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# THE REACTION BETWEEN TERTIARY AMINES AND ORGANIC ACIDS IN NONPOLAR SOLVENTS

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## ABSTRACT

Cryoscopic measurements in dilute benzene solution indicate that aliphatic tertiary amines of high molecular weight react with fatty acids to form products in which two equivalents of acid are combined with one of amine, and that these products are in equilibrium with free acid and free amine to a significant extent. These amine-acid complexes enter into secondary equilibria with additional acid to form less stable complexes wherein four equivalents of acid are combined with one of amine. The data agree quantitatively with the assigned equilibrium constants. Only one equivalent of picric acid combines with one of amine to form a stable salt; this salt associates to form dimers but, like the alkylammonium halides, does not dissociate appreciably in nonpolar solvents. In dilute benzene solutions less basic tertiary amines such as pyridine show only a slight tendency to react, while dimethylaniline, the least basic amine studied, shows no detectable evidence of reaction with fatty acids. Tertiary aliphatic amines will effectively neutralize strong acids, but they will only reduce to a controlled and low level the concentration of a carboxylic acid in a nonpolar solvent. The results of this investigation are directly applicable to the theory and practice of corrosion inhibition in oils, fuels, and other non-aqueous systems.

## PROBLEM STATUS

This is an interim report; work on other phases of the problem is continuing.

## AUTHORIZATION

NRL Problem C08-01R  
NR 408-010

## THE REACTION BETWEEN TERTIARY AMINES AND ORGANIC ACIDS IN NONPOLAR SOLVENTS

### INTRODUCTION

Amines of various types are frequently used as rust preventives and additives in lubricating oils. Recent work in this Laboratory (3, 4, 5) has indicated the possible usefulness of ashless rust inhibitors such as the compound formed between cetyldimethylamine and phenylstearic acid. Little information is available concerning the stability and the state of dispersion of the soluble compounds formed between amines and organic acids in non-aqueous solvents. Such information is needed to evaluate the neutralizing effect of amines on corrosion-promoting fatty acids of low molecular weight formed during the oxidation of lubricating oils in service, as well as to determine the mechanism by which amine-acid compounds function as inhibitors of rusting.

Maryott (15) has studied dilute benzene solutions of pure picrates of numerous primary, secondary, and tertiary amines. Except in the case of tribenzylammonium picrate he noted no appreciable dissociation into free amine and picric acid. He found that picrates of primary and secondary (but not of tertiary) amines were associated into bimolecular complexes having a stability slightly less than that found by Maryott, Hobbs, and Gross (16) for the dimers of long-chain fatty acids in the same solvent. Picric acid, however, differs so much in structure, strength and dipole moment from carboxylic acids that the behavior of amine picrates cannot be extrapolated with confidence to predict the behavior of similar amines with fatty acids of high molecular weight.

Prideaux and Coleman (23) studied the reaction between piperidine and propionic acid in benzene. They reported piperidine propionate to exist in 5 percent solution largely as double molecules with aggregation of increasing complexity at higher concentrations. They considered that the acid and amine combined only in equivalent proportions.

Hunter (13) prepared compounds by the reactions of a large number of carboxylic acids including lauric, palmitic and stearic with dodecylamine and octadecylamine. He combined equivalent proportions of amine and acid in both petroleum ether and alcohol solutions. Nitrogen analyses did not indicate the isolation of other than one-to-one compounds.

Matavulj (17) studied refractometrically the liquid binary systems formed by a number of primary, secondary, and tertiary amines of relatively low molecular weight with isobutyric and isovaleric acids. He reported evidence for the formation of compounds containing two equivalents of acid per equivalent of amine between triethylamine and isovaleric acid and between aniline and isobutyric acid, as well as compounds containing three equivalents of acid per equivalent of amine between pyridine and propionic, butyric, and valeric acids. Matavulj also reported that pyridine and quinoline showed no refractometric evidence of compound formation with fatty acids containing more than five carbon atoms, and

attributed the failure to react to the relatively greater association of the acids of longer chain length.

Lucasse, Koob, and Miller (14) investigated the binary system *p*-toluidine-acetic acid, and reported a maximum melting point for the mixture corresponding to two equivalents of acid per equivalent of amine.

O'Connor (19) studied the binary system dimethylaniline-acetic acid, and found little or no evidence of reaction between these two compounds.

