

Preparation of Some Mono- and Diesters of N,N-Disubstituted Amides and Their Evaluation as Plasticizers

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ABSTRACT

Mono- and diesters of fatty acid- and aromatic acid-derived N,N-disubstituted amides were prepared in which the acid moieties were alternately substituted to function as the basic amide moiety or the terminal ester moiety. Several of the ester-amides were evaluated as plasticizers for polyvinyl chloride (PVC). The plasticized stocks exhibited properties that equaled, and in some instances were superior to PVC plasticized with the common plasticizer, di-2-ethylhexyl phthalate (DOP). The monoesters were more compatible than the diesters. Thermal stability was enhanced by the presence of the benzoic acid moiety in the molecule. Brittle point temperatures were shown to be a predictable characteristic for specific terminal groups, based on structural similarity of the basic molecule.

INTRODUCTION

A variety of types of N,N-disubstituted fatty amides have been shown to have members that are effective plasticizers for polyvinyl chloride (PVC) resins. These include symmetrical and unsymmetrical N,N-dialkyl oleamides (1);

N,N-bis(2-alkoxyethyl) long chain fatty amides (2); N,N-bis(2-acyloxyethyl) long chain fatty amides (3); and others (4,5). Certain mixed esters of aliphatic diols containing at least one long chain fatty acyl group have also been shown to have excellent properties as plasticizers for PVC (6). In the present work, a number of mono- and diesters of N,N-disubstituted amides of some long chain fatty acids and of benzoic and toluic acids were prepared, characterized, and evaluated as plasticizers for PVC. Several of these ester-amides proved to be highly efficient plasticizers, and properties of the plasticized stock, in some cases, were superior to those of PVC plasticized with the conventional plasticizer, di-2-ethylhexyl phthalate (DOP).

EXPERIMENTAL PROCEDURES

Diethanolamine, N-methylethanolamine, the fatty acid methyl esters, and aromatic acids were all commercial products used without further purification. The acid chlorides were also commercial products, except for erucoyl chloride and *p*-toluoyl chloride, which were prepared from the acids by conventional procedures.

The fatty amides were prepared by dropwise addition of the fatty acid methyl ester into a vigorously stirred mixture of the hydroxy amine and metallic sodium, dissolved in absolute methanol maintained at 65-70 C and under 60 mm pressure as described in the literature (3). The reaction was judged complete upon cessation of the evolution of methanol. The product was neutralized with dilute HCl, dissolved in benzene, washed with water, and dried over anhydrous sodium sulfate. The hydroxyethyl benzamides and toluamides were prepared similarly, except that a saturated sodium chloride solution was used during the wash procedure to minimize losses because these compounds were found to be very soluble in water. The esters were prepared by the interaction of equimolar quantities of the hydroxy-ethyl amides and the acid chlorides in the presence of pyridine, with benzene as the solvent. The pyridine hydrochloride was filtered off, the filtrate washed with water, dried over anhydrous sodium sulfate, and eluted through an activated alumina column to remove residual free acids. The solvent was removed at reduced pressure. The intermediate and final products were characterized by infrared and nuclear magnetic resonance spectral analyses, as shown in Figures 1 and 2. Densities were deter-

