resins easily deactivate at high temperature for a long lime and show poor reusability. For solid supported catalysts, their application is limited on a large scale because of troubled preparation and high cost.

Esterifications of carboxylic acids and alcohols catalyzed by solid Lewis acids have also been reported in a few examples [21, 22]. Yamamoto et al. reported direct esterifications of equimolar mixture of carboxylic acids and alcohols catalyzed by hafnium(IV) and zirconium(IV) salts ($ZrCl_4$, $Zr(i\text{-}PrO)_4$, $HfCl_4$, $Hf(t\text{-}BuO)_4$) with azeotropic reflux to remove water from system [23]. Juan et al. researched $Zr(SO_4)_2 \cdot 4H_2O$ catalyzed esterifications of fatty acids and alcohols [24]. Besides those, Sugi et al. reported that various multivalent metal chlorides catalyzed esterifications of long chain aliphatic acids and long chain alcohols in mesitylene as solvent [25]. Although Hf(IV) and Zr(IV) salts are highly effective for esterifications of carboxylic acids and alcohols, they are enough expensive compounds.

In this work, we describe esterifications of various carboxylic acids and alcohols catalyzed by $Al_2(SO_4)_3 \cdot 18H_2O$ under solvent-free conditions. $Al_2(SO_4)_3 \cdot 18H_2O$ not only possesses high catalytic activity for esterification, but also is a cheap, low toxic compound. Moreover, it can be easily recovered by simple filter and reused to the further reaction. So $Al_2(SO_4)_3 \cdot 18H_2O$ should be a promising green catalyst for esterifications of carboxylic acids and alcohols.

EXPERIMENTAL

Materials

Ethanol, diethyl ether, 1-butanol, KOH, caprylic acid, chloroactic acid, and benzoic acid were purchased from Tianjin Fuyu Fine Chemicals Industry Co., Ltd (China); cyclohexanol, 2-butanol, *n*-butyric acid and acetic acid—from Tianjin Yuanli Chemical Reagent Co., Ltd (China). $MgSO_4 \cdot 7H_2O$,

[1] The article is published in the original.

Table 1. Esterification of equimolar mixture of stearic acid and 1-octanol catalyzed by various metal salts under solvent-free conditions

Entry	Catalyst	Conversion, %
1	$Al_2(SO_4)_3 \cdot 18H_2O$	94.6
2	$Al_2(SO_4)_3$	95.3
3	$CuSO_4 \cdot 5H_2O$	63.5
4	$ZnSO_4 \cdot 7H_2O$	43.3
5	$MgSO_4 \cdot 7H_2O$	41.1
6	$KAl(SO_4)_2 \cdot 12H_2O$	68.1
7	$Na_2SO_4 \cdot 10H_2O$	40.9
8	$NiSO_4 \cdot 6H_2O$	55.9
9	$LnNO_3 \cdot 6H_2O$	69.9
10	$AlCl_3 \cdot 6H_2O$	75.0
11	$SnCl_4 \cdot 5H_2O$	52.7
12	None	40.8

Note: Reaction condition: molar ratio of stearic acid to 1-octanol 1 : 1, amount of catalyst 10 mol %, reaction time 24 h, temperature 80°C.

$ZnSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, $Na_2SO_4 \cdot 10H_2O$. 3-phenylpropionic acid, isopentanol, isobutanol, and octanoic acid were obtained from Sinopharm Chemical Reagent (China); 1-octanol, 1-pentanol, cinnamic acid, β-phenethyl alcohol, $LnNO_3 \cdot 6H_2O$, $SnCl_4 \cdot 5H_2O$, $NiSO_4 \cdot 6H_2O$, $KAl(SO_4)_2 \cdot 12H_2O$, $AlCl_3 \cdot 6H_2O$, and $Al_2(SO_4)_3 \cdot 18H_2O$, from Beijing Chemicals Reagent Co., Ltd (China); oleic acid, linoleic acid, stearic acid and palmitic acid, from Tianjin Damao Chemicals Reagent Industry Co., Ltd (China). $Al_2(SO_4)_3$ was prepared from $Al_2(SO_4)_3 \cdot 18H_2O$ by calcining to 300°C for 2 h. All chemicals used were of analytical grade and were used without further purification.

