

## Research Article

### Preparation and Characterization of Stearyl (L-) Calcium Lactate

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**Abstract:** Domestic production of L-lactic acid is used as raw materials for the preparation of a new anionic emulsifier stearyl (L-) calcium lactate, in an index of the acid value and esters value of emulsifiers. It was studied that the effects of temperature, molar ratio, time and catalyst of four factors on the preparation process stearyl (L-) calcium lactate, with the orthogonal experiment method to determine the optimum conditions. Stearyl (L-) calcium lactate structures were identified by IR. Results of the study show the optimal conditions of stearyl (L-) calcium lactate synthesis: temperature 110°C, the molar ratio of L-lactic acid and stearic acid is 1.8:1, the amount of catalyst is added to account for 1.0%, the reaction time was 2 h. Using the above determined conditions to do validation experiments, the results show that stearyl (L-) calcium lactate esters and acid values are in line with standards, which is an emulsifier with good performance.

**Keywords:** Emulsifier, L-lactic acid, preparation, stearyl (L-) calcium lactate

#### INTRODUCTION

Currently there are emulsifiers commonly used in food sucrose fatty acid ester (Sarcose Fatty Acid Ester), xylitol anhydride stearate (LS-60M), polyoxyethylene stearates xylitol anhydride (LT-60M), Single Monoglycerides (GMS). But in recent years many experiments have shown that some emulsifier anti-aging effect is not ideal.

CSL is a common international food currently an anionic emulsifier (Liu, 1998), has the dual role of strengthening and flexibility in the face of fresh products. The study found that the human body can only metabolize L-lactic acid, so that only L-lactic acid can be absorbed by the body and microorganisms and no harmful effect, it has been proposed World Health Organization does not recommend the use of D- and DL-lactic acid in children's foods. Thus, in the food industry to gradually replace D-L-lactic acid and DL-lactic acid is inevitable (Xu and Zhang, 2002; Zhang, 1993).

In recent years, domestic synthetic methods on food emulsifiers CSL is mainly the "two-step" and "three-step", but the two methods, time-consuming, complicated preparation process, stearyl lactic acid produced calcium products are unstable, easily absorbing moisture, difficult storage and other shortcomings.

Using L-lactic acid, stearic acid and calcium hydroxide as a raw material, concentrated sulfuric acid as a catalyst, synthetic "one-shot" of new technology, made directly stearyl (L-) calcium lactate can be directly used in the food industry. Not only improve the

traditional synthesis, new synthetic method of stearyl (L-) calcium lactate is also raised.

#### MATERIALS AND METHODS

**Determination of the ester value of stearyl (L-) calcium lactate:** Accurately weigh 0.4~0.5 g sample (accurate to 0.0002 g). Two hundred and fifty milliliter bottle placed after esterification, accurate added 50 mL, 0.1 mol/L potassium hydroxide ethanol standard solution, fitted with a reflux condenser basic drying tube, maintain micro-boiling state under reflux for 30 min in a water bath until cool remove the drying tube, rinsed with 5 mL ethanol pipe wall and then added 0.3% cresol red indicator 2~3 drops of potassium hydroxide remaining with 0.1 mol/L hydrochloric acid standard solution titration, drop to disappear is purple end. At the same time a blank test under the same conditions. Ester value is calculated as follows:

$$\text{Ester value (mgKOH/g)} = V \times N \times 56.1 / W - \text{Acid value}$$

where,

V = Actual consumption in ml sample titration standard solution of hydrochloric acid

N = Molar concentration of hydrochloric acid standard solution

W = Weight of sample

56.1 = Molar mass of potassium hydroxide

**Structural identification of stearyl (L-) calcium lactate:** The structural identification of the raw material of stearic acid, L-lactic acid and Stearyl (L-) Calcium Lactate were done by infrared spectral.

