Synthesis and Properties of Fatty Imidazolines and Their N-(2-Aminoethyl) Derivatives[1]

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ABSTRACT

Cationic high molecular weight surfactants hold promise as water repellents for soil for water harvesting. Specifically, the products of the reaction of 2 moles of fatty acids with 1 mole of diethylenetriamine were investigated. Optimum conditions for the formation of imidazolines as well as the open-chain N-(2-aminoethyl) derivatives, i.e., the diamides, were determined. Saturated fatty acids, pelargonic through behenic, oleic acid, elaidic acid as well as tallow, tallow fatty acids, and hydrogenated tallow fatty acids, were converted in 6 hr at 150 C to form the diamides. The fatty imidazolines were synthesized by cyclizing the diamides at 150 C for 2 hr under reduced pressure in a 92% yield. The crude imidazolines were purified by crystallization. The fatty imidazolines were readily hydrolyzed at the C=N bond of the imidazoline ring with water or dilute alcohol. The resulting diamides, $RCON(CH_2CH_2NH_2)CH_2CH_2NHCOR$, were also purified by crystallization. Water repellency of these compounds was evaluated by contact angle measurements and percolation tests. The surface properties of these series of compounds are determined by four parameters. The open-chain diamides are more hydrophobic than the analogous imidazolines, and hydrophobicity increases with increasing molecular weight of derivatives of saturated fatty acids. Oleic acid derivatives are far more hydrophilic than the saturated acid derivatives or the analogous elaidic acid derivatives. The latter are more hydrophilic than stearic derivatives.

INTRODUCTION

Water harvesting through the use of soil treatment chemicals has received increased attention over the past decade (1). Many chemicals have been examined with varying degrees of success. The selection of a fat-based chemical suitable for this purpose would provide a potentially new application for fats and oils. The higher molecular weight nitrogen derivatives of fatty acids, such as imidazolines, were considered because of their remarkable properties and wide variety of uses (2). Production of imidazolines and their derivatives has been predicted to increase from 22.5 million pounds in 1977 to 50 million pounds in 1985 (3,4).

Since Hofmann prepared the first 2-alkyl-2-imidazoline (5), the homologous series from fatty acids and ethylenediamine have been synthesized and characterized (2,6,7). From the structure of such compounds, it can be concluded that the 2-alkyl-2-imidazolines would not impart sufficient hydrophobicity to soils. However, the fatty derivatives of higher molecular weight polyamines, such as diethylenetriamine (DETA) might be sufficiently hydrophobic.

Ackley (8) reacted fatty acids with DETA to prepare the fatty imidazolines, which, in crude form, were quaternized to produce fabric softeners. In the past four decades, many patents have been issued describing the fatty acid-DETA condensate as an intermediate for subsequent reaction. The few descriptions of the reaction mechanism, appearing in the chemical literature, are not entirely in agreement. Although Dobozy (9) did not report experimental details for the reaction of DETA with sperm oil fatty acids, he concluded that the synthetic compounds are imidazolines of the structure $R-\underline{C=N-CH_2CH_2-N}-CH_2CH_2NH_2$, and that fatty acid attachment actually occurred at one primary and/or one secondary nitrogen atom and not at the two primary amino nitrogen atoms of the DETA molecule. Krejcar et al. (10) similarly prepared $R-\underline{C=N-CH_2CH_2-N}-CH_2CH_2NH_2$ at 270 C under a vacuum of 5 mm Hg in 2 hr. When the reactants were mixed below 100 C, Butler and coworkers (11) observed amine salt formation which dehydrated at 130 C to a diamide-fatty acid complex and finally at 180 C to the liberated diamide, identified as $(C_{17}H_{35}CONHCH_2CH_2)_2NH$. Continued heating at 240-260 C for 48 hr yielded $C_{17}H_{35}\underline{C= NCH_2CH_2N}-CH_2CH_2NHCOC_{17}H_{35}$. It was concluded that the reaction followed a sequential pattern and that each successive step took place at a higher temperature. The high temperature requirements for synthesis, the inconsistency in the literature as to reaction conditions and the chemical structures of the intermediates and the imidazolines, and the inadequate description of their chemical properties were areas which merited further investigation.

