TABLE III

Effect of Amount of Heat on Values for Soap in Oil

Volts	Soap in p.p.m.	
	No. 1	No. 2
120	29	33
100	23	25
80	11	13
60	3.4	3.8

TABLE IV

Effect of Oil-H_2O Ratio on Values for Soap in Oil

Sample	Oil-H_2O ratio	Soap p.p.m.
1	1:1	50
1	5:1	29
2	1:1	51
2	5:1	33

The values obtained with a 5:1 ratio are approximately 60% of those found at a 1:1 ratio.

The fourth variable is the temperature at which the resistance of the water extract is measured. The original method measures resistance at 30°C. Three samples were measured at both 30°C. and 25°C.; the values are recorded in Table V.

TABLE V

Effect of Water-Extract Temperature on Values for Soap in Oil

Sample	Oil-H_2O ratio	Volts	Soap p.p.m.	
			30°C.	25°C.
1	1:1	120	50	48
2	1:1	120	51	45
3	1:1	120	74	61
1	5:1	60	3.4	2.8
2	5:1	60	3.8	3.6
1	5:1	120	29	27
2	5:1	120	33	29

Measurements at the two temperatures produced values which differed by 4–18% on the same sample; all other conditions remained constant.

Of all the variables mentioned, the amount of heat or voltage applied to reflux the oil-water mixture seems to have the greatest effect. The difference here is 880%. Of all the combinations whiich might be encountered by two laboratories using different variables, the greatest spread in values are condensed in Table VI.

TABLE VI

Oil-H_2O ratio	Volts	Temp.	Soap p.p.m.
1:1	120	30°C.	50
5:1	60	25°C.	2.8

From these data of Table VI it is entirely possible that one laboratory could report 50 p.p.m. of soap while the other laboratory would find only 2.8 p.p.m. of soap on the very same oil. This creates an error of 1700%.

One other thing might be pointed out, which has been mentioned in the literature reviewed, that soap concentrations in vegetable oil are not stable and analyses on the same oil vary after the oil has stood for a day or more.

In summation, we have in the course of this paper observed several things regarding the determination of soap in refined vegetable oil. First of all, we have realized that soap in oil is a necessary and important analysis for the oil chemist. Secondly, there is a wide variation of analytical methods suggested, most of which are time-consuming and, to varying degrees, unreliable. Thirdly, a rapid, easy method has been described, and observations have been made on the variables of this method.

In view of these facts it seems imperative that the vegetable-oil industry have an official method for the determination of soap in refined vegetable oil. Therefore we would like to propose that the Conductivity Method for the Determination of Soap in Refined Vegetable Oil, as set forth in this article, be given further study by a committee of the American Oil Chemists' Society in order to ascertain a standardized form and the feasibility of its adoption as the official method of the Society.

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The Chemistry of Lauric Acid-Diethanolamine Condensation Products

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THE CONDENSATION PRODUCTS of higher molecular weight carboxylic acids and diethanolamine have been of primary commercial interest as surface-active agents for the past quarter of a century. The most important class of alkanolamides are those obtained from the coconut fatty acids and, in recent years, from lauric acid. These products have been incorporated into formulations which find their greatest use in the textile and cosmetic fields.

The reaction of a carboxylic acid with diethanolamine is not a simple process primarily because of the presence of three functional groups on the alkanolamine and the inter-related reactivity of these groups both in the presence and absence of the reacting carboxylic acid. The complexity of this reaction was recognized by the U. S. Patent Office in 1937

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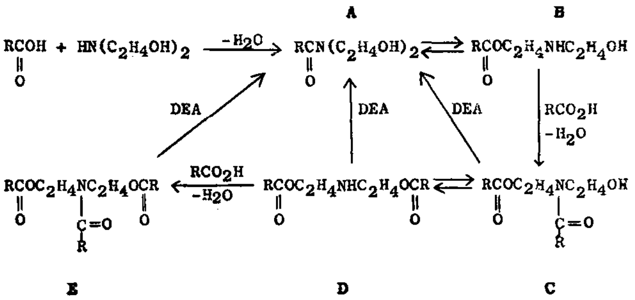
when Wolf Kritchevsky (1) was granted a patent on the product prepared by the reaction of one mole of a higher carboxylic acid with two moles of diethanolamine. This product was sufficiently different from that obtained from the condensation of equimolar amounts of higher carboxylic acid and diethanolamine so as to be protected by a U. S. Letters Patent. Since the issuance of the basic Kritchevsky patent, various modifications of the production of alkanolamides have appeared in the patent literature (2, 7).