Table 1: Relationship between molar ratio and acid value and ester value

Molar ratio	1.6	1.7	1.8	1.9	2.0
Acid value/mg KOH/g	71.24	65.85	69.30	65.27	66.06
Ester value/mg KOH/g	147.16	150.43	160.51	177.61	200.87

Table 2: Relationship between temperature and acid value and ester value

Temperature/°C	95	100	105	110	115
Acid value/mg KOH/g	83.13	81.34	75.97	75.63	66.91
Ester value/mg KOH/g	135.61	143.29	149.26	160.46	178.76

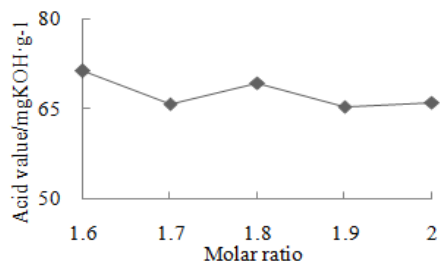


Fig. 1: Relationship between molar ratio and acid value

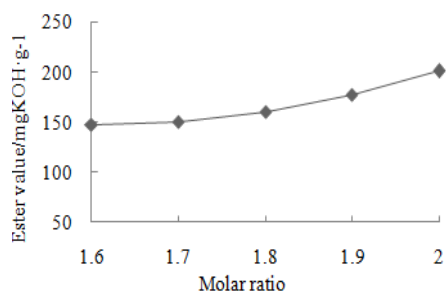


Fig. 2: Relationship between molar ratio and ester value

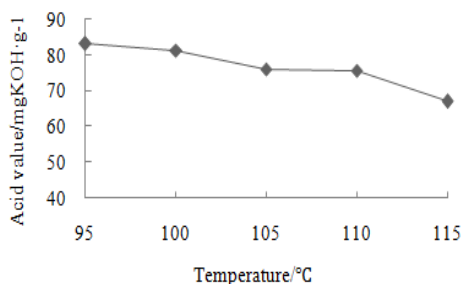


Fig. 3: Effect of temperature on acid value

**Infrared scanning method:** The solid was triturated infrared flash dryer to a fine powder, passed through a 60 mesh screen, infrared scan tablet; liquid wafer scanning after pressed into a sheet.

## RESULTS AND DISCUSSION

**Determination of the optimum synthesis conditions of calcium stearyl (L-) calcium lactate:**

**Effect of the molar ratio of (L-) lactic acid and stearic acid on esterification reaction:** In stearyl (L-) lactate synthesis reaction temperature of 105°C, the amount of catalyst is 1.5%, the reaction time was 4 h, the change L-lactic acid and stearic acid molar ratio, measured after synthesis stearyl (L-) lactate in 1.6 L-

lactic acid molar ratios: 1.7: acid and ester value under the conditions of: 1, 1.8: 1, 1.9: 1, 2.0.

As shown in Table 1 and Fig.1, synthesized stearyl (L-) lactate change L-lactic acid and stearic acid molar ratio, the acid value fluctuations, the reason may be due to all levels stearyl (L-) different calcium lactate finished drying time, drying temperature for a long time a large acid value also increased, so the fluctuations (Zhou *et al.*, 2001).

Table 2 and Fig. 2 shows that the process parameters of reaction temperature 105°C, catalyst dosage 1.5%, reaction time 4 h conditions, stearic acid (L-) lactate ester value mainly due to the molar ratio of L-lactic acid and stearic acid as raw material, the molar ratio is small, stearyl (L-) values low calcium lactate ester, the molar ratio increases, stearyl (L-) values increased lactate ester (Mima and Kitamori, 1964), but the molar ratio of over 1.9: 1 after stearyl (L-) lactate ester value significantly exceeds 200 mgKOH/g, more than the predetermined indicator (ester value of 135~180 mgKOH/g), L-lactic acid and stearyl so the molar ratio of acid control in 1.9: 1 or less is appropriate.

**Effect of reaction temperature on esterification:** The molar ratio of L-lactic acid is 1.8:1, the amount of catalyst is 1.5%, under the conditions of the reaction time was 3 h change stearyl (L-) calcium lactate synthesis reaction temperature, measured after the synthesis of stearyl (L-) calcium lactate at 95, 100, 105, 110°C, respectively acid value and the level value 115°C ester under reaction temperatures.