The objectives of this investigation were: (a) to prepare the intermediate diamides and imidazolines from the C_9-C_{22} saturated acids, oleic, and elaidic acids, tallow, tallow fatty acids and methyl tallowate, and DETA; (b) to study reaction variables, such as temperature, time, and reduced pressure; (c) to characterize the chemical nature of the intermediate amides; and (d) to measure their chemical and physical properties. The fatty imidazolines were prepared by running the reaction to completion under vacuum. The imidazolines were subsequently hydrolyzed to the diamides.

For brevity, the fatty imidazolines $R\underline{C=N-CH_2CH_2N}CH_2CH_2NHCOR$ will be referred to as imidazolines and the N-(2-aminoethyl) derivatives $RCON(CH_2CH_2NH_2)CH_2CH_2NHCOR$ as diamides in the following discussion.

EXPERIMENTAL PROCEDURES

Materials

The following chemicals were used: diethylenetriamine, Aldrich Chemical Co. (Milwaukee, WI); C_{10}, C_{12}, C_{14}, C_{16}, and C_{18} saturated fatty acids, Armak Industrial Chemicals Division (Chicago, IL); oleic acid, A. Gross & Co. (Newark, NJ); C_{20} and C_{22} fatty acids, Sigma Chemical Co. (St. Louis, MO); 11-undecenoic acid, Eastman Kodak Co. (Rochester, NY), elaidic acid, laboratory preparation (12); pelargonic acid, Emery Industries, Inc. (Cincinnati,

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OH); tallow, Corenco Corp. (Philadelphia, PA); tallow fatty acids T-11 and T-22 and methyl tallowate (TE1618), Proctor & Gamble, Industrial Chemical Division (Cincinnati, OH); hydrogenated tallow fatty acids, Acme-Hardesty Co., Inc. (Jenkintown, PA); Drierite, W.A. Hammond Drierite Company (Xenia, OH); Ottawa Sand ASTM, Arthur H. Thomas Co. (Philadelphia, PA); SYLON-CT Silylating Reagent, Supelco, Inc. (Bellefonte, PA).

Instrumentation

Parr pressure apparatus, Parr Instrument Co. (Moline, IL); infrared spectroscopy, Perkin-Elmer Model 257 infrared spectrophotometer, Perkin-Elmer Corp. (Norwalk, CT); ultraviolet spectroscopy, Perkin-Elmer Model 559 UV-vis spectrophotometer, Perkin-Elmer Corp., Coleman Instruments Div. (Oak Brook, IL); Fisher-Johns melting point apparatus, Fisher Scientific Co. (Pittsburgh, PA); contact angles, Gaertner goniometer, Gaertner Scientific Corp. (Chicago, IL); gas chromatography, Hewlett-Packard Model 5889A gas chromatograph, Hewlett-Packard Co. (Palo Alto, CA); 100M SP2340 glass capillary column, Quadrex Corp. (New Haven, CT).

Synthetic Procedures

Imidazoline preparation. The following procedure is typical of imidazoline preparations. Diethylenetriamine (DETA), 51.5 g (0.50 mol) was added to stearic acid, 270.4 g (0.95 mol) at 90 C. Temperature quickly increased to 120 C and gelling occurred, as a result of amine soap formation. This was overcome by warming above 125 C. Heating at 150 C was continued for 6 hr.

At this point, a typical analysis by titration showed 4.3% free fatty acid, 1.64 meq/g primary amine, 0.14 meq/g secondary amine, and 0.13 meq/g tertiary amine or 8.3% imidazoline present. Amine content, according to AOCS Test Method TF 1b-64 and TF 2b-64, "Quantitative Determination of Amines" was calculated as meq/g total amine = 1000/mol wt and determined by titration = mL HCl X N HCl/g sample. Heating was continued at 150 C for 2 hr under 0.3 mm Hg vacuum. Analysis of the crude imidazoline gave, in meq/g: primary amine = 0.25, secondary amine = 0.05, tertiary amine = 1.58. The hard, waxy material was recrystallized from 1 L 50%, v/v acetone/toluene mixture, producing $C_{17}H_{35}-\underline{C=N-CH_2CH_2-N}$ $CH_2CH_2NHCOC_{17}H_{35}$, a white crystalline powder in 87% yield, mp 84-85 C with the following amine analyses in meq/g: primary = 0.10, secondary 0.03, and tertiary = 1.49 corresponding to 93% purity. The lower molecular weight imidazolines were recrystallized from chemically pure acetone. All members of the homologous series were prepared accordingly. The diamides were obtained by hydrolysis of the imidazolines.