Pool, Harwood, and Ralston (22) studied the binary system, octadecylamine-acetic acid, and isolated crystalline solids with one and two equivalents of acid per equivalent of amine. Although the studies of these various binary systems are of considerable importance, they do not furnish direct evidence concerning the behavior to be expected in low concentrations in nonpolar solvents.

The present investigation was intended to establish the presence or absence of colloidal aggregates of amine-fatty acid compounds in benzene solutions. Preliminary cryoscopic observations indicated that micelle formation did not occur to a detectable extent, and suggested further that the amine-acid compounds were dissociated into free amine and free acid to a degree that permitted detailed study of the reaction. Since the extent and nature of such a dissociation bear significantly on the theory and practice of rust and corrosion inhibition, this further work was undertaken.

It was expected that the amine and acid might combine in equivalent proportions to form salts that could be purified by recrystallization for use in the cryoscopic study. Attempts to prepare such compounds, however, led to various crystalline products containing approximately two and three equivalents of acid per equivalent of amine. This variety of possible solid compositions does not of necessity furnish proof of the existence of corresponding molecular species in the liquid phase from which they separate. The combining ratio of acid to amine might be determined in the act of crystallization as a consequence of the geometry of the crystal lattice and the relative solubilities of the substances present, as in the case of such hydrated mixed salts as the alums. Therefore, the final examination of the equilibrium between acids and amines was made by adding amine and successive increments of acid to a quantity of benzene in which they would remain completely dissolved.

Although the attempts to prepare solid compounds were not pursued far enough to produce materials of high purity, the results are briefly reported because of their relation to the results later obtained with the liquid systems.

Four compounds of cetyldimethylamine were prepared with the following fatty acids:

- (a) Stearic acid, by reaction of equivalent proportions of amine and melted acid. The resulting crystal-containing mush was centrifugally filtered, and the solid recrystallized three times from acetone. The white crystalline product was dried in vacuo at 35°C.
- (b) Stearic acid, by mixing the acid with the amine in 95 percent ethanol in proportions which approximated the phenol red end point. The white crystalline product was recrystallized three times from alcohol and once from acetone.
- (c) Lauric acid, by reaction of equivalent proportions of amine and acid in ethyl acetate solution. The white crystals which separated were dried on a clay plate and recrystallized from acetone and from ethyl acetate.

- (d) Oleic acid, by reaction of equivalent proportions of acid and amine. The white crystals were centrifugally filtered from the resulting mush, washed with benzene, and dried in vacuo at 25°C.

The four products were analyzed for total nitrogen content. Results of the analyses and melting points are recorded in Table 1, together with the calculated nitrogen content for each of the corresponding compounds containing one, two, and three equivalents of acid per equivalent of amine. The two stearates prepared by different procedures differ in composition. The analysis of preparation (b) corresponds to an acid-amine combining ratio of 2:1, while that of preparation (a) corresponds more nearly to a ratio of 3:1. The laurate (c) and oleate (d) analyses both correspond to an acid-amine combining ratio of 2:1. These results indicate the possible formation of complexes having acid-amine combining ratios greater than 1:1, and in the case of the stearate, the possibility of more than one ratio.

TABLE 1  
Analyses of Cetyldimethylamine-Fatty Acid Compounds

Preparation Symbol	Acid	Analysis (% nitrogen)	Calculated Composition for Monoacid Complex (% nitrogen)	Calculated Composition for Diacid Complex (% nitrogen)	Calculated Composition for Triacid Complex (% nitrogen)	Melting Point (°C)
(a)	Stearic	1.31	2.53	1.67	1.24	64.2-64.5
(b)	Stearic	1.62	2.53	1.67	1.24	77-79
(c)	Lauric	2.13	2.98	2.09	1.61	56.8-57.5
(d)	Oleic	1.80	2.54	1.68	1.20	36.2-37.3

For the cryoscopic work, benzene was chosen as a representative nonpolar solvent with a convenient freezing point. Naphthalene was the solute used for comparison purposes, and for validation of the apparatus and technique. Cryoscopic determinations were made with solutions of cetyldimethylamine, triisoamylamine, pyridine, dimethylaniline, and acetic, myristic, and picric acids, respectively. Further observations were made with additions of myristic acid to solutions of cetyldimethylamine, triisoamylamine, pyridine and dimethylaniline, and with additions of picric and acetic acids to solutions of triisoamylamine.