In recent years the increasing use of the lauric acid-diethanolamine condensates in cosmetic and detergent formulations has prompted a closer study of the chemical reactions involved in this process. This work has been done in several laboratories, but only limited reports containing descriptive experimental data have been published (4). Since more than one product is obtained in the reaction, a series of abbreviations to minimize the use of formal nomenclature in naming these compounds is suggested in lieu of the more precise chemical designations. These abbreviations are listed in Figure 1.



	Systematic Name	*Abbreviated Name*
A	N,N-bis-(2-hydroxyethyl)lauramide	Di(hydroxyethyl)lauramide
B	2-(2-hydroxyethylamine)ethyl laurate	Amino ester
C	2[N-(2-hydroxyethyl)lauramide] ethyl laurate	Amido ester
D	2,2¹-imino-bis-(ethyl laurate)	Amino diester
E	N-lauroyl-2,2¹-imino-bis-(ethyl laurate)	Amido diester

FIG. 1

The reaction of one mole of lauric acid with two moles of diethanolamine at a temperature of 160°–180°C. gives a series of products indicated by the equations in Figure 1. This reaction sequence may be divided into three phases which are:

a) the monoacylation of diethanolamine by lauric acid with the elimination of water to give di(hydroxyethyl) lauramide (A), and the thermal rearrangement of the amide to amino ester (A → B);

b) the polyacylation step consisting of the acylation of amino ester by a second molecule of lauric acid to give the amido ester (B → C); the rearrangement of this product to amino diester (C → D); and the lauric acid acylation of this product to amido diester (D → E); and

c) the reaction of all compounds containing ester linkages with diethanolamine to yield di(hydroxyethyl) lauramide (C → A; D → A; E → A).

In order to develop the chemical data to describe the reaction system under discussion, it is necessary to have available an analytical scheme which will supply the needed information. Such a scheme is outlined in Table I. The analysis is based on established techniques and is readily reproducible (3). The determination of amino ester is subject to the greatest error because of the labile nature of the compound and the tendency of di(hydroxyethyl) lauramide to rearrange to the amino ester at slightly elevated temperatures.

TABLE I

Analytical Scheme for Alkanolamides

Component	Method
1. Free total amine	1. Perchloric acid titration of product in glacial acetic acid
2. Free fatty acid	2. Product titrated in isopropyl alcohol with standard alkali
3. Amino ester	3. Product dissolved in diethyl ether and washed with 10% sodium chloride; ether evaporated at room temperature and residue titrated with perchloric acid in glacial acetic acid
4. Free diethanolamine	4. 1 minus 3
5. Total fatty acid	5. Hydrolysis of product with 6N HCl, extraction of hydrolysate with diethyl ether, and determination of fatty acid in ether extract by titration
6. Total amine	6. Aqueous layer from 5 concentrated to dryness, and diethanolamine hydrochloride determined in residue by potentiometric titration
7. Combined fatty acid	7. 5 minus 2
8. Combined diethanolamine	8. 6 minus 4
9. Ratio of combined amine to combined fatty acid.	9. 8 divided by 7

In order to establish the course of the reaction, two moles of diethanolamine and one mole of lauric acid were reacted under the conditions specified by Kritchevsky (1). Samples were withdrawn at intervals, and the following analyses were carried out: determination of reacted lauric acid, determination of reacted diethanolamine, formation of amino ester, and the calculation of the ratio of combined diethanolamine to lauric acid. These data are shown in Table II.

TABLE II

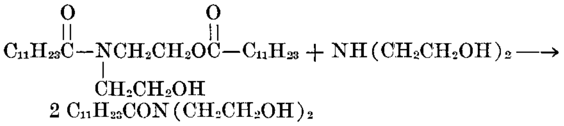
Analytical Results Obtained from Samples Withdrawn from a Lauric Acid-Diethanolamine Condensation [a]

Time (min.)	Temp. (°C.)	Combined Lauric Acid	Combined DEA	Amino Ester	$\frac{\text{Combined DEA}}{\text{Combined LA}}$
0	122	......	......	......	......
20	160	0.39	0.39	0.01	1
22	164	1.20	1.16	0.03	0.97
62	167	1.70	1.53	0.09	0.90
100	168	2.14	1.90	0.49	0.85
125	177	2.29	1.97	0.51	0.86
135	179	2.29	1.98	0.73	0.86

[a] Molar ratio of lauric acid to diethanolamine = 1:2
Diethanolamine = 4.76 me./g.
Lauric acid = 2.42 me./g.
Values are in milliequivalents/g.