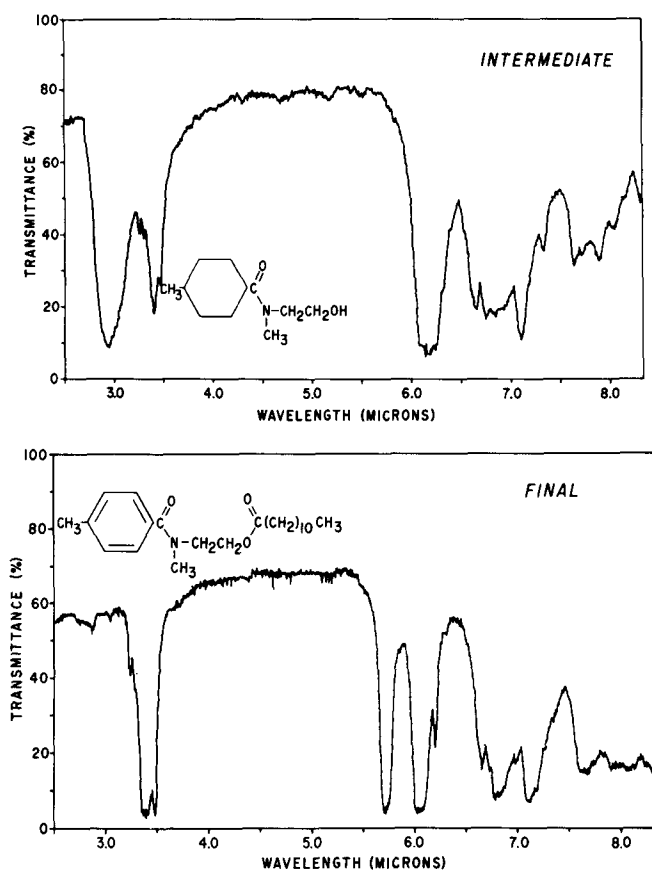


FIG. 1. Infrared spectra of intermediate and final product, between 2.5 and 8.3 microns, in typical preparation. A. N-Methyl-N-(2-hydroxyethyl)*p*-toluamide; B. N-Methyl-N-(2-lauroyloxyethyl)*p*-toluamide.

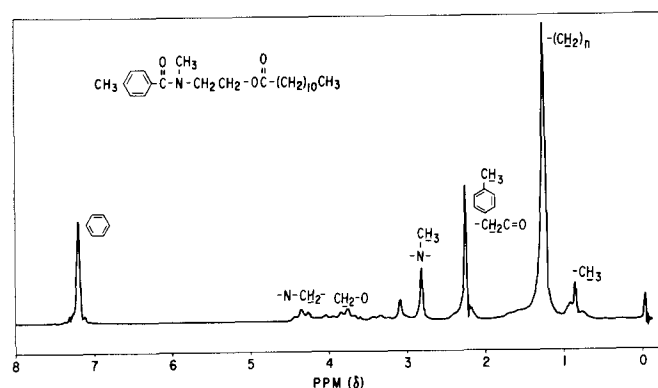


FIG. 2. Nuclear magnetic resonance spectrum (60 MHz) of N-methyl-N-(2-lauroyloxyethyl)*p*-toluamide.

TABLE I
Plasticizer Characteristics of Ester-Amide-Plasticized Polyvinyl Chloride (35% Plasticizer)