Preliminary tests demonstrated that neither stearic acid nor its amine complex was sufficiently soluble to permit cryoscopic determinations at the desired concentrations. Palmitic acid was unsuitable for similar reasons. Myristic acid was chosen as the representative high molecular weight acid because of its availability, the adequate solubility of the acid and of its amine complex, and its degree of dimerization (7), which is comparable to that of stearic and other high molecular weight aliphatic acids.

Acetic acid was selected as a representative low molecular weight aliphatic acid. It is also of interest as a common product of the oxidation of hydrocarbons and their derivatives.

Picric acid (trinitrophenol), on the other hand, represents a different class of acid, having greater strength, a noncarboxylate structure, and little or no tendency to dimerize

in dilute benzene solutions. It was selected for these reasons, and because the amine picrates have been investigated by other workers, thus permitting a check of our experimental technique by comparison with the results obtained elsewhere from measurements of dielectric properties (15) and from cryoscopic studies (6).

Because of the pronounced association of primary and secondary amines and their salts (15), the scope of this investigation was limited to tertiary amines in order to simplify the interpretation of the cryoscopic data. The four amines studied were chosen to provide a wide range of basicity, structural type and symmetry of substitution about the nitrogen atom. Cetyldimethylamine and triisoamylamine or their addition compounds represent a possible class of rust inhibitors for lubricating compositions; dimethylaniline and pyridine are distinct types of less basic aromatic nitrogen compounds which bear structural relationship to other types of additives used as oxidation inhibitors in lubricating oils.

## MATERIALS

The myristic acid used was the Eastman Kodak product No. 1116. As received, its melting point was 51.8°-52.7°C. It was prepared for use by heating in vacuo to about 60°C at 0.3 mm Hg for 0.5 hour and by cooling at the same pressure. The dried acid melted at 52.3°-53.0°C. Ralston (24) considers 54.4°C the most reliable melting point for this acid, but cites both higher and lower values. The neutral equivalent weight of the final product, determined by titration, was 232.8 (theoretical 228.36).

The cetyldimethylamine was prepared from hexadecylamine by the method of Ralston et al.(25). Hexadecylamine was fractionally distilled in vacuo from material supplied by Armour and Company (Armeen 16D). The melting point of the fraction used was 45.6°-46.6°C. Ralston et al.(26) report the freezing point of hexadecylamine as 46.77°C. The cetyldimethylamine prepared from the primary amine was fractionally distilled in vacuo. The fraction reserved for cryoscopic work distilled at 118°-119°C and 0.3 mm Hg. This product was stored in sealed ampoules. Before use, it was dried by heating to 80°C at 0.3 mm Hg for 0.5 hour and cooled at the same pressure. Its neutral equivalent was 278.7 (theoretical 269.5).

If the discrepancy in equivalent weight is explained by assuming the presence of some octadecyldimethylamine, the amount of C<sub>18</sub> required is found to be improbably high. The starting material (hexadecylamine) is reported to contain six percent of octadecylamine and three percent of a neutral impurity. It is likely that an appreciable amount of this neutral impurity was carried over to the tertiary amine. The equivalent weight obtained could result from the mixture of 3.4 percent of such a material with pure cetyldimethylamine. Spot tests (11) on a semiquantitative basis indicated that primary and/or secondary amines were present to the extent of less than 0.1 percent.

The triisoamylamine was the Eastman Kodak product No. 1880. After dehydration with solid potassium hydroxide, it was filtered through sintered glass and fractionally distilled in vacuo. The fraction reserved for cryoscopic work distilled at 111.5°-112.0°C and 10 mm Hg. Its refractive index ( $n_D^{20}$ ) was 1.4330. Its neutral equivalent was 228.4 (theoretical 227.4).

The dimethylaniline was the Eastman Kodak product No. 97. After dehydration with potassium hydroxide it was filtered through sintered glass and fractionally distilled in vacuo. The fraction reserved for cryoscopic work distilled at 92.0°-92.6°C and 20 mm Hg. Its refractive index ( $n_D^{20}$ ) was 1.5589 (ICT value,  $n_D^{20} = 1.5587$ ).