Esterification

The esterifications were carried out at atmospheric pressure in a 50 mL two-neck round-bottom flask equipped with a reflux condenser and a thermometer. An equimolar mixture of carboxylic acid and alcohol and 10 mol % catalyst were added into the flask without any solvent and dehydrating agent. The reaction mixture was continuously stirred using a teflon-coated magnetic stirrer for 24 h at 80°C. Paraffin liquid was used as heat conduction medium.

Analysis

After completion of the reaction, the percentage conversion of carboxylic acids was measured by standard titration. The catalyst was separated from product by simple filter. Then the product was dissolved in ethanol–diethyl ether mixture (1 : 2, v/v) and phenolphthalein solution in ethanol (10 g/L) as indicator was added. The titration was performed by means of about 0.1 mol/L KOH solution in ethanol. The volume of KOH solution consumed was recorded, and the percentage conversion of carboxylic acids was calculated using the following expression:

$$\text{Conversion to carboxylic acid} = \left[1 - \frac{V}{V_1 M_1}\right] \times 100\%,$$

where V represents the volume in mL of reaction mixture consumed after completion of the esterification, V_1—the volume of KOH solution in mL consumed by 1 g of carboxylic acid, which was titrated by KOH–ethanol solution solely according to the same method, M_1(g)—the weight of carboxylic acid added into flask.

After the titration, low-boiling solvents and water in the reaction mixture were removed by a rotary evaporator, and the pure esters were obtained by decompression distillation. The product ester structures were confirmed by IR (Varian 800 FT-IR). The IR spectra of some products are presented in Appendix.

The analytical procedures are described in publications [26–29].

Reuse of the Catalyst

The recycle performance of catalyst $Al_2(SO_4)_3 \cdot 18H_2O$ was researched by esterification of stearic acid and 1-octanol under identical conditions. The $Al_2(SO_4)_3 \cdot 18H_2O$ catalyst filtered was reused to catalyze the further esterification without any further treatment. The same amount of carboxylic acid, alcohol and catalyst were used for each of the recycled esterification.

RESULTS AND DISCUSSION

Catalytic Activities of Various Metal Salts in Esterification

The results of testing of various metal salts catalysts in the esterification of stearic acid with 1-octanol as typical substrates are summarized in Table 1. To develop green chemistry, stearic acid and 1-octanol reacted without using any solvent and agent. By comparing various metal salts, it can be found that $Al_2(SO_4)_3 \cdot 18H_2O$ and $Al_2(SO_4)_3$ are the most efficient catalyst to esterification. Furthermore, catalytic activity of $Al_2(SO_4)_3$ appreciably excel over $Al_2(SO_4)_3 \cdot 18H_2O$ (95.3 and 94.6%, respectively). We consider that the distinction should be attributed to $Al_2(SO_4)_3$ absorbability to water. Anhydrous $Al_2(SO_4)_3$ can adsorb water formed during esterification from product ester and shift the equilibrium towards product side. However, conversions on other metal salts such as $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, $MgSO_4 \cdot 7H_2O$, $KAl(SO_4)_2 \cdot 12H_2O$, $Na_2SO_4 \cdot 10H_2O$, $NiSO_4 \cdot 6H_2O$, $LnNO_3 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$, and $SnCl_4 \cdot 5H_2O$ are evidently low comparing to that on $Al_2(SO_4)_3 \cdot 18H_2O$ and $Al_2(SO_4)_3$ under the same conditions. Although

Table 2. $Al_2(SO_4)_3 \cdot 18H_2O$ catalyzed esterifications of linear carboxylic acids and alcohols

