

A New Approach to the Analysis of Fatty Alkanolamides

JOSEPH J. HEJNA, M.S., and DIANE DALY, B.S.*

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Synopsis—COLUMN CHROMATOGRAPHY in conjunction with INFRARED SPECTROSCOPY can be used to elucidate the composition of the SUPERAMIDE and the KRITCHEVSKY AMIDE. The method is quantitative and yields information pertaining to the secondary products along with reverting and rearranging of the various components.

INTRODUCTION

The synthesis and properties of the alkanolamides have been known for some time and there has been a great deal of speculation about the course of reaction and possible interactions concerning the molecular rearrangement to give the secondary products. The complexity of the reaction is due to the bifunctional activity of the diethanolamine, a secondary amine with two hydroxyl groups, which accounts for the various by-products.

There have been a number of chemical and instrumental methods suggested for the analysis of the alkanolamide condensates. The chemical method proposed by Kroll and Lennon (1) is designed for the analysis of the Kritchevsky type of amide. The analytical scheme employs the standard wet methods.

A similar method has been proposed by Livengood and Johnson (2). The wet methods have certain shortcomings in that the results are based on speculative assumptions. The methods do not distinguish between the mono- and diesters of the amines, if present, or between the mono- and diesters of the amide. There is also no distinction between the

* Helene Curtis Industries, 4401 West North Avenue, Chicago, Ill.

amine and amide esters. No procedure has been proposed for the determination of 1,4-diethanol piperazine, which may be present in the Kritchevsky type of amide. In the work described here, the amides have been separated chromatographically and then analyzed by infrared spectroscopy.

The chromatographic method of separation of fatty alkanolamides was developed using an extension of Rosen's method (3) for separating surface active agents and has proven to be a valuable analytical tool.

EXPERIMENTAL

A chromatographic column, 20 in. long and 1 in. in diameter, was packed with 75 g of silica gel (Davison No. 992, 100 to 200 mesh) by pouring a chloroform slurry into the column. It is essential that no air is entrapped in the column. A 1.25- to 2.0-g sample was dissolved in 20 ml of chloroform and was added to the column. All the chemicals were of reagent grade and they were not treated in any way prior to their use. The column was eluted by solvent series increasing in polarity as follows:

- (1) 70 ml of chloroform,
- (2) 100 ml of a mixture of 1 ml of ethyl ether and 99 ml of chloroform,
- (3) 70 ml of a mixture of 35 ml of ethyl ether and 35 ml of chloroform,
- (4) 80 ml of a mixture of 40 ml of acetone and 40 ml of chloroform,
- (5) 100 ml of a mixture of 5 ml of methyl alcohol and 95 ml of chloroform,
- (6) 70 ml of a mixture of 7 ml of methyl alcohol and 63 ml of chloroform,
- (7) 75 ml of a mixture of 25 ml of methyl alcohol and 50 ml of chloroform,
- (8) 100 ml of methyl alcohol.

The above eluents were not polar enough to remove free amines; however, amines can be eluted from the column by using a 2% solution of hydrochloric acid in water. The amines are eluted as the hydrochloride salt.

The eluted material was collected in 10-ml fractions into 50-ml beakers at a flow rate of 1 ml every 1.5 min. The solvents were evaporated on a steam bath under a stream of air. In general, 60–75 such fractions were collected. After the solvent was removed, the beaker was wiped to remove any moisture on the outside, cooled, and weighed. Samples of the various fractions were then examined by infrared spectroscopy.

RESULTS

Five different samples from three different suppliers were examined. Four of the samples were considered fresh in that they were made two weeks prior to their analysis. One sample analyzed was two years old. Two of the samples were the superamide type and three were of the Kritchevsky type. One sample was analyzed twice because it was received as a liquid and after a few weeks it started to solidify. There was interest in knowing what, if any, chemical change took place in changing from a liquid to a solid. The results of the six samples are shown in Table I.

Table I
Comparative Analysis of Various Amides
(Values shown as percentages)

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Free fatty acid	1.21	1.14	7.94	4.00	2.60	3.74
DEA amide diester	5.36	0.58	0.00	0.00	5.45	0.80
DEA amide monoester	0.00	0.63	0.00	2.44	6.94	2.65
Amine diester	0.00	0.00	0.00	0.00	0.97	0.00
MEA amide ester		0.53	0.90	0.40	0.45	0.50
MEA amide		2.27	1.35	2.50	2.40	
DEA amide	86.31	88.65	49.02	53.85	52.16	62.26 ^a
Free amine			35.60	32.41	27.00	27.20
Amido-amine	4.12		5.18	4.10	2.04	
Free amine plus soap	3.00	6.20				

^a Contained piperazine derivative.