Table 2, Fig. 3 shows that synthetic stearyl (L-) lactate with increasing reaction temperature, acid value decreased, but the temperature exceeds 115°C. Synthesized stearyl (L-) lactate color was deepened, affecting the quality, so stearyl (L-) lactate synthesis reaction temperature should be below 115°C.

Stearyl (L-) lactate synthesis reaction is carried out from an endothermic reversible reaction chemical equilibrium theory shows favorable reaction at elevated temperatures (Srinivasan *et al.*, 2001), it can be seen from Table 2, Fig. 4, in the mole ratio of 1.8:1, 1.5% of the amount of catalyst, reaction time 3 h under conditions of changing temperature on the reaction of ester value is not obvious, but the temperature is too high will cause product color deepened, affecting stearyl (L-) lactate finished color, so the reaction temperature should be controlled below 110°C, otherwise affect the quality of the product.

**Effect of catalyst dosage on esterification reaction:** L-lactic acid and stearic acid in a molar ratio of 1.8:1, reaction temperature of 105°C, the reaction time of 3 h under the condition, the change in the amount of catalyst, the synthesis of stearyl (L-) calcium lactate, stearyl measured (L-) calcium lactate respectively in the catalyst in an amount of 0.5, 1.0, 1.5, 2.0%, respectively and acid value of the ester 2.5% level.

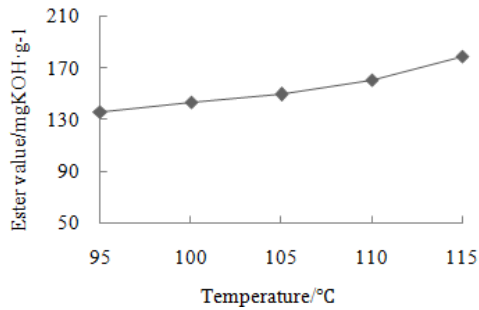


Fig. 4: Relationship between ester value and temperature

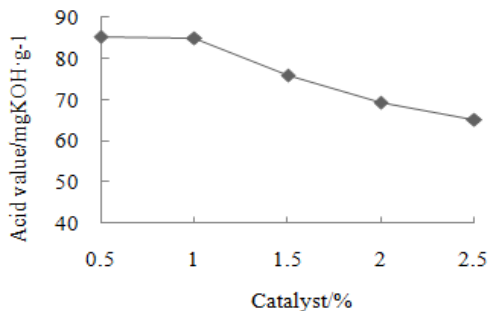


Fig. 5: Effect of catalyst dosage on acid value

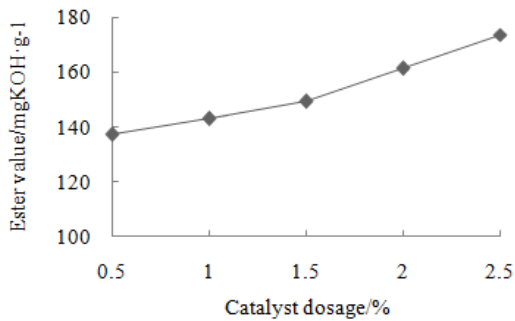


Fig. 6: Relationship between ester value and catalyst

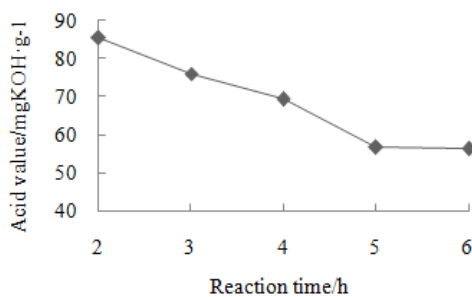


Fig. 7: Relationship between acid value and reaction time

Catalyst dosage/%	0.5	1.0	1.5	2.0	2.5
Acid value/mg KOH/g	85.44	85.11	75.97	69.33	65.27
Ester value/mg KOH/g	137.21	142.94	149.26	161.26	173.61

Reaction time/h	2	3	4	5	6
Acid value/mg KOH/g	85.34	75.97	69.30	56.60	56.26
Ester value/mg KOH/g	135.61	149.26	160.51	174.12	184.98