Entry	Carboxylic acid	Alcohol	Conversion, %
1	$CH_3(CH_2)_{16}COOH$	$CH_3(CH_2)_6CH_2OH$	94.6
2	$CH_3(CH_2)_{16}COOH$	$CH_3CH_2CH_2CH_2OH$	90.2
3	$CH_3(CH_2)_{14}COOH$	$CH_3(CH_2)_6CH_2OH$	91.6
4	$CH_3(CH_2)_{16}COOH$	CH_3CH_2OH	82.7
5	$CH_3(CH_2)_6COOH$	$CH_3(CH_2)_6CH_2OH$	86.5
6	CH_3COOH	$CH_3(CH_2)_6CH_2OH$	83.2
7	CH_3COOH	CH_3CH_2OH	76.1

Note: Reaction condition: molar ratio of carboxylic acid to alcohol 1 : 1, amount of catalyst 10 mol %, reaction time 24 h, temperature 80°C.

both $Al_2(SO_4)_3$ and $Al_2(SO_4)_3 \cdot 18H_2O$ have excellent catalytic activity, the preparation of $Al_2(SO_4)_3$ is troubled and it is more expensive than $Al_2(SO_4)_3 \cdot 18H_2O$. So we deep investigate $Al_2(SO_4)_3 \cdot 18H_2O$ catalyzed esterifications of carboxylic acids and alcohols.

Esterifications of Linear Carboxylic Acids and Alcohols

The reaction was examined with structurally diversed fatty carboxylic acids and alcohols as shown in Table 2. For linear carboxylic acids and alcohols, esterifications catalyzed by $Al_2(SO_4)_3 \cdot 18H_2O$ can be smoothly carried out with moderate to excellent yield. Long chain fatty compounds generally prepared using acyl chlorides [30]. They are esterified with over 90% conversion (entries 1–3). Conversions of short chain linear substrates are relative low compared to that of long chain fatty substrates (entries 4–7).

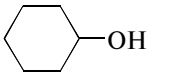
Esterification of Hindered Alcohols and Carboxylic Acids

The esterifications of various hindered alcohols with stearic acid $CH_3(CH_2)_{16}COOH$ catalyzed by $Al_2(SO_4)_3 \cdot 18H_2O$ are also investigated under the same condition as shown in Table 3. The results indicate that the conversion of hindered alcohols (entry 1), especially tertiary alcohols, are distinctly low as compared to that of primary alcohol. The conversion of stearic acid and tertiary butyl alcohol is only 9.4% even after prolonged reaction time 48 h (entry 3). The low conversion should be attributed to the alcohols' strong steric hindrance. The conversion of cyclohexanol and octanoic acid is up to 67.8% for 24 h (entry 2), which is better than that of 2-butanol because the close alkyl chain reduces steric hindrance. The conversion of *iso*-amyl alcohol catalyzed by $Al_2(SO_4)_3 \cdot 18H_2O$ can be up to 91.3% under the same condition (entry 4), and it indicates that hindrance effect of the methyl group is not obvious to esterification.