In Table I, Sample Nos. 1 and 2 were the superamides, and the other four were the 2:1 ratio amides.

Histograms of the six samples were made in which the weights of the eluted fractions were plotted *versus* the fractions. The histograms indicate the number of major components that were in the product. The infrared spectra of the peaks of the plotted fractions when carefully evaluated revealed the composition of the components. It was found that in several instances it was necessary to obtain an infrared spectrum of not only the peaks, but also of the fractions before and after the peaks. This was necessary because some of the components are similar in polarity and as a result they will be eluted close to each other. The infrared spectra were able to show the distinguishing functional groupings of the components.

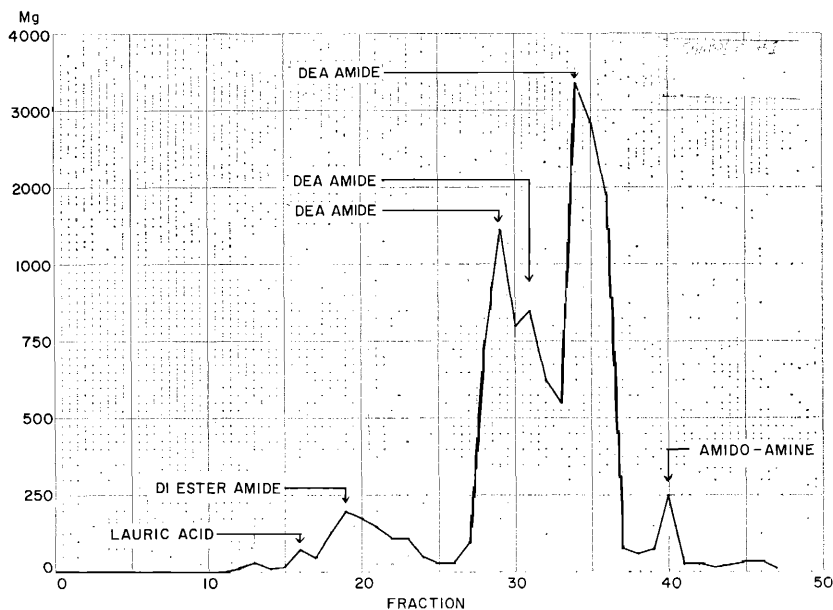


Figure 1. Superamide made from methyl esters, 1:1 ratio

The various fractions were also dissolved in neutral alcohol and then a few drops of bromcresol green indicator were added. The color change corresponded with the degree of acidity or basicity of the various components and, as such, can be used as a guide to help determine the nature of the components.

As stated, it was found that the diethanolamine could be eluted from the column as the hydrochloride salt by using water containing hydrochloric acid. This procedure is possible with 2:1 ratio amides but not with the 1:1 ratio amides. These latter amides contain soap which, along with small amounts of free diethanolamine, could not be eluted from the column. The acidic water cannot be used in the case of the 1:1 ratio amides because the soap would be decomposed by the acid.

The analysis of Sample No. 1, a 1:1 adduct, is presented in Fig. 1. In this example, infrared curves on the major fractions were run. From these fractions the composition of the amide was summarized (Table I).

With Sample No. 2, another 1:1 adduct (Fig. 2), more fractions were examined by infrared spectroscopy to obtain a more precise evaluation of the composition of the amide.

The diethanolamide was not eluted as a single peak which indicates that the amide is made from a methyl ester of mixed fatty acids. This was