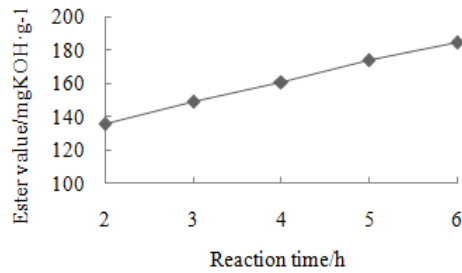


Fig. 8: Relationship between ester value and reaction time

The catalyst is generally added to increase the reaction rate, from Table 3, Fig. 5 shows that with the gradual increase of the amount of catalyst, stearyl (L-) calcium lactate acid value decreases, but the amount of catalyst is greater than 2.0% stearic acid (L-) lactate color black, affecting the quality of the product, so stearoyl (L-) lactate synthesis reaction catalyst should be controlled at 2.0%.

This reaction is an esterification reaction with concentrated sulfuric acid as a catalyst is preferable, from Table 3, Fig. 6 shows that the reaction conditions are the same in other cases, when the amount of catalyst exceeds 2.0%, accelerating the rate of carbon up deepen the color of products, so stearoyl (L-) lactate synthesis, catalyst dosage 2.0% stearic acid quality suitable.

**Effect of reaction time on esterification reaction:** L-lactic acid and stearic acid in a molar ratio of 1.8:1, reaction temperature of 105°C, catalyst dosage 1.5%, the synthesis of stearyl (L-) lactate, measured stearoyl (L-) calcium lactate under the above conditions remain unchanged, the reaction time was 2, 3, 4 and 5 h, respectively when 6 h, acid value and ester value stearoyl (L-) lactate.

Table 4 and Fig. 7 shows, stearyl (L-) lactate synthesis reaction time increases, stearic acid (L-) lactate acid number gradually reduced, but the reaction time is lengthened acid value is not within the specified range (acid value 60~180 mgKOH/g) and the color gradually deepened, affecting the quality of the product, therefore, the reaction time should be less 6 h, as appropriate.

The esterification reaction was carried out entirely or not the reaction time of a great relationship (Zhao *et al.*, 2002), in the case of other conditions are the same, from Table 4 and Fig. 8 shows, when stearyl (L-) lactate synthesis reaction time gradually extended when, ester value significantly increased, when the reaction time is more than 5 h, the ester is greater than 180 mgKOH/g, more than the standard used, therefore, stearyl (L-) calcium lactate synthesis reaction time is preferably 6 h or less.

**Test of optimal reaction conditions:**

**Determination of the optimal levels of acid value and ester value in stearyl (L-) lactate synthesis:** From the

Table 5: Levels and factors of L<sub>16</sub> (4<sup>5</sup>) orthogonal test

Levels	A	B	C	D
	Molar ratio	Temperature /°C	Catalyst dosage/%	Reaction time/h
1	1.6	95	0.5	2
2	1.7	100	1.0	3
3	1.8	105	1.5	4
4	1.9	110	2.0	5