No.	Ester-Amide	Compatibility ^a	Tensile strength (psi)	100% modulus (psi)	Elongation 100%	Brittle point (° C)	Volatility loss (%)	Density (30 C) ^b
1	N-Methyl-N-(2-benzoyloxyethyl)lauramide	C	3024	1607	329	-18	2.38	0.993
2	N-Methyl-N-[2-(2-furoyloxyethyl)lauramide	C	2911	1731	264	-20	0.99	1.008
3	N-Methyl-N-[2-(<i>p</i> -toluoyloxyethyl)lauramide	C	2965	1590	296	-18	1.07	0.998
4	N-Methyl-N-(2-trimethylacetoxylethyl)lauramide	I	-----	-----	---	-32	---	0.921
5	N-Methyl-N-(2-benzoyloxyethyl)oleamide	I	2996	1776	341	-34	0.63	0.960
6	N-Methyl-N-[2-(2-furoyloxyethyl)oleamide	I	2966	1754	338	-36	1.15	0.965 ^c
7	N-Methyl-N-[2-(<i>p</i> -toluoyloxyethyl)oleamide	C	3265	1546	319	-33	0.99	0.955
8	N-Methyl-N-(2-trimethylacetoxylethyl)oleamide	I	-----	-----	---	---	0.916	---
9	N-Methyl-N-(2-benzoyloxyethyl)erucamide	I	2897	1929	355	-42	0.71	0.936 ^c
10	N-Methyl-N-(2-furoyloxyethyl)erucamide	C	2993	2018	319	(-43) ^d	0.40	-----
11	N-Methyl-N-[2-(<i>p</i> -toluoyloxyethyl)erucamide	C	3056	2189	275	(-41)	0.83	-----
12	N-Methyl-N-(2-lauroyloxyethyl)benzamide	C	2934	1424	352	-22	0.80	0.988
13	N-Methyl-N-(2-oleoyloxyethyl)benzamide	C	2965	1604	335	-32	1.38	0.962
14	N-Methyl-N-(2-lauroyloxyethyl) <i>p</i> -toluamide	C	-----	-----	---	-28	3.2	0.955
15	N-Methyl-N-(2-oleoyloxyethyl) <i>p</i> -toluamide	C	-----	-----	---	-16	1.8	0.965
16	N,N-Bis(2-benzoyloxyethyl)lauramide	C	-----	-----	---	-2	0.4	1.047
17	N,N-Bis[2-(2-furoyloxyethyl)lauramide	C	-----	-----	---	-5	1.1	1.082
18	N,N-Bis(2-trimethylacetoxylethyl)lauramide	I	-----	-----	---	-16	---	0.947
19	N,N-Bis(2-lauroyloxyethyl)benzamide	I	-----	-----	---	---	---	---
20	N,N-Bis(2-oleoyloxyethyl)benzamide	C	-----	-----	---	-7	---	0.962
21	N,N-Bis(2-erucoyloxyethyl)benzamide	I	-----	-----	---	---	0.945	---
22	N,N-Bis(2-benzoyloxyethyl)oleamide ^e	C	-----	-----	---	-9	---	1.010
23	N,N-Bis(2-trimethylacetoxylethyl)oleamide	I	-----	-----	---	-24	---	0.940
24	Di-2-ethylhexyl phthalate (DOP, Control)	C	3082	1785	349	-31	1.62	-----

^aC = compatible; I = incompatible.

^bOf ester-Amide plasticizer.

^cDetermined at 40 C.

^dValues in parentheses are predicted.

^eCompound previously reported, see reference 3.

mined pycnometrically in a thermostated bath controlled to ± 0.1 C.

The ester-amides were screened as plasticizers for vinyl chloride homopolymer, Geon 101, and were compared with a control plasticizer, DOP. The formulation was as follows: resin, 63.5%; plasticizer, 35%; basic lead carbonate stabilizer, 1.0%; and stearic acid, 0.5%. Milling, molding, and testing procedures were those described by Magne et al. (5). Volatilities were determined by the activated carbon method (7). Thermal stabilities were established in terms of the reflectances of the plasticized stock after it was subjected in increasing exposure periods in a forced draft oven maintained at 176 C. These values were determined by means of a Photoelectric Reflection Meter, Model 610 (Photovolt Corp., New York, NY), with the amber 0° , 45° directional reflectance. Compositions which showed no signs of exudation during 90 days of shelf storage were rated compatible.

RESULTS AND DISCUSSION

Plasticizer evaluation data and densities are presented in Table I. Several of the compounds that proved compatible yielded plasticized materials with very good properties, when compared with DOP-plasticized PVC. The compounds we chose for preparation and evaluation were based on their molecular similarity so that the effects of specific moieties on compatibility and brittle point temperature could be observed. Of the two general classes, the monoesterified amides were more compatible than the diesterified amides. The reduced compatibility was probably due more to the larger molecular weight of the diester amides than to the structure, as others (8) have noted incompatibility when two long chain acyl groups were present. Although no plasticizer evaluation data were developed for the *N,N*-bis(2-benzoyloxyethyl) and *N,N*-bis[2-(2-furoyloxy)ethyl] lauramides and for *N,N*-bis(2-oleoyloxyethyl)benzamide, the fact that these compounds are compatible is in itself significant.