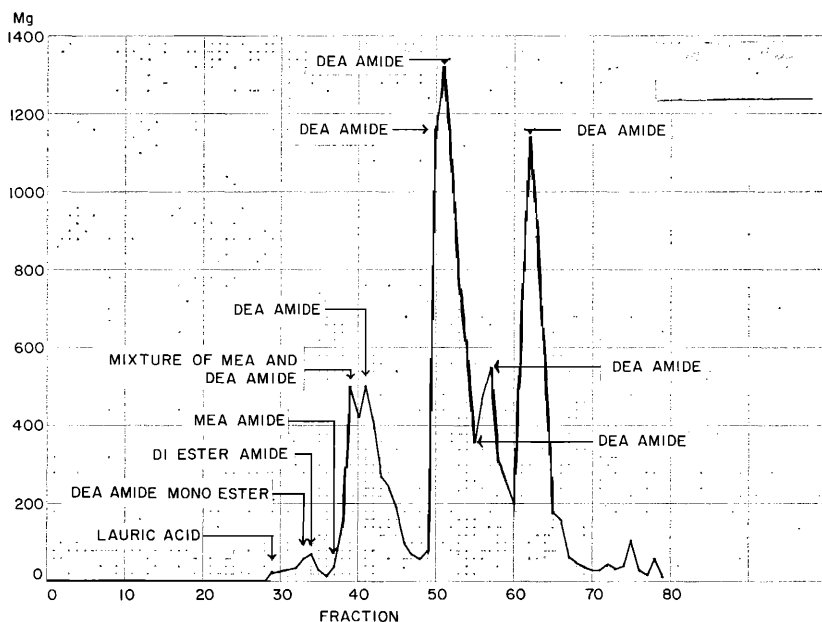


Figure 2. Superamide made from methyl esters, 1:1 ratio

substantiated by examining the spectra in relation to the CH band at 2915 and 2840 cm^{-1} to the "amide I" band at 1620 cm^{-1} of the various fractions. The ratio of the CH band to the "amide I" and the melting points of the fractions are presented in Table II. The variability in the melting points of the fractions is indicative of a eutectic mixture.

The superamides are usually made from a mixture of methyl myristate and methyl laurate which are C_{14} and C_{12} fatty acid esters, respectively, the ratio being $\text{C}_{12}/\text{C}_{14}$ or 0.86. If the ratio of CH to amide of the average of fractions 50 and 51 is taken in relation to the average of fractions 55 and 57, we obtain 0.83, indicating that the amide is made from a mixture of methyl myristate and methyl laurate.

Samples of the fractions were dissolved in alcohol and a few drops of bromocresol green indicator were added. Fractions 29 through 32 were yellow, indicating acidic groups; 33 through 36 (green) indicated neutral molecules; 37 was a blue-green showing the presence of the NH or amine group of the monoethanolamide. Fractions 38 through 73 were green, 74 was blue-green, and from 75 to the end were blue. The blue color is due to the presence of the amido-amine.

Sample No. 3, a 2:1 adduct, was examined similarly to Nos. 1 and 2.

Table II
Ratio of CH/Amide Indicating Relative Chain Length

Fractions	Melting Point, °C	CH Absorption, %	Amide Absorption, %	Ratio of CH/Amide
41	36	56	66	0.85
42	36			
43	40			
44	40			
45	40			
47	40			
49	40			
50	46	52	57	0.91
51	47	45	50	0.90
52	47			
53	42			
54	43			
55	46	56	74	0.76
56	46			
57	42	60	78	0.77
58	41			
59	46			
60	46			
61	43			
62	45	44	55	0.80
63	46			
64	46			
65	44			

Figure 3 shows the histogram; of particular interest were Fractions 22 and 24 which were identified as monoethanolamide ester and monoethanolamide. With this as background, Sample No. 4 was analyzed in greater detail.

Sample No. 4, a 2:1 adduct, is presented in Fig. 4. This was a fresh sample which was liquid when it was received. Fractions 1 through 17 were combined and examined by infrared; the material was found to be di(2-ethylhexyl)phthalate. It is not included in Table I because it is not one of the components. The phthalate ester came from the plastic cap and liner and was also found in other samples which were packaged in plastic containers. Fraction 18 is lauric acid, 23 is the ester of monoethanolamide, 25 is a diethanolamide. Fraction 32 is also a diethanolamide; however, this fraction also contains a small amount of an ester amide. Fractions 33 and 39 are diethanolamide; Fraction 36 shows the diethanolamide with a trace of ester. Fraction 47 is also a diethanolamide; however, the spectrum does not have the detail of a pure amide,