An examination of these data indicate that, in the first half of the reaction, lauric acid combines with approximately equivalent amounts of diethanolamine. The second half of the reaction is characterized by a more rapid disappearance of lauric acid than diethanolamine so that an appreciable amount of a product is formed in which the ratio of carboxylic acid to alkanolamine is equal to 2:1. This is indicated in the last column of Table II. A further observation is the increasing amino ester content of the product as the reaction progresses. The significance of this increase will be discussed subsequently.

Since the analytical determinations indicate the presence in the final product of a material containing two moles of lauric acid per mole of diethanolamine, it is apparent that a fraction of the combined lauric acid is bound to the diethanolamine through an ester linkage. This was verified by the isolation of amido ester from the condensation product which was freed of excess diethanolamine and fractionally crystallized from hexane-ethyl alcohol mixtures. The presence of amido ester in the condensation product indicates that di(hydroxyethyl) lauramide is being converted to an amido ester at a rate somewhat faster than the aminolysis of the amido ester by reaction a.

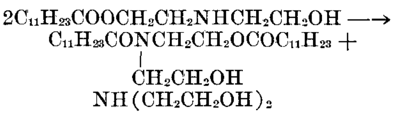


$$C_{11}H_{23}\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_2CH_2OH}{|}}{N}CH_2CH_2O\overset{\overset{O}{\|}}{C}-C_{11}H_{23}+NH(CH_2CH_2OH)_2\longrightarrow 2\,C_{11}H_{23}CON(CH_2CH_2OH)_2$$

(a)

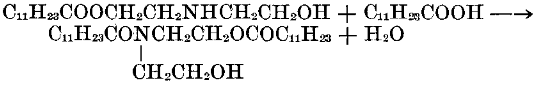
A clue to the possible route by which di(hydroxyethyl) lauramide is converted to the amido ester is the increasing amino ester concentration in the reaction product as the reaction progresses. The following series of reactions indicate the probable mechanism:

$$C_{11}H_{23}CON(CH_2CH_2OH)_2 \overset{\Delta}{\rightleftarrows} C_{11}H_{23}COOCH_2CH_2NHCH_2CH_2OH \qquad (b)$$



$$2C_{11}H_{23}COOCH_2CH_2NHCH_2CH_2OH\longrightarrow C_{11}H_{23}CO\underset{\underset{CH_2CH_2OH}{|}}{N}CH_2CH_2OCOC_{11}H_{23}+NH(CH_2CH_2OH)_2$$

(c)



$$C_{11}H_{23}COOCH_2CH_2NHCH_2CH_2OH+C_{11}H_{23}COOH\longrightarrow C_{11}H_{23}CO\underset{\underset{CH_2CH_2OH}{|}}{N}CH_2CH_2OCOC_{11}H_{23}+H_2O$$

(d)

$$C_{11}H_{23}COOCH_2CH_2NCH_2CH_2OH \xrightarrow{HN(CH_2CH_2OH)_2} C_{11}H_{23}CON(CH_2CH_2OH)_2 \qquad (e)$$

The thermal conversion of di(hydroxyethyl) lauramide to amino ester (reaction b) appears to be the pivotal process in the formation of amido esters. This rearrangement, which takes place rapidly, can be demonstrated by heating di (hydroxyethyl) lauramide at 165°C. under an inert atmosphere and by determining the basic nitrogen liberated in the formation of the amino ester (reaction b). The experimental data are plotted in Figure 2, which indicates that the amino ester content reaches an equilibrium value in approximately 10 min. after the initiation of the experiment.