Preparation of diamide derivatives. The following is a typical synthesis: The imidazoline from stearic acid, 75 g, 0.12 mol, was dissolved in 600 mL 80% ethanol and heated in a Parr pressure reactor to 150 C at 100 psig for 1 hr. The product was recrystallized from 95% ethanol, yielding 62.1 g $C_{17}H_{35}CON(CH_2CH_2NH_2)CH_2CH_2NHCOC_{17}H_{35}$, a white crystalline powder (mp 118-119 C) in 83% yield. Expressed as meq/g, the following amine analyses were found: primary = 1.49, secondary = 0.02, tertiary = 0.01 corresponding to a purity of 95%. The diamide derivatives whose values are reported in Table I were prepared according to this procedure. Two alternative methods were also used: (a) heating a 50% alcoholic solution of the imidazoline on the steam bath for 2 hr; (b) adding 20% water to the imidazoline in the reaction flask and refluxing for 2 hr. However, when products of the latter two procedures were analyzed, 3% unhydrolyzed imidazoline was found in the diamide derivatives.

cis-trans fatty acid determination. Tallow fatty acids were methylated, using the BF_3/methanol procedure of Metcalfe (13). Samples were injected automatically into the gas chromatograph, fitted with a glass capillary column. The column was temperature programmed from 150 to 200 C at 0.5 C/min (14). The peaks were identified by peak enhancement with known standards.

Ultraviolet absorption studies. Ultraviolet absorption studies were conducted on 0.01 g samples dissolved in 100 mL absolute ethanol. An aliquot was placed in 10 mm quartz cell, together with absolute ethanol in the reference cell. Using an absorbance maximum = 1.25, the range was scanned from 270-190 nm and absorptions for imidazoline at 230 nm and diamides at 202 nm recorded. The absorbance at 230 nm of mixtures of different ratios of the palmitic imidazoline and diamide was plotted to obtain the composition curve (Figure 1).

Contact angle determination. A test sample of product was melted on a microscope slide to cover a circle of at least 1 cm diameter. Using the sessile drop technique (15), a 3 μl drop of water was placed on the solidified sample. The maximum angle observed after 60 sec on a Gaertner goniometer was reported as the contact angle of the compound. Compounds that possess contact angles $> 90^\circ$ were considered to be water repellent.

Percolation test. A bed was prepared, mixing 30 mL of a 0.1% alcoholic suspension of test solution into 80 g ASTM Ottawa sand (20-30 mesh), allowing alcohol to evaporate under a stream of nitrogen, and then drying further in an oven at 60 C for 3 hr. Ten g indicating Drierite was placed in a silylated 4-oz round jar, followed by the treated sand. Eight mL distilled water was then placed on the surface of the sand. The time required to change the indicating Drierite completely from blue to pink was recorded as the penetration time. Water remained on the surface of hydrophobe-coated sand for as long as 30 days, although its vapor turned Drierite pink after seven days.

RESULTS AND DISCUSSION

Synthesis

A literature survey of the fatty acid-DETA reaction revealed many contradictions (2,9-11). The high temperatures (250-300 C) reported earlier by Waldmann and Chwala (16) have generally been accepted by subsequent investigators, despite the fact that DETA boils at 199-209 C. The reaction was reported to be an equimolar reaction, although the only investigator (11) who identified the isolated imidazoline found it to be a product containing two fatty acid groups. The assumption that primary amino groups were more reactive than secondary ones has resulted in the intermediate product being incorrectly reported as $(RCONHCH_2CH_2)_2NH$. The spectral data and physical properties of purified members of the series of fatty acid-DETA reaction products have not been recorded so far. These areas were investigated to determine information