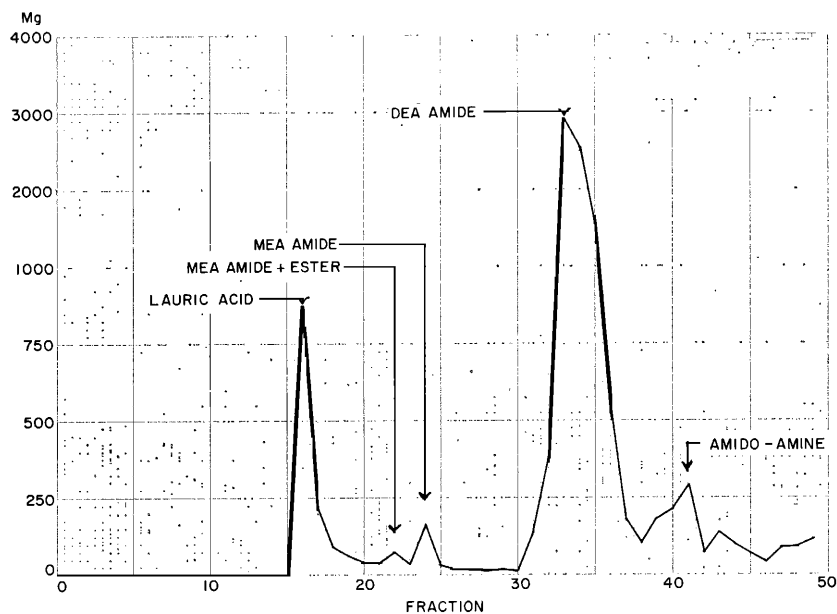


Figure 3. Kritchevsky amide, 2:1 ratio

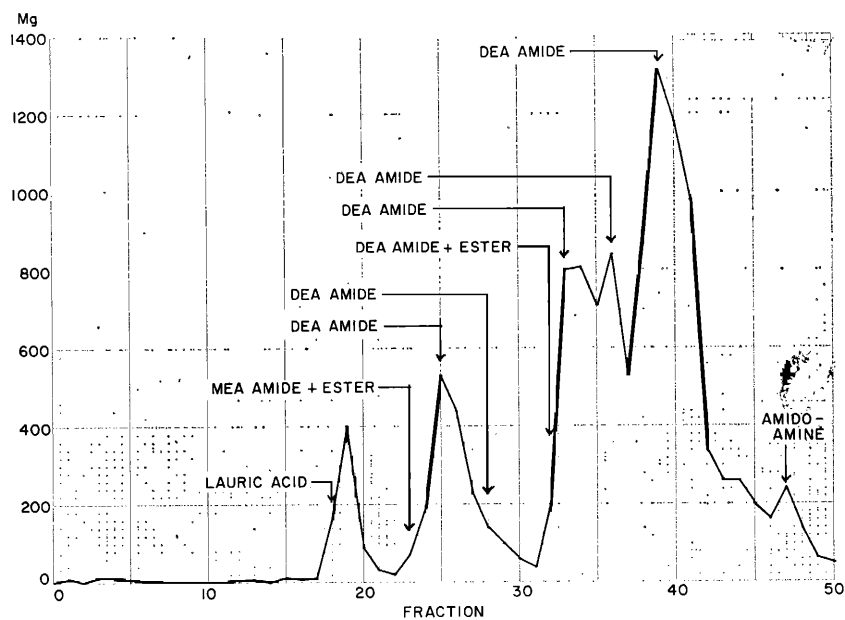


Figure 4. Kritchevsky amide, 2:1 ratio

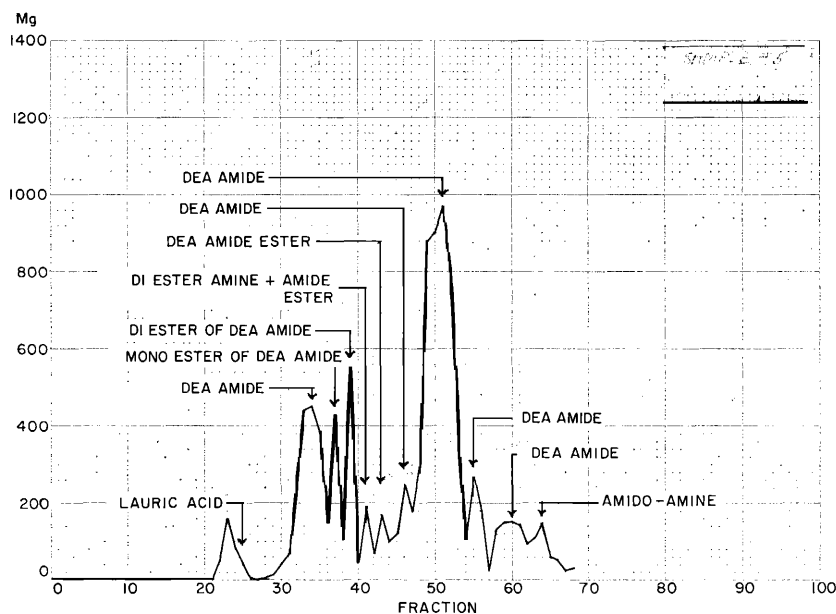


Figure 5. Kritchevsky amide, 2:1 ratio

indicating contamination from the amido-amine. This was also evident from the fact that the fraction turned blue-green when bromocresol green was added to the sample in alcohol. The melting points of the fractions of the amide peaks varied from 39° to 47°C indicating that the fractions were possible eutectic mixtures of varying carbon chain length.

Sample No. 5 was a repetition of No. 4 after it changed from a liquid to a solid. It will be noted that Fig. 5 is quite different from Fig. 4. There has been a rearrangement of the components as evidenced by the increased number of peaks. Samples 37 through 46 showed discrete infrared differences and indicated the presence of amide ester, amide diester, and amine diester. Fraction No. 37 was an ester amide, 39 was a diester amide. It analyzed similarly to No. 37 but had a higher ester content. The infrared spectrum showed the