The pyridine was Baker's cp grade. It was fractionally distilled at atmospheric pressure (774 mm Hg) with appropriate safeguards against the absorption of moisture. Since pyridine forms an azeotrope with water (bp 92°C) no preliminary dehydration was necessary. The fraction reserved for cryoscopic measurements distilled at 115.4°-115.8°C. Its refractive index ( $n_D^{20}$ ) was 1.5101 (ICT value,  $n_D^{20} = 1.509$ ).

The picric acid was the Eastman Kodak product No. 210. It was recrystallized once from aqueous alcohol solution, and twice from benzene and was desolvated in vacuo at 62°C. The final crystals were a very pale yellow and melted at 122.3°-122.9°C.

The acetic acid was Baker's cp ACS grade. It was purified in a dry atmosphere by four partial freezings with rejection of the liquid phase after each freezing. The fraction reserved for cryoscopic work froze at 16.4°C.

Thiophene-free benzene meeting ACS specifications was percolated through activated silica gel to remove polar material and moisture, and was stored over sodium until used. Its freezing point was 5.37°C.

The naphthalene was the Eastman Kodak product No. 168, which is recrystallized from alcohol. It was prepared for use by double resublimation in vacuo at 0.3 mm Hg, and was heated to about 50°C and allowed to cool in vacuo just before use.

To avoid contamination by moisture, all unsealed materials were kept in tightly covered desiccators over suitable desiccants except during necessary transfers.

#### EXPERIMENTAL PROCEDURE

A Beckmann cryoscopic apparatus was used for the freezing point measurements. The temperature of the jacket was maintained constant to  $\pm 0.1^\circ\text{C}$  by circulating liquid coolant from a thermostatically controlled reservoir. The mean jacket temperature was held at 3.3°C for measurements of the freezing point of pure benzene, and at 3.3°C minus the depression when solutes were present. The contents of the inner tube were agitated by an externally driven glass stirring screw, rotating in the direction which lifted the separating crystals from the bottom of the tube. Reciprocal vertical stirring, which is commonly used, was found to pump out solvent vapor at an appreciable rate, so that the concentration of the solution could not be held sufficiently constant. The losses of benzene with rotary stirring were measurable, but small, amounting to about 0.05 gram per hour with the arrangement employed. It was assumed that these losses were distributed evenly with respect to time, and corrections to observed data were made on this basis when the losses were significant.

The stirrer shaft traversed the stopper of the inner freezing tube in a glass sleeve having a side arm, through which nitrogen dried over magnesium perchlorate was passed. The omission of the current of dry nitrogen past the stirrer shaft was found to allow the slow entry of moisture, which progressively depressed the freezing point. A differential thermometer indicated the temperature of the contents of the freezing tube. To eliminate parallax, the thermometer was read with a suitably mounted microscope.

Before use, the inner freezing tube was flushed with dried nitrogen for one hour or more to remove the contained air and the moisture held by the walls. Omission of the flushing produced a variable and marked depression of the freezing point of the pure solvent.

The amount of supercooling was controlled so that its magnitude was  $0.2 \pm 0.05^\circ\text{C}$  except in a few cases. The solutions were inoculated with minute crystals of benzene

introduced through the side arm of the freezing tube by means of a platinum wire. The seed crystals of benzene were protected from moisture until transfer, and the transfer was made in ten seconds or less. Corrections were made for withdrawal of solvent by freezing (2) according to the equation

$$y = \frac{t_s \times s}{l_f},$$

where  $y$  = the fraction of benzene removed by freezing,

$t_s$  = the extent of supercooling in  $^{\circ}\text{C}$ ,

$s$  = specific heat of benzene in  $\text{cal/g}/^{\circ}\text{C}$ , and

$l_f$  = latent heat of fusion of benzene in  $\text{cal/g}$ .

With the exception of picric acid, pellets of the solids were introduced into the side arm of the freezing tube from tared vials. Picric acid was introduced in small tared cups of fragile glass which were shattered by the rotating stirrer. Liquids were introduced by means of tared hypodermic syringes of suitable sizes. The observations were made in a constant-temperature room at  $25^{\circ}\text{C}$  and 20 to 50 percent relative humidity.

Measurements were made with  $26.0 \pm 0.2$  g of benzene. The temperature of the solution was read at half-minute intervals preceding freezing and after freezing began, until the temperature showed no detectable change during a minimum interval of four minutes. This constant temperature was taken as the observed freezing point. The measurements produced results which were satisfactorily concordant. When all of the data for a given solute were combined in a single plot of the freezing-point depression,  $\Delta T$ , vs. concentration, the average deviation of the experimental points from the best smooth curve was  $\pm 0.002^{\circ}\text{C}$ .

