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160. Kazuya Kunugi : Deacidification of Sucrose Fatty Acid Ester by Treatment with Ion Exchange Resins.

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Since sucrose fatty acid esters were permitted for food-additives in Dec. 1959 in this country, interests about these compounds were increased in their application to food emulsifiers. Although Osipow, *et al.*[1] developed the process of syntheses of these compounds, there still remained some problems in the process of purification. For instance, the elimination of dimethylformamide, used as a solvent in the syntheses or the elimination of free fatty acid or soap formed by side-reaction, is preferable.

Of the latter problem, the acid value of final product must be less than five according to the standard specifications for food-additives in Japan, and it is apparent that the less acid value is the more preferable. In many cases an acid value of a raw product of sucrose ester is more than five.

The process in synthesis of sucrose ester developed by Osipow, *et al.* is application of alcoholysis of fatty acid ester of volatile alcohol, *e.g.*, methyl stearate, by sucrose. In this process, relatively large amount of basic catalyst, *e.g.*, potassium carbonate, is used and, as a result of side-reaction, soap is formed. Furthermore, by neutralisation of basic catalyst after reaction, a part of the soap is converted to fatty acid, and then, the soap and free acid are mixed in the product.

In the present work, the author attempted to investigate the method of deacidification[*2] of sucrose ester by treatment with ion exchange resins. Owing to their surface activities, it is very difficult to remove soap or fatty acid from sucrose ester by usual method. For instance, a trial to filter off an insoluble calcium salt of fatty acid from aqueous solution of product was not successful, because considerable amount of calcium salt was solubilized in the solution of sucrose ester.

From the view-point that sucrose ester is nonionic and, soap or fatty acid is ionic compound, it seems to be possible to eliminate soap or fatty acid by ion exchange resins. In this case, however, there are another difficulties that non-aqueous solvent must be used. As the aqueous solution of sucrose fatty acid ester with an adequate concentration is very viscous, it is not suitable for treatment with ion exchange resins. Although the application of non-aqueous solution for treatment with ion exchange resins is relatively undeveloped, Inoue[2] reported that deacidifications of oil and fats were carried out effectively in non-aqueous solution by ion exchange and the presence of polar solvent, *e.g.*, methanol, was preferable.

Butanol was good solvent for sucrose fatty acid ester, and the author investigated of butanol solution.

As the soap and free fatty acid were mixed in raw product, it was considered to use both anion and cation exchange resins. In this case, since the first application of anion exchange resin caused the formation of alkali, *e.g.*, potassium hydroxide, and soap was again formed by saponification of sucrose ester, cation exchange resin must be applied at first.

The butanol solution of raw product of sucrose ester was treated with cation and then anion exchange resin in batch process during a various period. The butanol

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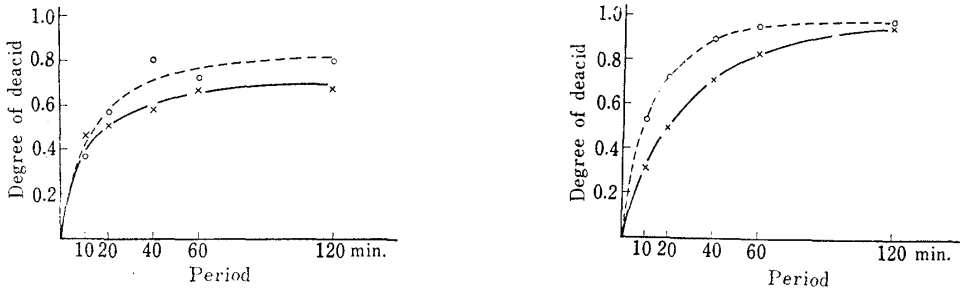
*2 In this paper, "deacidification" means the removal of soap as well as free fatty acid.

1) L. Osipow, *et al.* : Ind. Eng. Chem., 48, 1459 (1956).

2) H. Inoue : Yukagaku 8, 402 (1959).