amide peak to be smaller than the ester peak and the hydroxyl peak decreased, indicating more diester. Fraction No. 41 was a mixture of both amine diester and an amide diester. The spectrum had a small amide peak at 1620 cm^{-1} and an amine peak at 1572 cm^{-1} ; the ester peak was very large in proportion to the amide peak and again the hydroxyl peak was small. Fraction No. 43 was the monoester of diethanolamide, but of less ester content than No. 37. Fraction No. 46 shows the diethanolamide with a trace of an ester amide. The spectra of peak Nos. 51, 55, and 60 were of the typical

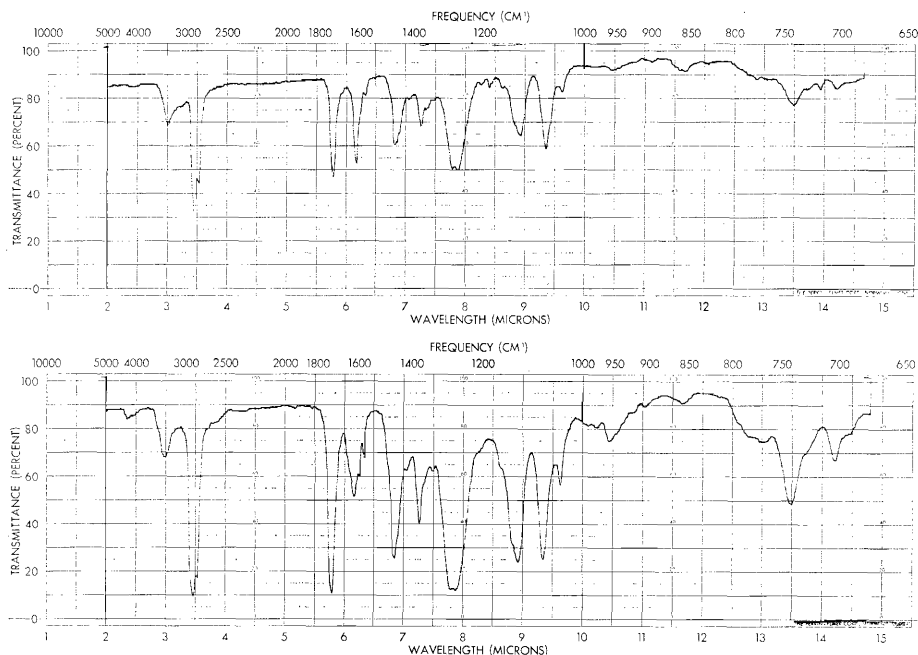
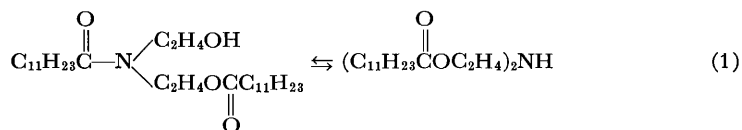


Figure 6. Infrared spectra of a diester amide before heating (top) and after heating (bottom) diethanolamide. Again, the spectra when comparing the "CH" band with the "amide I" band showed the presence of varying length carbon chains. Fraction No. 64 is a mixture of an amide and amido-amine. This was demonstrated when an alcoholic solution of this fraction turned blue upon adding bromcresol green indicator, whereas the fractions prior to it were green.