Esterifications of Substrates with Functional Groups

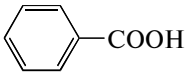
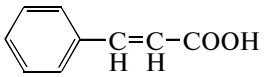
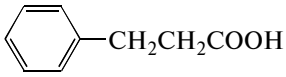
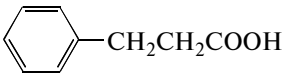
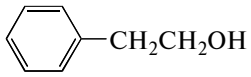
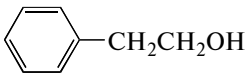
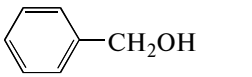
Additionally, we investigated the $Al_2(SO_4)_3 \cdot 18H_2O$ catalyzed esterifications of substrates with functional groups such as chlorines, double bonds, and phenyl groups under solvent-free condition as shown in Table 4. For esterifications of benzoic and cinnamic acids (entries 1, 2), conversions are only 50.3 and 65.6%, respectively. The low conversions should be attributed to the conjugation effect of the carbonyl and ethylene or phenyl groups, which increase stability of the carbonyl and go against formation of tetrahedral intermediate. However, for 3-phenylpropionic acid in which carboxylic carbonyl can not conjugate with phenyl, the conversion is over 90% (entries 3, 4). Therefore, esterificaton of 3-phenylpropionic acid is not affected by phenyl group. Esterifications of stearic acid with β-phenethyl alcohol and benzyl alcohol give over 90% conversions (entries 5, 6). It indicates that phenyl also does not affect on esterification activity of alcohol in which hydroxyl group does not directly link phenyl group. Esterifications of oleic acid and linoleic acid (entries 7, 8), where double bonds arc away from the carboxylic acid group, with 1-octanol give excellent conversion under the same condition. It shows that the effect of the double bond on the esterifications is negligible. Chloroactic acid can smoothly react with 1-octanol and gives 89.2% conversion (entry 9). The

Table 3. $Al_2(SO_4)_3 \cdot 18H_2O$ catalyzed esterification of hindered alcohols with stearic acid

Entry	Reaction time, h	Alcohol	Conversion, %
1	24	$CH_3CH_2CH(OH)CH_3$	54.2
2	24		67.8
3	48	$(CH_3)_3COH$	9.4
4	24	$(CH_3)_2CH_2CH_2CH_2OH$	91.3

Note: Reaction condition: molar ratio of carboxylic acid to alcohol 1 : 1, amount of catalyst 10 mol %, temperature 80°C.

Table 4. $Al_2(SO_4)_3 \cdot 18H_2O$ catalyzed esterifications of substrates with functional groups

Entry	Carboxylic acid	Alcohol	Conversion, %
1		$CH_3(CH_2)_3CH_2OH$	50.3
2		$CH_3(CH_2)_6CH_2OH$	65.6
3		$CH_3(CH_2)_6CH_2OH$	90.6
4			91.2
5	$CH_3(CH_2)_{16}COOH$		93.6
6	$CH_3(CH_2)_{16}COOH$		90.1
7	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	$CH_3(CH_2)_6CH_2OH$	91.2
8	$CH_3(CH_2)_4CH{=}CHCH_2{-}CH{=}CH(CH_2)_7COOH$	$CH_3(CH_2)_6CH_2OH$	92.0
9	$ClCH_2COOH$	$CH_3(CH_2)_6CH_2OH$	89.2
10	$CH_3(CH_2)_{16}COOH$	$ClCH_2CH_2OH$	68.7

Note: Reaction condition: molar ratio of carboxylic acid to alcohol 1 : 1, amount of catalyst 10 mol %, reaction time 24 h, temperature 80°C.

excellent conversion should be attributed to the pull inductivity of the chlorine, which increase positive charge of the carbonyl carbon and favor form of tetrahedral intermediate. For 2-chloroethanol (entry 10), the 68.7% conversion of stearic acid is attributed to the pull inductivity of the chlorine, which decrease the alcohols' nucleophilicity.

Reusability of Catalyst $Al_2(SO_4)_3 \cdot 18H_2O$

In order to investigate the recycle performance of $Al_2(SO_4)_3 \cdot 18H_2O$ catalyst, a recycle esterification of stearic acid and 1-octanol under the same condition was conducted. The same amounts of oleic acid and 1-octanol were used for each of the recycled esterifications. As shown in Table 5, in the first recycle conversion decrease from 94.6 to 85.3%. It shows that the activity of $Al_2(SO_4)_3 \cdot 18H_2O$ catalyzed esterification slightly declines. The conversion does not further decrease in the second and third recycles. The catalyst $Al_2(SO_4)_3 \cdot 18H_2O$ is easily separated from the reaction system by simple filtration. These results indicate that $Al_2(SO_4)_3 \cdot 18H_2O$ can be expediently recycled without special treatment, such as calcination or rinse.