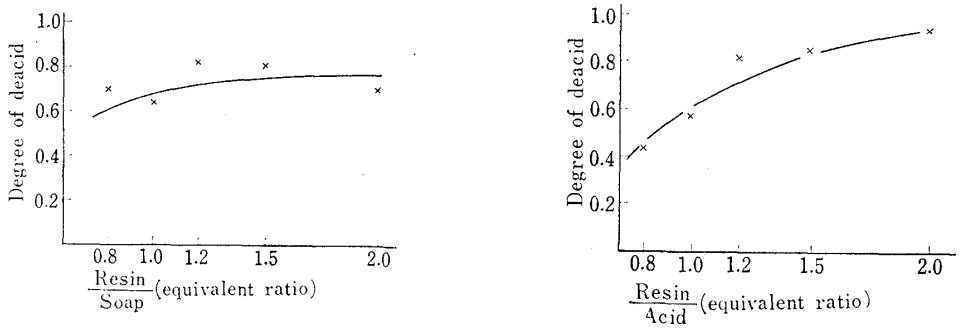
contained water was also applied. The experimental results were shown in Fig. 1. To obtain satisfactory result, the treatment should be continued for one hour or more. With cation exchange resin, maximum degree of deacidification obtained was 70~80%, but with anion exchange resin, it reached to 97%. Water blended in the solvent was effective to accelerate the velocity of exchange.



(a) By cation exchange (b) By anion exchange

×—× in BuOH (Exper. No. 1)
○---○ in BuOH contained H_2O (5%) (Exper. No. 2)

Fig. 1. Effect of Period on the Deacidification of Sucrose Ester



(a) By cation exchange (b) By anion exchange

Fig. 2. Effect of Resin Amount on the Deacidification of Sucrose Ester in BuOH (Exper. No. 3~7)

The effect of the amount of exchange resin was also tested. Results obtained at various ratios of resin/soap or acid in batch process were given in Fig. 2. In cation exchange, an equivalent or slightly more resin to soap was enough to obtain the maximum degree of deacidification. In anion exchange, 1.5~2.0 times of resin in equivalency to fatty acid was necessary for satisfactory results.

A test of continuous removal of soap and fatty acid by mixed bed consisted of both resins gave unsuccessful results. It was regarded that the failure in this process was due to the decrease of the effect by formation of alkali and soap with anion exchange mentioned above. Therefore, it seemed that cation and anion exchange resins must be applied succeedingly in the process.

The soap can be converted to fatty acid by neutralising with acid, *e.g.*, hydrochloric acid, equivalent to the soap. The solution, in which the soap was converted to fatty acid by neutralisation and resulted salt, *e.g.*, potassium chloride, was washed out with water gently, and was treated with anion exchange resin, to obtain the best result. In this process, considerable amount of water solubilized in the solution was regarded to be effective.

It was concluded that the deacidification of sucrose ester was able to be carried out by treatment with ion exchange resins in non-aqueous solvent such as butanol. In this work, decoloration of sucrose ester by ion exchange resins was also observed.

Table I. Experimental Conditions in the Cation Exchange

Exper. No.	Content of soap (w%)	Content of fatty acid (w%)	Concentration of sucrose ester (w/v%)	Amount of the solution (cc.)	Amount of resin (g.)	Solvent	Period (hr.)
1	4.46	6.79	10.04	500	2.6	BuOH	various
2	2.48	8.29	12.0	570	1.9	BuOH-H_2O (5%)	〃
3～7	4.19	8.23	7.91	80	various	BuOH	1

Table II. Experimental Conditions in the Anion Exchange

Exper. No.	Content of fatty acid (w%)	Amount of the solution (cc.)	Amount of resin (g.)	Solvent	Period (hr.)
1	9.85	430	15.5	BuOH	various
2	9.55	490	19.5	BuOH-H_2O (5%)	〃
3～7	11.61	80	various	BuOH	1

Table III. Effect of Period on the Deacidification of Sucrose Ester by Ion Exchange in BuOH (Exper. No. 1)

Cation exchange			Anion exchange		
Period (min.)	Content of soap (w%)	Degree of deacid.	Period (min.)	Content of fatty acid (w%)	Degree of deacid.
original	4.46		original	9.85	
10	2.54	0.431	10	6.75	0.315
20	2.14	0.520	20	4.94	0.498
40	1.83	0.590	40	2.82	0.713
60	1.48	0.668	60	1.69	0.829
120	1.43	0.680	120	0.34	0.966

Table IV. Effect of Period on the Deacidification of Sucrose Ester by Ion Exchange in BuOH contained Water (5%) (Exper. No. 2)