TABLE I

Physical Properties of Diethylenetriamine Reaction Products

R	$R{-}\underbrace{C{=}N{-}CH_2CH_2N}{-}CH_2CH_2NHCOR$			$RCON(CH_2CH_2NH_2)CH_2CH_2NHCOR$		
	mp (C)	Contact angle (°)	Percolation test	mp (C)	Contact angle (°)	Percolation test
C_8H_{17}	45–46	62	i[c]	91–92	94	i
C_9H_{19}	48–49	59	i	101–102	104	i
$\Delta^{10}{-}C_{10}H_{19}$	40–41	37	i	92–93	76	i
$C_{11}H_{23}$	67–68	95	1 hr	110–111	99	1 hr
$C_{13}H_{27}$	70–71	89	1.5 hr	112–113	99	7 days
$C_{15}H_{31}$	78–79	97	7 days	116–117	96	> 7 days
$C_{17}H_{35}$	84–85	103	> 7 days	118–119	98	> 7 days
$\Delta^9{-}C_{17}H_{33}$ *cis*	liquid	0	5 min	52–53	50	5 min
$\Delta^9{-}C_{17}H_{33}$ *trans*	46–47	55	5 min	91–92	62	1 day
$C_{19}H_{39}$	88–89	104	> 7 days	110–111	104	> 7 days
$C_{21}H_{43}$	92–93	103	> 7 days	98–99	109	> 7 days
Tallow derivatives						
Tallow	35–45	23	i	50–60	37	i
Tallow fatty acid[a]	40–50	54	i	45–55	63	i
Tallow fatty acid[b]	45–55	97	i	55–65	97	i
Hyd. tallow FA	65–75	78	> 7 days	90–95	94	> 7 days
Methyl tallowate	45–55	40	30 min	55–65	46	1 hr

[a] T-22 fatty acids C_{18} *cis* = 36%; C_{18} *trans* = 7%.

[b] T-11 fatty acids C_{18} *cis* = 6%; C_{18} *trans* = 24%.

[c] i = instantaneous.

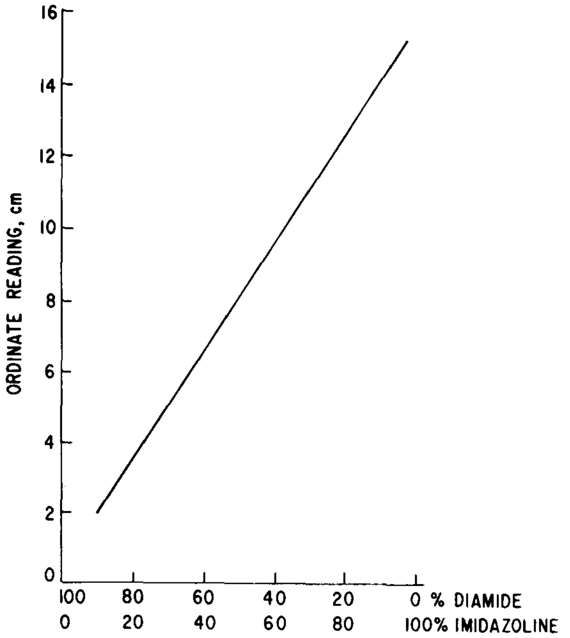


FIG. 1. Percentage composition of imidazoline in mixtures of imidazoline and diamide. 0.01% concentration in ethanol.

concerning the fatty acid-DETA reaction.

A series of fatty acid-DETA reactions was carried out at 120 C, 150 C, 175 C, and 200 C and the distillates collected for analysis. Results showed that excessive amounts of DETA codistilled with the water formed from the reaction at 175 C and 200 C. Only small amounts of DETA were found in the distillate from the 150 C reaction. It was concluded that 150 C was the optimum temperature for the reaction.

A reaction rate study was then conducted at 150 C under atmospheric pressure, using 2 mol tallow fatty acids and 1 mol DETA. Initially and at 2 hr intervals, samples were withdrawn for analysis of free fatty acid, primary, secondary, and tertiary amine, and the results are shown in Figure 2. Within the first 2-hr period, the amount of available fatty acid decreased to 1/3 of the original value, thus indicating that DETA and fatty acid did not react in a 1:1 mole ratio. However, during the same period, the meq/g of secondary amine dropped to an insignificant amount, while only a 1/3 reduction was detected for primary amine. This indicated clearly that in a nonaqueous system the secondary amino group was more reactive than the primary one as has been reported in aqueous systems (17). After the reaction had proceeded for 6 hr at 150 C, the free fatty acid content was less than 5% and the meq/g of primary amine reached a constant value roughly equivalent to one free amino group. Thus, the structure of the intermediate is $RCON(CH_2CH_2NH_2)CH_2CH_2NHCOR$ and not the previously reported $(RCONHCH_2CH_2)_2NH$ (11). If vacuum was applied during the first 2 hr of reaction, unreacted DETA distilled out, resulting in an excess of fatty acid remaining in the reaction mixture.