Table 5. Reusability of catalyst $Al_2(SO_4)_3 \cdot 18H_2O$ for esterification of equimolar mixture of stearic acid and 1-octanol

Number of cycle	Conversation, %
Fresh catalyst	94.6
1	85.3
2	85.2
3	85.3

Note: Amount of catalyst 10 mol %, reaction time 24 h, temperature 80°C.

Effect of Various Reaction Conditions on Esterifications

In order to research effect of reaction variables on the esterifications and optimize reaction condition, the solvent-free esterification of stearic acid and 1-octanol as typical substrates catalyzed by $Al_2(SO_4)_3 \cdot 18H_2O$ was carried out under various conditions.

As shown in Table 6, when the amount of alcohol is doubled regarding to carboxylic acid, conversion increases slightly (entry 2). It shows that effect of molar ratio of carboxylic acid and alcohol on esterification is insignificant. The esterifications can smoothly process in equimolar mixture of carboxylic acid and alcohol.

Table 6. Effect of various reaction conditions on esterifications catalyzed by $Al_2(SO_4)_3 \cdot 18H_2O$

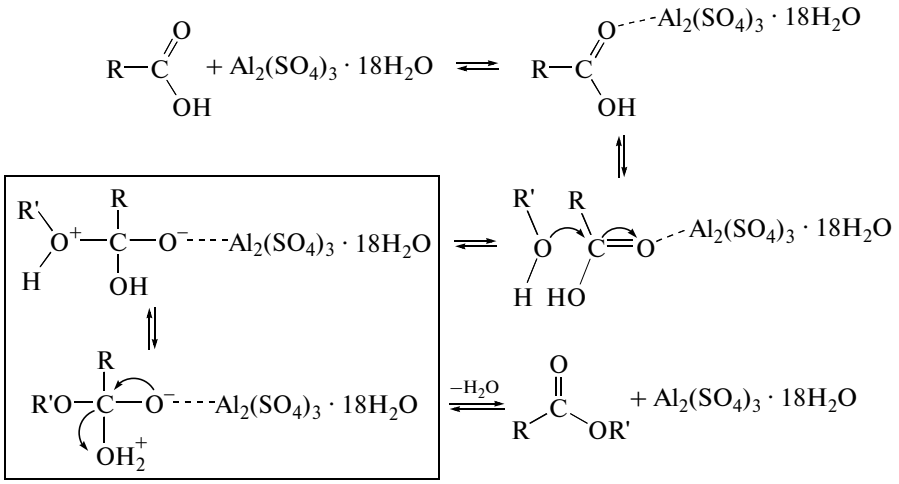
Entry	Carboxylic acid : alcohol (mol/ratio)	Catalyst amount, mol %	Temperature, °C	Time, h	Conversion, %
1	1 : 1	10	80	24	94.6
2	1 : 2	10	80	24	95.2
3	1 : 1	10	70	24	79.7
4	1 : 1	10	90	24	96.1
5	1 : 1	5	80	24	72.4
6	1 : 1	15	80	24	95.5
7	1 : 1	10	80	18	86.3
8	1 : 1	10	80	30	95.9

It is well known that temperature is a key factor for organic chemical reaction. Similarly, temperature can evidently influence on the esterifications: when reaction temperature is 70°C (entry 3), conversion (79.7%) is obviously lower than at 80°C (94.6%). When temperature is 90°C, the conversion only adds up to 96.1% (entry 4). It indicates that 80°C is appropriate reaction temperature. When temperature is below 80°C, conversion decreases; when temperature is over 80°C, energy is waste.

Effect of catalyst amount on reaction is also investigated. When amount of catalyst $Al_2(SO_4)_3 \cdot 18H_2O$ used is 5, 10, and 15 mol %, reaction conversions are 72.4, 94.6, and 95.5%, respectively (entries 5, 1, and 6). The increasing of amount of catalyst used over 10 mol %, weakly raise the conversion. When amount of catalyst used is below 10 mol %, decreasing of reaction conversion is evident. 10 mol % should be an appropriate amount.