Table 6: L<sub>16</sub> (4<sup>5</sup>) orthogonal experiment acid value result

Level	A	B	C	D	Acid value /mg KOH/g
1	1 (1.6)	1 (95)	1 (0.5)	1 (2)	95.72
2	1 (1.6)	2 (100)	2 (1.0)	2 (3)	85.17
3	1 (1.6)	3 (105)	3 (1.5)	3 (4)	71.42
4	1 (1.6)	4 (110)	4 (2.0)	4 (5)	54.36
5	2 (1.7)	1 (95)	2 (1.0)	3 (4)	51.13
6	2 (1.7)	2 (100)	1 (0.5)	4 (5)	53.19
7	2 (1.7)	3 (105)	4 (2.0)	1 (2)	46.96
8	2 (1.7)	4 (110)	3 (1.5)	2 (3)	86.71
9	3 (1.8)	1 (95)	3 (1.5)	4 (5)	52.69
10	3 (1.8)	2 (100)	4 (2.0)	3 (4)	47.75
11	3 (1.8)	3 (105)	1 (0.5)	2 (3)	73.77
12	3 (1.8)	4 (110)	2 (1.0)	1 (2)	50.41
13	4 (1.9)	1 (95)	4 (2.0)	2 (3)	50.43
14	4 (1.9)	2 (100)	3 (1.5)	1 (2)	90.12
15	4 (1.9)	3 (105)	2 (1.0)	4 (5)	56.14
16	4 (1.9)	4 (110)	1 (0.5)	3 (4)	71.04
K <sub>1</sub>	306.67	249.97	293.72	241.85	
K <sub>2</sub>	237.99	276.23	242.85	297.08	
K <sub>3</sub>	224.63	248.29	300.94	241.34	
K <sub>4</sub>	267.73	262.52	199.50	216.38	
k <sub>1</sub>	76.668	62.492	73.430	70.803	T = 1037.01
k <sub>2</sub>	59.489	69.058	60.713	74.020	$\bar{x}$ = 64.81
k <sub>3</sub>	56.155	62.072	75.235	60.335	
k <sub>4</sub>	66.933	65.030	49.875	54.095	
R	20.153	6.986	25.360	19.925	
Optimal levels	A <sub>2</sub>	B <sub>4</sub>	C <sub>1</sub>	D <sub>3</sub>	

Table 7: L<sub>16</sub> (4<sup>5</sup>) orthogonal experiment ester value result

Level	A	B	C	D	Ester value /mg KOH/g
1	1 (1.6)	1 (95)	1 (0.5)	1 (2)	104.51
2	1 (1.6)	2 (100)	2 (1.0)	2 (3)	172.48
3	1 (1.6)	3 (105)	3 (1.5)	3 (4)	160.51
4	1 (1.6)	4 (110)	4 (2.0)	4 (5)	222.33
5	2 (1.7)	1 (95)	2 (1.0)	3 (4)	167.77
6	2 (1.7)	2 (100)	1 (0.5)	4 (5)	195.22
7	2 (1.7)	3 (105)	4 (2.0)	1 (2)	195.17
8	2 (1.7)	4 (110)	3 (1.5)	2 (3)	175.48
9	3 (1.8)	1 (95)	3 (1.5)	4 (5)	207.95
10	3 (1.8)	2 (100)	4 (2.0)	3 (4)	223.63
11	3 (1.8)	3 (105)	1 (0.5)	2 (3)	162.76
12	3 (1.8)	4 (110)	2 (1.0)	1 (2)	164.24
13	4 (1.9)	1 (95)	4 (2.0)	2 (3)	175.68
14	4 (1.9)	2 (100)	3 (1.5)	1 (2)	144.41
15	4 (1.9)	3 (105)	2 (1.0)	4 (5)	189.45
16	4 (1.9)	4 (110)	1 (0.5)	3 (4)	173.44
K <sub>1</sub>	659.83	655.91	635.93	608.33	
K <sub>2</sub>	733.64	735.74	693.94	686.40	
K <sub>3</sub>	758.58	707.89	688.35	725.35	
K <sub>4</sub>	682.98	735.49	816.81	814.95	T = 2835.03
k <sub>1</sub>	164.958	163.978	158.983	152.083	$\bar{x}$ = 177.19
k <sub>2</sub>	183.410	183.935	173.485	171.600	
k <sub>3</sub>	189.645	176.972	172.088	181.337	
k <sub>4</sub>	170.745	183.873	204.202	203.738	
R	24.687	19.957	45.219	51.655	
Optimal levels	A <sub>3</sub>	B <sub>4</sub>	C <sub>2</sub>	D <sub>1</sub>	

above discussion of individual factors variables to determine the acid value and ester value index factors and orthogonal experiment to determine the following

L<sub>16</sub> (4<sup>5</sup>) orthogonal design factor level in Table 5 and L<sub>16</sub> (4<sup>5</sup>) orthogonal test acid the value of the results in Table 6 and L<sub>16</sub> (4<sup>5</sup>) orthogonal test ester value results shown in Table 7.