The disproportionation of amino ester to amido ester and diethanolamine by reaction c is based on the analysis of the product obtained by heating di(hydroxyethyl) lauramide at 165°C. for several hours. These data, which are presented in Table III, indicate that di(hydroxyethyl) lauramide is thermally unstable under the conditions of the Kritchevsky reaction and undergoes a transformation which results in the formation of products in which the molar ratio of fatty acid to diethanolamine is greater than unity. The water-soluble amine which is liberated on heating di(hydroxyethyl) lauramide has been tentatively identified as diethanolamine. The possibility that a piperazine derivative is present in this fraction has not been excluded (5, 6).

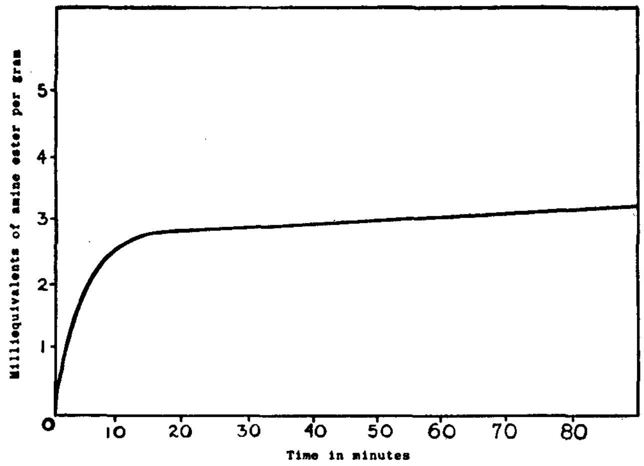


FIG. 2

TABLE III

Thermal Treatment of N,N-(2-dihydroxyethyl)lauramide at 165°C.

	Before Heating me./g.	After Heating me./g.
Titratable amine	0.052	1.16
Free fatty acid	0.031	0
Water-insoluble amine	......	0.83
Water-soluble amine	......	0.34
Combined fatty acid	3.68	3.64
Combined amine	3.68	2.44

A similar set of reactions can be postulated for the rearrangement of amide ester to amino diester and for the conversion of this compound to amido diester. It is to be expected that uncombined fatty acid can condense with amino ester to yield amido ester by reaction d.

Reactions a and e indicate that amido ester and amino ester react with diethanolamine to form di(hydroxyethyl) lauramide. The combined effect of these two reactions on the composition of the condensation product of lauric acid and diethanolamine can be evaluated by carrying out the reaction in the presence of increasing amounts of diethanolamine. The results of these experiments are tabulated in Table IV. The data show that the ratio of combined amine to combined acid increases from 0.73 to 0.99, indicating that the increased diethanolamine concentration favors the formation of di(hydroxyethyl) lauramide and decreases the amido ester content of the product. These data do not permit a separate evaluation of reactions a and e or the effect of increasing amounts of diethanolamine on the thermal rearrangement of di(hydroxyethyl) lauramide to amine ester.

TABLE IV

Effect of Varying Amounts of Diethanolamine on the Lauric Acid-Diethanolamine Condensation

	Ratio of DEA to Lauric Acid		
	2.0	2.2	2.4
Combined DEA (me./g.)	2.67	3.26	3.28
Combined lauric acid (me./g.)	3.65	3.46	3.30
Amino ester (me./g.)	0.90	0.78	0.69
$\frac{\text{Combined DEA}}{\text{Combined LA}}$	0.73	0.94	0.99

Young and Rubinstein (7) have indicated that conditioning a lauric acid-diethanolamine condensate at 90°–120°C. for prolonged periods of time improves the surface-active properties of the product, especially for soap formulations. An examination of the rate of reaction between lauric acid and diethanolamine indicates that very little condensation takes place in this temperature range, and the beneficial results obtained in the conditioning phase of the reaction must be concerned with the condensation product and diethanolamine. This effect is illustrated by

TABLE V

The Effect of Conditioning a Lauric Acid-Diethanolamine Condensation Product at 90–120°C.[a]

Sample Number	Time[b] Hr.	Time[b] Min.	Temp. °C.	Free Fatty Acid (me./g.)	Amino Ester (me./g.)	Combined Fatty Acid	Combined DEA	Combined DEA / Combined Acid
5	4	50	170	0.31	0.16	2.44	2.04	0.84
7	6		168	0.23	0.51	2.53	2.28	0.90
8	6	40	167	0.23	0.56	2.43	2.24	0.92
9	7	20	120	0.23	0.52	2.34	2.20	0.94
11	19	40	110	0.25	0.15	2.34	2.20	0.94

[a] Molar ratio of DEA to Lauric Acid = 2.2.