We further investigated effect of reaction time on the conversion under fixed other conditions (entries 7, 8). The conversion evidently increases from 86.3 to 94.6% when reaction time is prolonged from 18 to 24 h. However, when reaction time is prolonged from 24 to 30 h, the increasing of conversion is only 1.3%. It shows that the esterification is basically close to balance for 24 h. So, we think that optimum condition of the esterification should be as follows: 1 : 1 molar ratio of carboxylic acid to alcohol, 10 mol % of $Al_2(SO_4)_3 \cdot 18H_2O$ catalyst, 24 h reaction time and 80°C reaction temperature.

Solid Lewis acids such as Cu^{2+}, Mg^{2+}, Al^{3+}, and Zr^{2+} have been used as catalysts for esterification in a few works [31–33]. Barbosa et al. provided a plausible mechanism for esterification reaction on $SiO_2/ZnCl_2$ [21]. Based on previous works, we presume the mechanism of $Al_2(SO_4)_3 \cdot 18H_2O$ catalyzed esterifications of carboxylic acids and alcohols as shown in Scheme 1.



Scheme 1. Proposed mechanism of esterification catalyzed by $Al_2(SO_4)_3 \cdot 18H_2O$.

This mechanism is described as follows: the carbonyl oxygen of the carboxylic group combines with $Al_2(SO_4)_3 \cdot 18H_2O$ to form an activated complex, which is attacked by the nucleophile alcohol to form a tetrahedral intermediate. The product ester is obtained after the intermediate eliminates water.

The results of our research show that $Al_2(SO_4)_3 \cdot 18H_2O$ can effectively catalyze esterifications of various carboxylic acids and alcohols, including substrate with functional group, such as phenyl, halogen and double bond. The esterification, does not demand any solvent and drier and one of the reactants excess. The $Al_2(SO_4)_3 \cdot 18H_2O$ catalyst is a low toxicity, low-cost compound, and is easily separated from the reaction mixture by simple filtration. Moreover, the catalyst can be recycled and the conversion does not evidently decrease. So $Al_2(SO_4)_3 \cdot 18H_2O$ compound should be a promising green catalyst for esterification of carboxylic acids and alcohols.

APPENDIX

IR Spectra of Part Product Esters

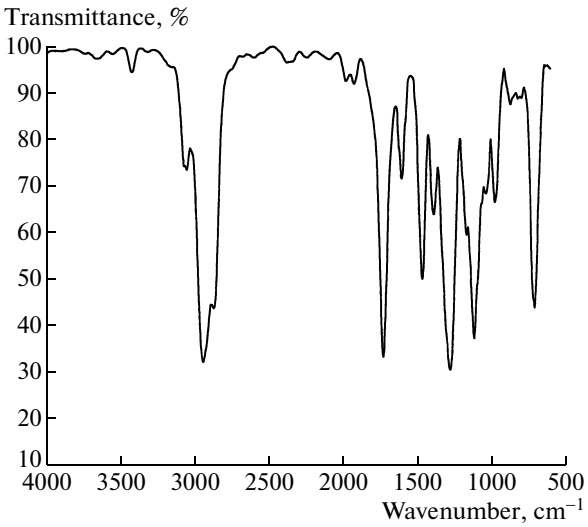


Fig. 1. IR spectrum of 1-amyl benzoate.