The plasticizer data for the monoesterified amides show that two general groups can readily be identified—amides derived from a fatty acid that contain a terminal aromatic acid moiety and amides derived from an aromatic acid that contain a terminal fatty acid moiety. Inclusion of the aromatic moiety enhances compatibility, whether it occurs as the terminal ester substituent or in the basic amide group. It would be difficult to rate the plasticizing efficiency of the ring structures on the basis of the limited data; however, the furoic acid moiety appears to have a slight advantage over the benzoic and toluic acid moieties, probably a result of the oxygen in the ring. All of the compounds that were compatible exhibited relatively good plasticizing characteristics when compared with DOP. One of the better of them is *N*-methyl-*N*-[2(*p*-toluoyloxy)ethyl] oleamide. *N*-methyl-*N*-(2-benzoyloxyethyl)- and *N*-methyl-*N*-[2(2-furoyloxy)ethyl] oleamide, and *N*-methyl-*N*-(2-benzoyloxyethyl)erucamide also gave plasticized stocks with excellent properties when freshly milled, but gave exudation on standing, indicating incompatibility. These compounds might be useful as secondary plasticizers, or perhaps, as primary plasticizers at a lower level of application. Unfortunately, no brittle point temperatures were obtained for PVC plasticized with *N*-methyl-*N*-[2(*p*-toluoyloxy)ethyl]- and *N*-methyl-*N*-[2(2-furoyloxy)ethyl]erucamide. There are indications that they would be superior to PVC plasticized with DOP. Volatility of all but one of the compounds evaluated were superior to that of DOP.

Thermal stability of PVC plasticized with the esterified *N,N*-disubstituted amides can be considered poor, in general, though there were exceptions. Most of the samples tested darkened rapidly during the first hour; however,

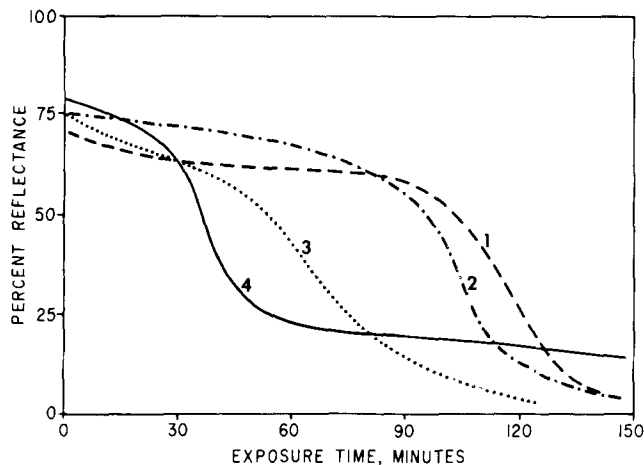


FIG. 3. Thermal stability of ester-amide compositions with polyvinyl chloride (standard formulation). Curve 1 = *N,N*-Bis(2-benzoyloxyethyl)lauramide; Curve 2 = *N*-Methyl-*N*-(2-lauroyloxyethyl)benzamide; Curve 3 = *N*-Methyl-*N*-(2-benzoyloxyethyl)erucamide; Curve 4 = Di-2-ethylhexyl phthalate (DOP).

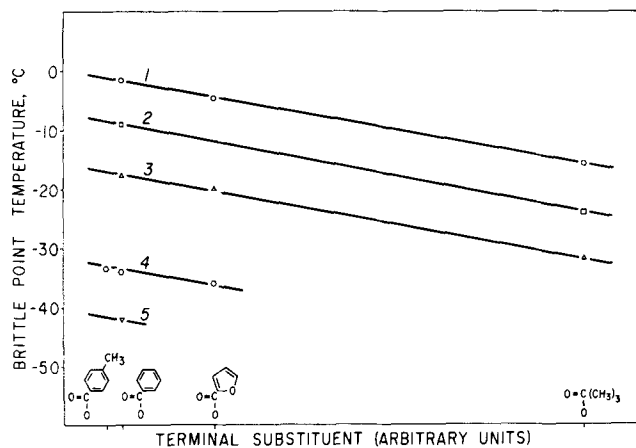


FIG. 4. Relationship between brittle point temperature and esterifying moiety for esterified *N,N*-disubstituted amides: \circ = Lauramides, samples 16, 17, 18 (line 1); \square = Oleamides, samples 22, 23 (line 2); \triangle = *N*-Methyl-lauramides, samples 1, 2, 4 (line 3); \diamond = *N*-Methyl-oleamides, samples 7, 5, 6 (line 4); ∇ = *N*-Methyl-erucamide, sample 9 (line 5).