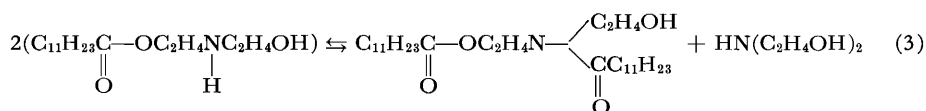
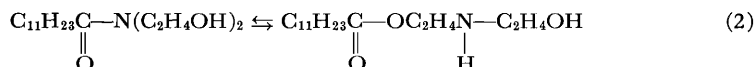
Sample No. 4 changed into what is called Sample 5 in the course of three weeks at room temperature. The change is due to a rearrangement of some of the components of the sample. The change was demonstrated by taking two of the fractions, namely Nos. 39 and 51 from sample No. 5 and heating them for 20 hours at 105°C to accelerate any possible rearrangement. Fraction No. 39, which was a mixture of diester amide and monoester amide, upon rearrangement gave a sample whose infrared curve showed diester amine contaminated with diester amide, proving the monoester amide is thermally unstable. The pH increased by the color test with bromcresol green.

Figure 6 shows the infrared curves of Sample 39 before heating, and after heating. It is interesting to note that the infrared curve after heating is very similar to Fraction 41.

The chemistry of the reaction is shown below (equation 1):



Fraction No. 51, which is a diethanolamide, when heated rearranged to a monoester amide. Figure 7 shows the infrared curves before and after heating. The reactions were:



The rearrangement takes place in two steps. The fraction was very basic, turning blue, when tested with the indicator. The melting points of the amide fractions indicated eutectic mixtures.

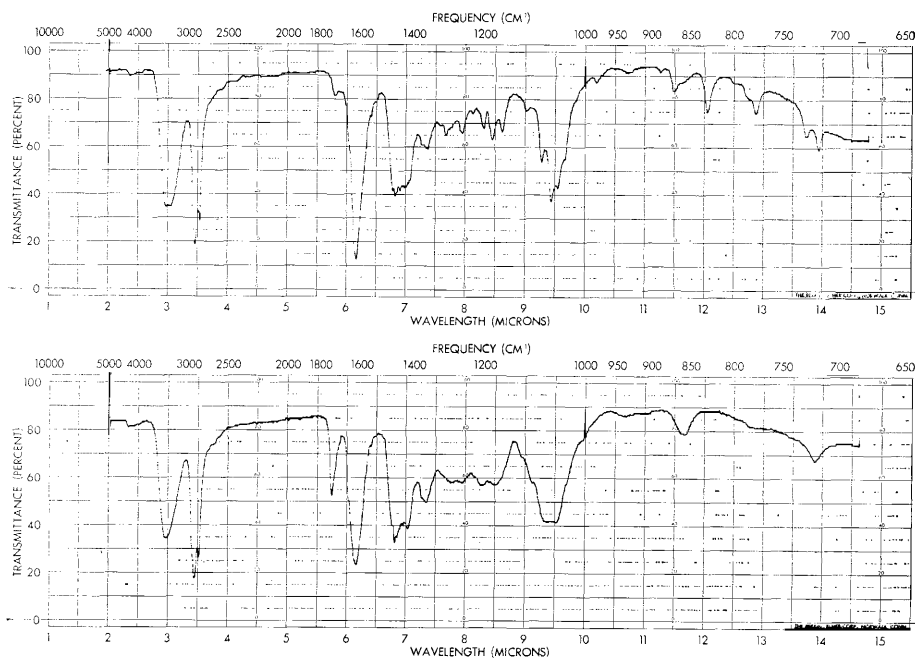


Figure 7. Infrared spectra of a pure diethanolamide before heating (top) and rearranged to a monoester after heating (bottom)

Sample No. 6 is a 2:1 amide which was more than two years old. The material was liquid and it had a precipitate which was suspected to be *N,N*-bis(2-hydroxyethyl)piperazine. When subjected to the analytical technique, the piperazine was found and it is eluted near the end of the chromatographic analysis. Figure 8 shows the histogram and the piperazine is in Fraction 55. The amido-amine which was detected in both 1:2 and superamides is shown in Fig. 9.