Cyclization to the imidazoline was completed after heating 2 hr at 150 C under 0.2 mm Hg pressure in a 92% yield. Further heating for 6 hr increased the conversion to 95%. The amount of tertiary amine rapidly increased, approaching the theoretical value for the fatty imidazoline, while only traces of primary and secondary amine

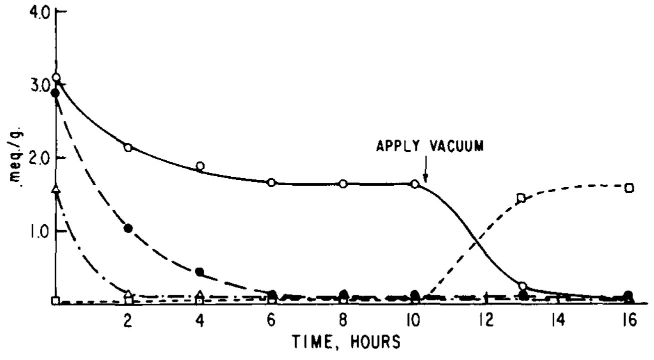
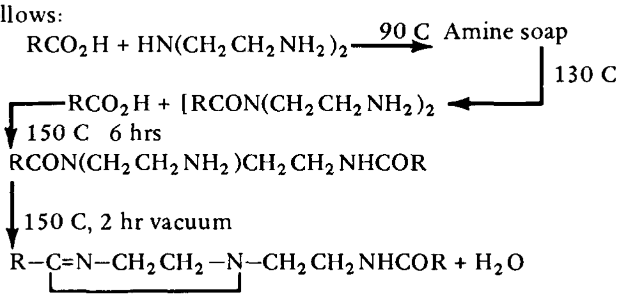


FIG. 2. Reaction rate study, 2 mol tallow fatty acid per mol diethylenetriamine. ● Tallow fatty acid; ○ primary amine; △ secondary amine; □ tertiary amine (imidazoline).

were found in the reaction product. The structure for the imidazolines is presumably $R{-}C{=}NCH_2CH_2N{-}CH_2CH_2NHCOR$, with only one of the two tertiary amino groups being titratable, as previously reported by Tornquist (7). This study thus shows the imidazolines can be synthesized under much milder reaction conditions than previously reported (10,11). The reaction proceeds as follows:



$$RCO_2H + HN(CH_2CH_2NH_2)_2 \xrightarrow{90\ C} \text{Amine soap}$$

$$\xrightarrow{130\ C} RCO_2H + [RCON(CH_2CH_2NH_2)_2$$

$$\xrightarrow{150\ C\ \ 6\ hrs} RCON(CH_2CH_2NH_2)CH_2CH_2NHCOR$$

$$\xrightarrow{150\ C,\ 2\ hr\ vacuum} R{-}C{=}N{-}CH_2CH_2{-}N{-}CH_2CH_2NHCOR + H_2O$$

The physical properties of the purified imidazolines and their diamide derivatives are tabulated in Table I.

The reactions of DETA with tallow and methyl tallowate were similarly investigated and the results shown in Figures 3 and 4. The amount of ester present, as determined by IR spectroscopy (18) and amine distribution by titration, were also determined at regular intervals. Since infrared (IR) determination of ester content is accurate only up to 10%, higher percentages have been estimated, based on the consumption of secondary amine, and are indicated by the dotted line on Figure 4. Tallow reacted rapidly with DETA Figure 3 at a rate similar to that of the above reaction with fatty acid (Figure 2). The content of secondary amine quickly dropped to a low level, the primary amine to a plateau value, and the tertiary amine increased, showing 28% of imidazoline after 6 hr reaction time at atmospheric pressure. In this reaction period the glyceride ester content decreased to less than 6%.

The reaction of DETA with methyl tallowate (Figure 4), proceeded more slowly and required 13 hr to reach the same end-point. It is not known why the methyl ester is less reactive than triglyceride or fatty acid. Alkali-catalyzed amidation of methyl esters usually proceeds rapidly. Perhaps the water from the ring closure inhibited the reaction, since 16% imidazoline was found in the reaction carried out under atmospheric conditions. The use of methyl esters was eliminated on the basis of high energy and time requirements.