## RESULTS

Figure 1 presents the experimental data for the cryoscopic effect of naphthalene in benzene solution, together with that for the amines studied. The data for naphthalene and the corresponding calculated values for the molal freezing point constant,  $K_f$ , of benzene are tabulated in Table 2. The average value of  $K_f$  is  $5.17^{\circ}\text{C}$ . The equation employed at the Bureau of Standards for the cryoscopic determination of the purity of benzene (12) is consistent with a value of  $K_f = 5.13$  at infinite dilution.

TABLE 2  
Cryoscopic Effect of Naphthalene in Benzene

Concentration ( $\frac{\text{formula wt}}{\text{kg solvent}}$ )	$\Delta T$ ( $^{\circ}\text{C}$ )	$K_f$ ( $^{\circ}\text{C}$ )
0.0626	0.324	5.18
0.1008	0.521	5.17
0.1340	0.692	<u>5.16</u>
		avg 5.17

The constant obtained in the present measurements is thought to differ from the accepted value because of small systematic errors derived from the materials and techniques employed; it was used for the treatment of other data obtained under the same conditions in order to reduce the effects of such systematic errors.

The cryoscopic effect of the amines in benzene (Table 3 and Figure 1) is very near that of the naphthalene, except for the case of pyridine, which is known to be abnormal in its cryoscopic behavior (8).

The excellent accordance of the measurements on the carboxylic acids (Table 4) is apparent from Figure 2, which also carries for reference purposes the plot of the freezing-point measurements on naphthalene. Picric acid shows nearly ideal behavior. The dotted line, drawn for comparison purposes, represents one-half the freezing point depressions expected for naphthalene, and corresponds to the slope for an acid which is totally dimerized. Inspection of the graph suggests that appreciable quantities of the carboxylic acids are in the monomeric form, but that the dimeric form preponderates. There is little difference between the behaviors of myristic and acetic acids in this respect.

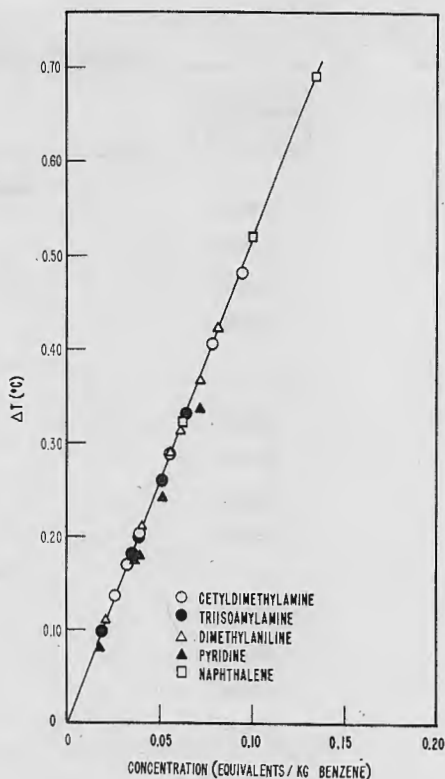


Figure 1 - Depressions of the freezing point of benzene by amines and by naphthalene

TABLE 3  
Cryoscopic Effect of Amines in Benzene

Concentration (equivalents/kg solvent)	ΔT (°C)	Concentration (equivalents/kg solvent)	ΔT (°C)
Cetyltrimethylamine		Triisooamylamine	
0.0260	0.137	0.0189	0.099
0.0326	0.170	0.0326	0.169
0.0393	0.205	0.0350	0.182
0.0556	0.289	0.0380	0.200
0.0787	0.406	0.0384	0.200
0.0947	0.482	0.0513	0.261
		0.0646	0.332
Pyridine		Dimethylaniline	
0.0175	0.081	0.0209	0.111
0.0366	0.175	0.0403	0.212
0.0393	0.180	0.0556	0.290
0.0514	0.243	0.0614	0.314
0.0721	0.337	0.0817	0.423