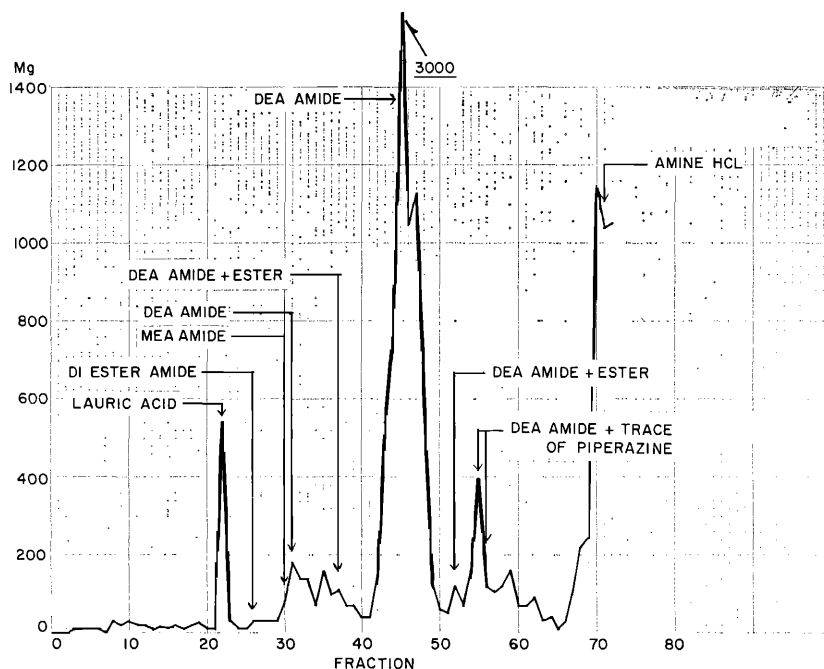


Figure 8. Kritchevsky amide, 2:1 ratio after aging

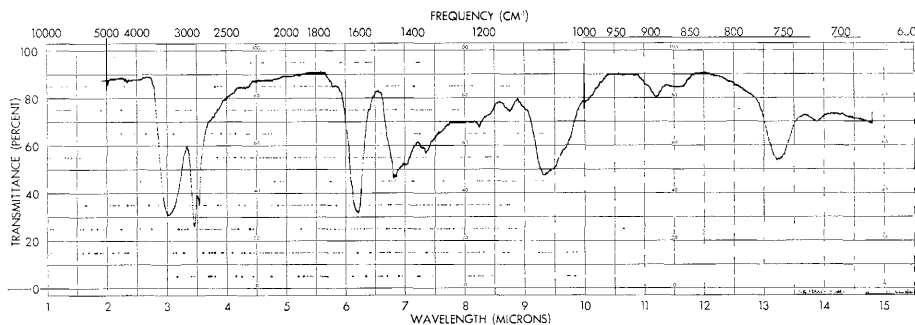


Figure 9. Infrared spectrum of amido-amine

SUMMARY

Column chromatography in conjunction with infrared spectroscopy can be used to elucidate the composition of both the superamide (1:1) and the Kritchevsky type (2:1) amides. The method not only substantiates the presence of the various secondary products, but yields quantitative information and also reveals the presence of monoethanolamide and the ester of monoethanolamide. This shows that commercial diethanolamine contains monoethanolamine as an impurity. The method can be used to study the effect of aging on the composition insofar as to the rearrangement of some of the components and the appearance of *N,N*-bis (2-hydroxyethyl) piperazine. The method also indicates the presence of impurities which were not part of the raw materials but were due to the solubility effect of the amides on such things as plastic bottles and caps with plastic liners. None of the 1:1 samples that were analyzed revealed any methyl esters but in subsequent work not covered by this paper small amounts of methyl ester were found to be present in several 1:1 amides. Thermal rearrangement of components was ascertained, whereby a diethanolamide was converted to a monoester diethanolamide and the subsequent conversion of the monoester diethanolamide to a diester amine. The soap component in the 1:1 amides is not eluted from the column as such. The method will indicate the presence of free fatty acid in the 1:1 amides which usually is not determined by the standard method of titration.

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