The DETA-tallow reaction also had a serious disadvan-

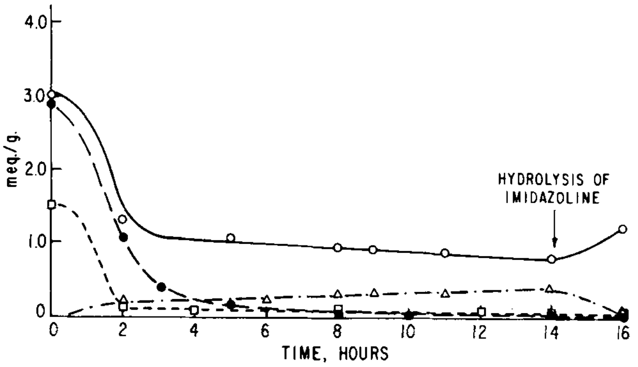


FIG. 3. Reaction rate study, tallow, and diethylenetriamine. ● Ester; ○ primary amine; △ secondary amine; □ tertiary amine (imidazoline).

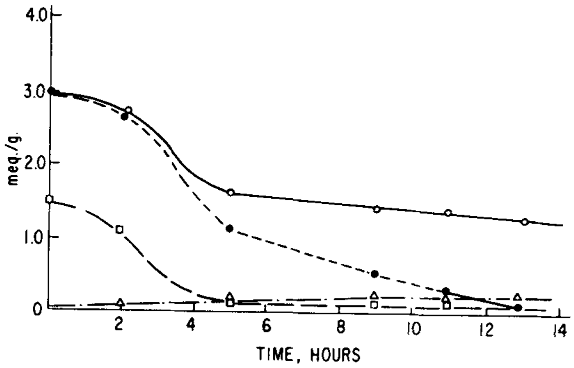


FIG. 4. Reaction rate study, 2 mol methyl tallowate per mol diethylenetriamine. ● Ester; ○ primary amine; □ secondary amine; △ tertiary amine (imidazoline); — — estimated.

tage: the problem of separation of ca. 10% glycerine formed in the reaction product. Glycerine retention resulted in a product with undesirable hydrophilic properties, and glycerine removal proved difficult and very time-consuming.

The diamides formed from each of the above reactions were readily cyclized to the imidazolines by applying vacuum for 2 hr at 150 C. In the reactions of DETA with the tallow, tallow fatty acid, or methyl tallowate in which the reaction product was not crystallized, a 5% excess of fatty material was used to minimize the formation of $RCON(CH_2CH_2NH_2)_2$. This low-melting waxy material has wetting properties similar to those of the dialkanolamides, $RCON(CH_2CH_2OH_2)_2$, and, if present in large amounts, would counteract water repellency.

Solubility Behavior

The higher molecular weight components of the two series were not very soluble in organic solvents at room temperature. Data showing the solubility behavior of the palmitic acid derivatives in various organic solvents are given in Table II. The table shows the temperature at which a 10% solution becomes clear. The more polar imidazoline is more soluble than the diamido compound, and the imidazoline is most soluble in ethanol, whereas the less polar diamide is most soluble in toluene.

TABLE II

Solubility Behavior of Palmitic Acid Derivatives in Various Solvents

Solvent	Imidazoline (C)[a]	Diamide (C)[a]
Acetone	49	55
Carbon tetrachloride	35-40	60-63
Ethanol	25	53-59
Isopropanol	30	45-50
Toluene	35	35-40

[a] Temperature at which 10% solution became clear.

Spectral Properties

In the IR region, the imidazolines displayed characteristic NH absorption at 3.03 μ with a shoulder at 3.15 μ amide band and a shoulder at 6.03 μ on the 6.12 μ amide band. Absorption for the diamide derivatives was observed at 3.03 μ and 6.12 μ. In the ultraviolet (UV) region, the imidazolines displayed a broach C=N band at 250-220 nm (peak at 230 nm) with a shoulder, CONH, at 202 nm. The diamide derivatives exhibited a strong CONH peak at 202 nm (19). The imidazoline content of an imidazoline diamide mixture can be determined by measuring in cm the UV absorbance at 230 nm of an absolute 0.01% ethanolic solution, and comparing this value with that of the calibration curve (Figure 1). UV absorbance thus is extremely useful in measuring composition of the compounds of this report and it can be used in determining very low concentrations of imidazoline. The imidazoline absorbance at 230 nm could be used to detect dilutions as low as 1 ppm, and the diamide absorbance at 202 nm can be used to determine concentration as low as 10 ppb.