TABLE 4  
Cryoscopic Effects of Acids in Benzene

Concentration (equivalents kg solvent)		$\Delta T$ ( $^{\circ}C$ )
	Myristic Acid	
0.0404		0.115
0.0826		0.231
0.1240		0.337
0.1649		0.442
	Acetic Acid	
0.0153		0.048
0.0363		0.108
0.0703		0.199
0.1037		0.288
	Picric Acid	
0.0177		0.092
0.0317		0.165
0.0503		0.277
0.0671		0.342

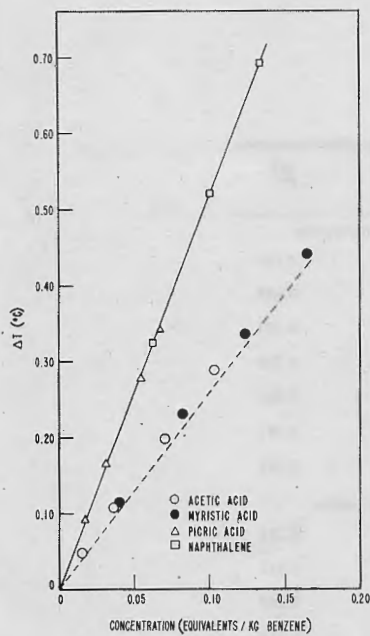


Figure 2 - Depressions of the freezing point of benzene by acids and by naphthalene

Concentrations recorded in the tables and figures were computed from measured neutral equivalent weights for cetyldimethylamine, triisoamylamine, and myristic acid, and from formula weights for the remaining compounds.

The dissociation constants,  $K_{A_2}$ , of the dimeric acids were calculated from  $K_f$  and from the data in Table 4 and are presented in Table 5. The following reaction was assumed:



where A represents the monomeric acid. Thus,

$$K_{A_2} = \frac{[A]^2}{[A_2]}$$

The brackets signify concentrations expressed as moles per kilogram of solvent.

The values of  $K_{A_2}$  show a scatter which is not greater than is to be expected from the experimental uncertainty of the freezing point measurement. If the concentrations are expressed as mole fractions instead of molalities,  $k_{A_2}$ , for myristic acid is  $6.0 \times 10^{-5}$ , and for acetic acid is  $1.25 \times 10^{-4}$ , where  $k_{A_2}$  is the dissociation constant computed on the mole fraction basis. The corresponding  $k_{A_2}$  for stearic acid at  $30^\circ\text{C}$  has been derived from measurements of the dielectric constant to be  $1.7 \times 10^{-4}$  (16). The constant for myristic acid at  $30^\circ\text{C}$  may be assumed to have the same approximate value as that for stearic acid. We may estimate from Maryott's data the corresponding value of the dimerization constant at the freezing point of benzene, if we assume the heat of dissociation of the myristic acid dimer in benzene to be approximately constant between  $30^\circ\text{C}$  and  $5^\circ\text{C}$ , and equal to that of benzoic acid in the same solvent. Pauling (20) gives for this heat of dimerization a value of 8.6 kilocalories per mole of dimer. The application of the Van't Hoff equation for the variation of the equilibrium constant with temperature leads to an estimate for myristic acid of  $k_{A_2} = 4.8 \times 10^{-5}$  at  $5.4^\circ\text{C}$ .

The value of  $k_{A_2}$  at  $30^\circ\text{C}$  for acetic acid has been reported (16) to be  $2.4 \times 10^{-4}$ . A computation similar to that above leads to an estimate of  $k_{A_2} = 0.68 \times 10^{-4}$  at  $5.4^\circ\text{C}$ . These estimated constants are in reasonable agreement with those obtained from the cryoscopic measurements, considering the fact that the actual heats of dimerization of the two acids may differ from each other and from that of benzoic acid.

Table 6 and Figures 3 and 4 present data resulting from the addition of successive increments of various acids to benzene solutions containing fixed amounts of different amines. For each amine-acid combination, enough amine first was added to the benzene to produce a depression of  $0.20^\circ\text{C}$  as nearly as it was practical to do so. After determination of the resulting freezing point, successive increments of acid were added, and the respective cryoscopic effects were observed.