Table 6 shows that the optimal reaction conditions for the orthogonal experiment L-lactic acid value stearic acid molar ratio of 1.7:1, reaction temperature was 110°C, the catalyst was 0.5%, reaction time 4 h, which the reaction catalyst for the greatest impact, the impact is minimal amount of catalyst.

According to Table 7 shows the results of the orthogonal experiment, the optimal reaction conditions for the orthogonal experiment molar ratio of 1.8:1, reaction temperature was 110°C, the amount of catalyst is 1.0%, the reaction time was 2 h, where the greatest impact on the reaction of the reaction time and the smallest is the amount of catalyst.

According to the product effect of practical application proved that the ester value, acid value, the impact to product application effect is larger, especially the ester value, its value is too high or too low will affect the product in the emulsifying properties of dough (Zhu and Chen, 2003), in bread production, can cause the bread organization close enough, poor flexibility, so that the specific volume of bread quality indicators owes and small faults, so the ester value as the main indicator of measuring the quality of the products (Liu *et al.*, 2001). So, the best synthetic reaction conditions to determine the optimal reaction conditions for the ester value.

**Verification experiment:** Determined by orthogonal experiments superior level: the molar ratio of L-lactic acid and stearic acid is 1.8: 1, reaction temperature was 110°C, the amount of catalyst is 1.0%, the reaction time was 2 h, do the verification test, the results show, acid value, ester value are within a predetermined range, to meet the requirements.

**Structural identification of stearyl (L-) calcium lactate:** From peaks in Fig. 9 to 11, the structure of stearyl (L-) lactate can be identified, indicating that this material is stearyl (L-) lactate.

Figure 9 and 10 are infrared spectrums of stearic acid and L-lactic acid as material respectively, Fig. 11 is a IR spectra of synthetic product stearyl (L-) calcium lactate, the three diagrams comparison shows that the product spectrum hydroxy L-lactic acid (3500 cm<sup>-1</sup>) the disappearance of the absorption peak, resulting in a very weak carbonyl group (3450 cm<sup>-1</sup>) esters overtone peaks and the carbonyl peak (1720 cm<sup>-1</sup>) and carbonyl peak (1580 cm<sup>-1</sup>) appears carbonyl carboxylic ester carbonyl bee. And stearic acid carbonyl peak shifts to longer wavelengths count proved reactant has been converted to product ester, to give the desired product.