Imidazoline Stability

Imidazolines are not stable chemical entities. Butler (20) observed cleavage of the imidazoline ring under atmospheric conditions within 2-9 days for compounds containing the *cis*-olefinic moiety. We have found that the tertiary amine content of saturated imidazolines decreased by 5-8% over an 18-month period, even when the product was stored in a closed glass container. Furthermore, the addition of 2% water to a reaction product, containing 38% imidazoline, resulted in a decrease to 6% in 72 hr with a further reduction to 4.5% after 6 days. Therefore, when used as intermediates, imidazolines should be reacted promptly and prolonged storage should be avoided.

Melting Properties

The melting point data are shown in Table I. The imidazolines melted at lower temperature and over a much wider temperature range (45-90 C) than the corresponding primary amides (98-112 C), (21). The imidazoline of oleic acid was liquid at room temperature (cf. oleamide 75-76 C), whereas its elaidic counterpart melted at 46-47 C (cf. elaidamide 93-94 C). In contrast, the diamides had higher melting points (92-119 C) which were closer to those of the primary amides. The oleic diamide was solid, melting at 52-53 C, whereas the elaidic diamide melted at 91-92 C. The melting points of the tallow derivatives were dependent upon the fatty acid composition of starting materials, byproducts formed, and amount of glycerine retained during processing.

Surface Properties

Hydrophobicity of the imidazolines and diamides were determined by contact angle measurements and percolation times and these are recorded in Table I. In general, contact angles increased as a function of molecular weight. Usually, the diamides possessed higher contact angles than the corresponding imidazolines. Unsaturation in the fatty acid chain caused a drastic reduction in contact angle and the angle for the *cis*-derivative was much lower than that for the *trans* compound.

The contact angle measurement for the derivatives of lauric acid and its saturated higher homologs were so close together that no clear distinction could be made between them with respect to hydrophobicity. It was therefore necessary to devise a more discriminating test, the percolation test. Differences between the C_{11}, C_{13}, and C_{15} derivatives were now observed. Water penetration rates through beds of treated sand were determined for the derivatives of the individual pure fatty acids, as well as for those from commercial fatty materials.

Water passed quickly through sand coated with the C_9, C_{10} and C_{11} derivatives and also the imidazolines of the oleic and elaidic acids. Although water penetrated the oleic diamide-coated sand within 5 min, a period of 1 day was required for penetration of the elaidic diamide-coated sand, showing the effect of *cis-trans* isomerism. In the *cis* configuration, the molecule is bent back upon itself, resulting in properties roughly analogous to those of a C_9 fatty acid derivative.

Although the elaidic diamide derivative is more linear in configuration, the *trans* unsaturation disarranges the molecules, resulting in surface properties which are inferior to those of the saturated stearic acid derivatives. Sand coated with derivatives of the C_{16} and higher molecular weight saturated fatty acids prevented water percolation for a month, demonstrating the influence of saturation and molecular weight on hydrophobicity. A delineation between hydrophilic and hydrophobic properties was observed between the lauric and myristic diamide derivatives, i.e., 1 hr vs 7 days. These data made it possible to interpret the results obtained from the tallow derivatives.

Contact angle measurements and percolation tests indicated that the tallow-DETA derivatives were hydrophilic, due to the high oleic acid content. Contact angles obtained from the methyl tallowate were slightly higher. Since these two compounds had similar fatty acid composition, the difference was due to the glycerine retained in the product prepared directly from tallow. The tallow fatty acid (T-22)-DETA reaction product, high in oleic acid content, had slightly higher contact angles, and gave instantaneous wetting of sand. It was thought that a more hydrophobic product would be obtained by the elaidinization of tallow fatty acids. Although high contact angles (97°) were obtained for the thus-treated fatty acid (T-11)-DETA reaction product, the percolation test indicated its inadequate hydrophobic properties. The hydrogenated tallow fatty acid-DETA reaction product, being completely saturated, was found to have a high contact angle and water failed to penetrate a bed of sand coated with this material in a 30-day period. Thus the fatty acid-DETA reaction products prepared from the C_{16}, C_{18}, and hydrogenated tallow fatty acids possessed optimum hydrophobic properties.

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