Cation exchange			Anion exchange		
Period (min.)	Content of soap (w%)	Degree of deacid.	Period (min.)	Content of fatty acid (v%)	Degree of deacid.
original	2.48		original	9.55	
10	1.57	0.367	10	4.65	0.513
20	1.08	0.565	20	2.76	0.720
40	0.50	0.799	40	1.01	0.894
60	0.69	0.722	60	0.48	0.950
120	0.50	0.799	120	0.23	0.976

Table V. Effect of Resin Amount on the Deacidification of Sucrose Ester by Ion Exchange in BuOH (Exper. No. 3～7)

Exper. No.	Cation exchange			Anion exchange		
	Resin/Soap equivalent ratio	Content of soap (w%)	Degree of deacid.	Resin/Acid equivalent ratio	Content of fatty acid (w%)	Degree of deacid.
original		4.19			11.61	
3	0.8	1.25	0.701	0.8	6.45	0.444
4	1.0	1.50	0.643	1.0	4.96	0.571
5	1.2	0.75	0.820	1.2	4.04	0.823
6	1.5	0.79	0.811	1.5	1.78	0.845
7	2.0	1.25	0.701	2.0	0.79	0.931

Experimental

Ion Exchange Resins——Cation exchange resin used was Dowex 50 WX8 (50～100 mesh) and anion exchange resin used was Dowex 1 X8 (20～30 mesh). These resins were converted to H-type and OH-type respectively by ordinary method, dried up to constant weight by IR drying (at about 60° of surface temperature) and reserved in desiccator.

The capacities of these resins determined were as the following :

Dowex 50 WX8 : 4.13 meq./g.

Dowex 1 X8 : 1.57 meq./g.

Sucrose Ester——Sucrose esters with relatively high acid values were used, which were synthesized by the alcoholyses of methyl ester of mixed fatty acid with sucrose. The mixed fatty acid was obtained from tallow, which was consisted of stearic acid and palmitic acid. The average molecular weight of the mixed fatty acid was 275.

These sucrose esters contained about 75～80% of mono acyl esters.

Treatment with Cation Exchange Resin——To the solution of sucrose ester, Dowex 50 WX8 was added, and the system was stirred at 50°. At a certain period, an aliquot of the solution was pipetted out, and after removal of the solvent the contents of potassium soap and fatty acid in dried product were determined. The content of soap and fatty acid in original sucrose ester, the concentration of sucrose ester in the solution, the amounts of the solution and the resin, the solvent used, and the period of ion exchange were given in Table I.

The experimental results were shown in Tables III, IV, V, Figs. 1 and 2. In these Tables and Figures, the "degree of deacid." represented the following value :

$$\text{degree of deacid.} = \frac{\text{the amount of soap or fatty acid removed (\%)}}{\text{the content of soap or fatty acid in original sample (\%)}}$$

Treatment with Anion Exchange Resin——Dowex 1X8 was added to the solution of sucrose ester, which was treated with cation exchange resin in the corresponding experiment. The determination of the content of fatty acid was carried out in the manner similar to the case of cation exchange. Experimental conditions were given in Table II, in which an experimental number corresponded to the same one in Table I.

The experimental results were shown in Tables III, IV, V, Figs. 1 and 2.

Treatment with Hydrochloric Acid and Anion Exchange Resin——Sucrose ester, in which the content of potassium soap was 3.64% and the content of free fatty acid was 8.71%, was dissolved in BuOH. To 200 cc. of BuOH solution of sucrose ester (7.91 w/v %), 3.1 cc. of 0.5*N* HCl was added, and then the solution was washed gently with 200 cc. of hot water twice. To the solution after washing, 6.3 g. of Dowex 1X8 was added and the system was stirred at 50° for 1 hr. After removal of the solvent from the solution, the contents of soap and fatty acid in the dried product were determined.

The content of potassium soap : 0.58%

The content of free fatty acid : 0.00%

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Summary

As one of the important problems in purifications of sucrose fatty acid ester, a new food-additive, its deacidification was investigated. The method of ion exchange in a non-aqueous medium was carried out, and it was concluded that the deacidification of sucrose ester was performed by treatment with anion exchange resin after treatment with cation exchange resin or inorganic acid. A small amount of water contained in the solvent was effective to accelerate the exchange reaction. Decoloration by the ion exchange resins was also observed.

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