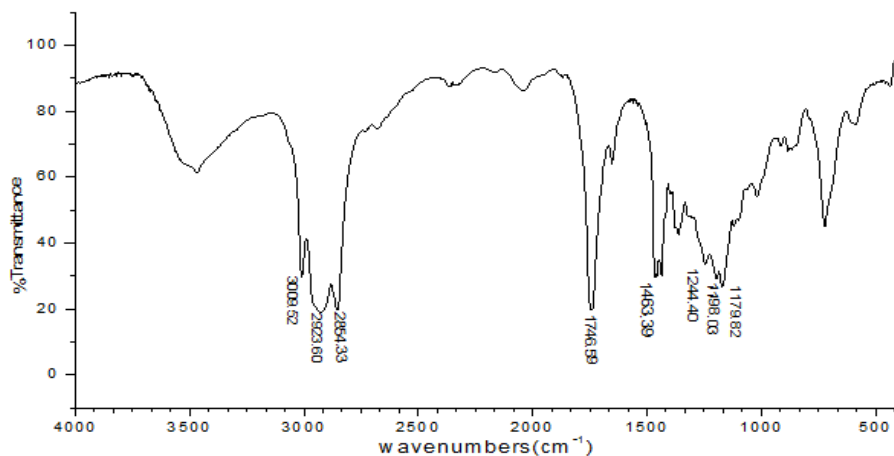


Fig. 9: Infrared spectrogram of stearic acid

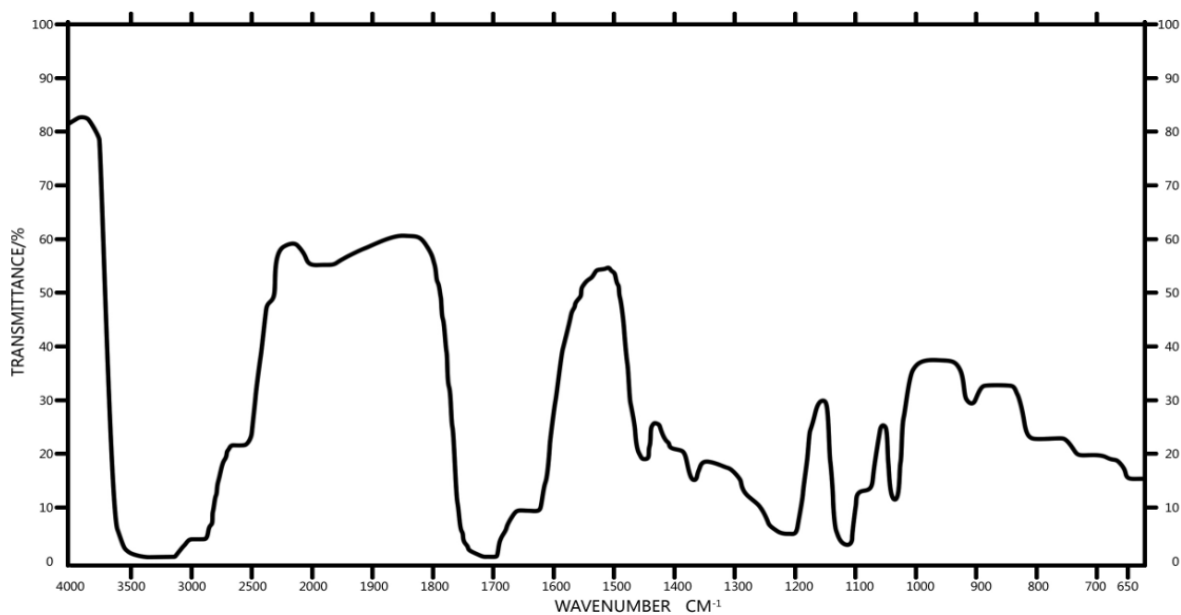


Fig. 10: Infrared spectrogram of L-lactic acid

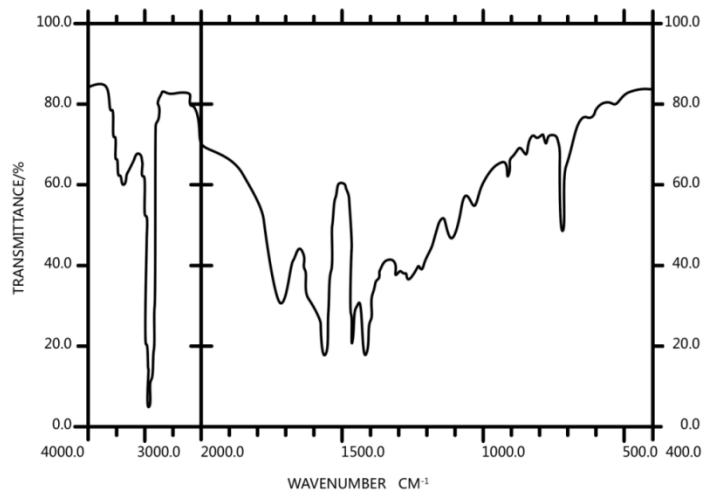


Fig. 11: Infrared spectrogram of stearyl (L-) calcium lactate

## CONCLUSION

Through the above single factor experiment, the optimum conditions of the synthesis of stearyl (L-) calcium lactate was determined by orthogonal experiment, the molar ratio of L-lactic acid and stearic acid is 1.8:1, reaction temperature 110°C, catalyst amount was 1.0%, the reaction time was 2 h. Determined using the above conditions do validation experiments, the results show that stearyl (L-) calcium lactate esters and acid values are in line with standards and determine its structure by infrared spectrophotometry, IR spectra show that this substance is stearyl (L-) calcium lactate. Experimental results show that stearyl (L-) calcium lactate is an emulsifier with good performance.

## ACKNOWLEDGMENT

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