[b] Represents the elapsed time from the initiation of the experiment.

the data in Table V, which were obtained from a reaction in which a 2.2 molar ratio of diethanolamine to lauric acid was employed.

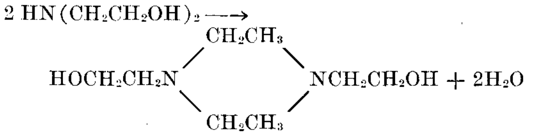
The conditioning of the condensation product at the reduced temperature of 120°C. produces two results. First, the ratio of combined amine to combined fatty acid tends to approach unity, indicating a conversion of a 2:1 condensate of lauric acid and alkanolamine to a 1:1 product, and secondly, the amino ester value decreases.

These changes can be explained in terms of reactions a to e, inclusive. The heating of di(hydroxyethyl) lauramide at 80°C. to 100°C. in an inert atmosphere results in about a 25% conversion to amino ester, and the maintenance of the resulting mixture at 100°C. does not produce any marked changes in the ratio of combined amine to combined fatty acid. Furthermore allowing the molten di(hydroxyethyl) lauramide to cool slowly to room temperature results in a decrease in the amino ester content to approximately the starting value. Recently Trowbridge (6) and co-workers have isolated the amino ester through the hydrochloride and observed a very rapid decrease in amine function of the compound in melts at 50°C. Recrystallization of a sample of amino ester which had been allowed to stand at room temperature for one year yielded di(hydroxyethyl) lauramide. These data indicate that at 100°C., the equilibrium of the acyl rearrangement of reaction b favors the di(hydroxyethyl) lauramide, and the shift is still farther in favor of the amide as the temperature of the reaction mixture is decreased still more. This accounts for the decrease in amino ester content of the condensation product on conditioning at the reduced temperature of 100°C. Furthermore, since heating di(hydroxyethyl) lauramide at 100°C. does not affect the combined diethanolamine and fatty acid ratio of the product, it is not expected that reaction c will contribute to the composition of the condensation product. Reaction d will have only a slight effect since the temperature is not sufficiently high enough for the fatty acid to condense with amino ester.

The aminolysis of amido ester by diethanolamine at 100°C. to yield di(hydroxyethyl) lauramide (reaction a) has been demonstrated by Kroll (2), and it is this process which accounts for the improvement of the condensation product of lauric acid and excess diethanolamine by conditioning at 100°C.

The formation of tertiary amines in the condensation reaction of lauric acid and diethanolamine has been suggested by Kritchevsky (1). More recently Trowbridge, Falk, and Krems (6) have briefly summarized the available literature, which contains references to the presence of tertiary amines in alkanolamides.

In the reaction of lauric acid with diethanolamine, if the reaction is forced, more than one mole of water per mole of lauric acid is eliminated. To explain the formation of the excess water it is necessary to postulate a reaction involving the hydroxyl groups of diethanolamine. The thermal intermolecular condensation of diethanolamine to give N,N′-bis(2-hydroxyethyl)piperazine (6) has been described by Small (5).



(f)

In order to effect an appreciable conversion of diethanolamine to the piperazine, it is necessary to heat the alkanolamine for over 200 hrs. at 204°C. Under the usual conditions of condensing lauric acid with excess diethanolamine, the formation of N,N′-bis(2-hydroxyethyl)piperazine is probably small. Reliable quantitative data are lacking. Potentiometric curves of the amine constituent isolated from lauric acid-diethanolamine condensates indicate the presence of a diamine which amounts to a few per cent of the total amine present. It is doubtful whether the lauric acid condensates of the piperazine products contribute to the surface-active properties of the alkanolamides.

Summary

The reaction of lauric acid with diethanolamine in the presence of excess alkylolamine results initially in the formation of N,N′-bis(2-hydroxyethyl)lauramide. This compound is responsible for the surface-active properties of the alkanolamides. Under the conditions of the reaction the amide undergoes a thermal rearrangement to the lauroyl ester of diethanolamine, which in turn is converted to the dilauroyl amido ester of diethanolamine. The excess diethanolamine converts both amino ester and amido ester to N,N′-bis(2-hydroxyethyl)lauramide.

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