N,N-bis(2-benzoyloxyethyl)lauramide, *N*-methyl-*N*-(2-lauroyloxyethyl)benzamide, and *N*-methyl-*N*-(2-benzoyloxyethyl)erucamide all gave plasticized stocks that appeared to resist thermal degradation better than DOP-plasticized PVC did, which probably resulted from the benzoic acid moiety in the molecule. Data on thermal stability are presented graphically in Figure 3.

Effect of Structure on Brittle Point Temperature

The simple solubility equation for ideal dilute solutions is written

$$\ln N = \Delta H_f / R(1/T) + C_1 \quad (I)$$

where N is the mole fraction of the solute, ΔH_f is the heat of fusion in calories per mole, T is the primary freezing point, R is the gas constant, and C_1 is a constant dependent on the system. When a resin is plasticized, the plasticizer plays the role of the solvent and the resin that of the solute (9). A similar equation can be written for a second compound,

$$\ln N' = \Delta H'_f / R(1/T') + C_2 \quad (II)$$

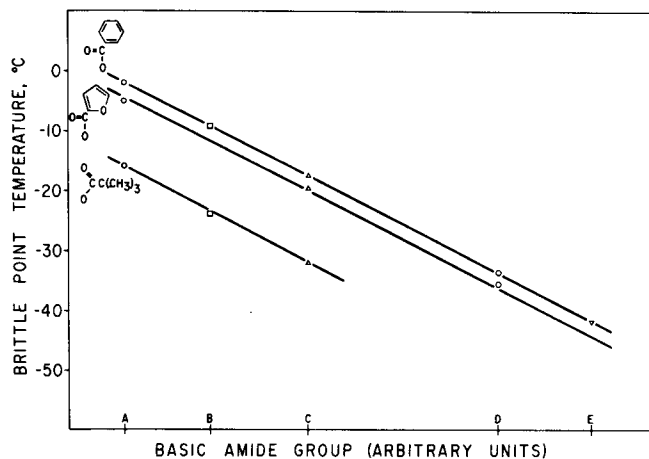


FIG. 5. Relationship between brittle point temperature and amide moiety: A = Lauramide grouping, samples 16, 17, 18; B = Oleamide grouping, samples 22, 23; C = N-Methylauramide grouping, samples 1, 2, 4; D = N-Methyloleamide grouping, samples 5, 6; E = N-Methylerucamide grouping, sample 9.

At the same solute concentration, i.e., when $N = N'$, the two equations can be combined to give, on rearranging,

$$T' = \Delta H_f' / \Delta H_f(T) + C_3 \quad (\text{III})$$

Since the brittle point is the temperature at which the plasticizer-resin combination undergoes a transition (9), it follows that for any given analogous or homologous fatty acid-derived compound (plasticizer), the brittle point temperature would be positively or negatively influenced by the electrophilic character of the compound, and also by that of the terminal substituent. The change would not be expected to vary greatly from one fatty acyl group to another and would be expected to vary uniformly. Figure 4 was developed on this premise. Brittle point temperatures (the highest and the lowest) were plotted on the ordinate scale at either end of the abscissa, and a straight line was drawn between them. The remaining brittle point tempera-

tures for each of the ester-amides were plotted along the straight line and thus were utilized to establish the coordinate position along the abscissa for each of the terminal substituents. Plots are then constructed for each of the substituted amide groups utilizing the coordinates so obtained. It is obvious, even with the limited number of observations, that the resulting brittle point depression for a given substituent on a basically similar compound is very nearly constant. Further, this brittle point temperature can be predicted for a series of structurally similar compounds based on a single determination, once brittle points have been obtained for two complete series. Brittle point temperatures that had not been experimentally determined for two of the erucamides have been predicted from Figure 4, and are included in Table I.

A second relationship, the brittle point change for a given terminal substituent for structurally similar basic compounds, also exists, as is illustrated in Figure 5. This relationship allows the brittle point temperatures to be predicted for different substituents with any given basic structure.

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