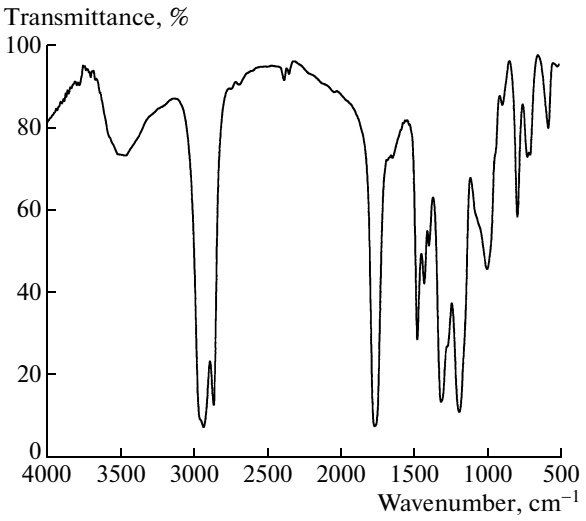


Fig. 2. IR spectrum of 1-octyl chloroacetate.

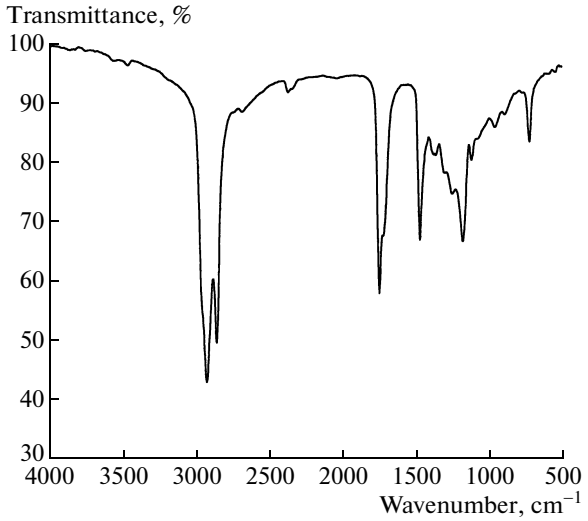


Fig. 3. IR spectrum of 1-octyl stearate.

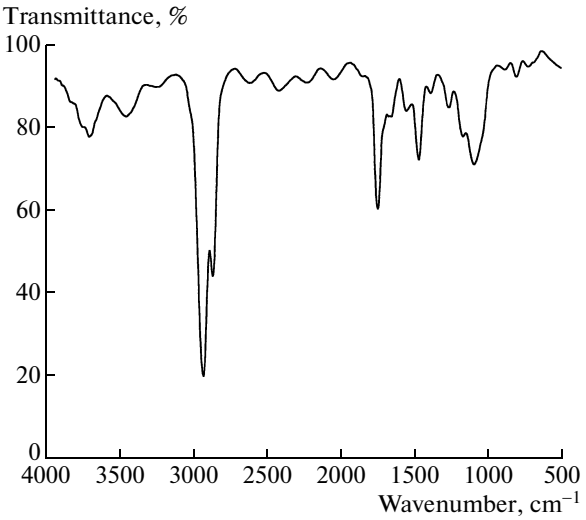


Fig. 4. IR spectrum of 1-octyl oleate.

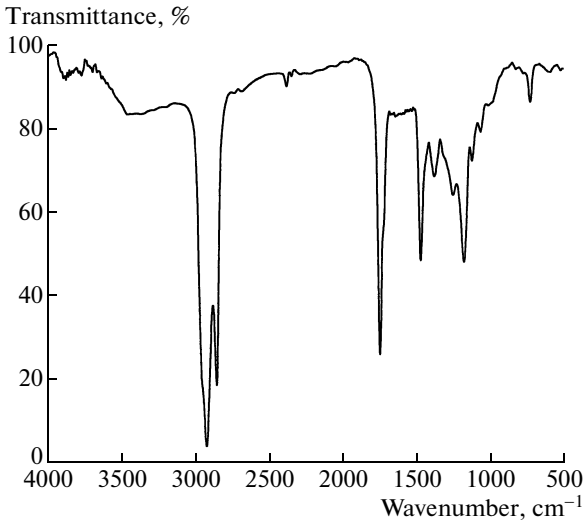


Fig. 5. IR spectrum of isoamyle stearate.

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