Figure 3 assembles the data obtained from combinations of various amines with myristic acid, while Figure 4 assembles the data obtained from combinations of triisoamylamine with various acids. Plots of  $\Delta T$  vs. solute added for these systems are not directly comparable, since the initial concentrations of the pure amine solutions were not precisely equal. For purposes of comparison the data have been plotted with the relative cryoscopic effect,  $\Delta T_{\text{total}}/\Delta T_{\text{amine 1}}$ , as the ordinate, and the ratio of equivalents of

total acid added to equivalents of amine added, equivalents acid/equivalent amine, as the abscissa. Thus, all the plots on each graph are directly comparable as to the equivalence points, relative amounts of acid present, and slopes of the curves representing the effects of acid additions.

Although it could be argued that mass-action effects for a given system will vary with the level of absolute concentration, the discrepancies are of little consequence for the variations in absolute concentration here involved. This point was tested by comparing the plots of similarly treated data of two like sets of measurements wherein the initial amine concentration of one set was 200 percent of that of the other. The two plots, though not identical, diverged only slightly. Inasmuch as the initial concentrations treated here varied by a maximum of about 10 percent and by an average of about 5 percent, the plots are substantially comparable.

The dotted lines represent, in the same coordinate scale, the hypothetical cases wherein the reaction of an amine with an acid attains irreversible completion at 0, 1, 2, or 3 equivalents of acid per equivalent of amine, following which additions of excess carbóxylic acid exert an independent cryoscopic effect.

The data for myristic acid (Table 4) were used for plotting the diagonal dotted lines in both figures. The difference between the cryoscopic behaviors of myristic and acetic acids is so slight as to be imperceptible in these graphs.

Because pyridine does not conform to the cryoscopic behavior of the other amines studied, the pyridine-myristic acid data in Figure 3 were treated differently from the rest to permit convenient visual comparison. The ordinate in this case is

$$1 + \frac{\Delta T_{\text{acid}}}{[N_1] \times K_f}$$

where  $\Delta T_{\text{acid}}$  is the total additional depression found after additions of acid to the amine solution, and  $[N_1]$  is the concentration of amine in the solution to which the acid was added. This treatment gives a curve whose coordinate scale, slope, and location are consistent with those of the other curves and auxiliary dotted lines.

TABLE 5  
Dissociation of Acid Dimer in Benzene  
From Cryoscopic Observations

Myristic Acid		Acetic Acid	
Concentration (equivalents) (kg solvent)	Dissociation Constant ( $K_{A_2}$ )	Concentration (equivalents) (kg solvent)	Dissociation Constant ( $K_{A_2}$ )
0.0404	$9.2 \times 10^{-4}$	0.0153	$1.8 \times 10^{-3}$
0.0826	$12.0 \times 10^{-4}$	0.0363	$2.0 \times 10^{-3}$
0.1240	$7.2 \times 10^{-4}$	0.0703	$1.4 \times 10^{-3}$
0.1649	$4.7 \times 10^{-4}$	0.1037	$1.2 \times 10^{-3}$
	avg $8 \times 10^{-4}$		avg $1.6 \times 10^{-3}$

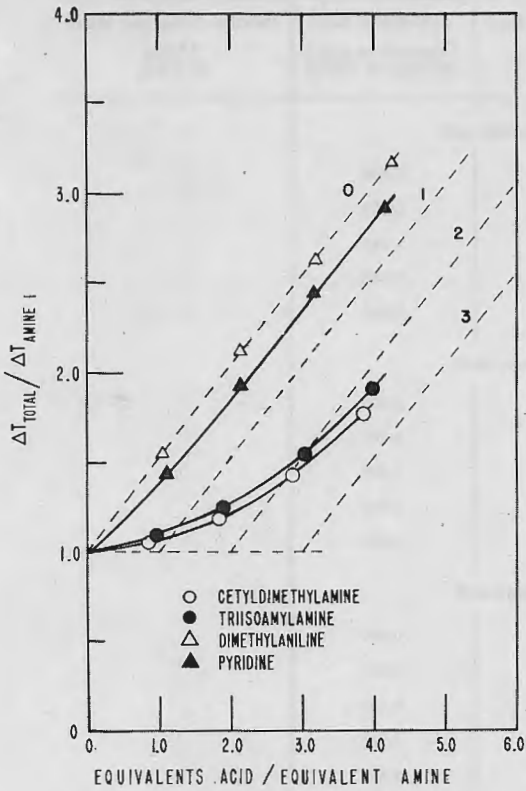


Figure 3 - Relative cryoscopic effects resulting from additions of myristic acid to solutions of various amines

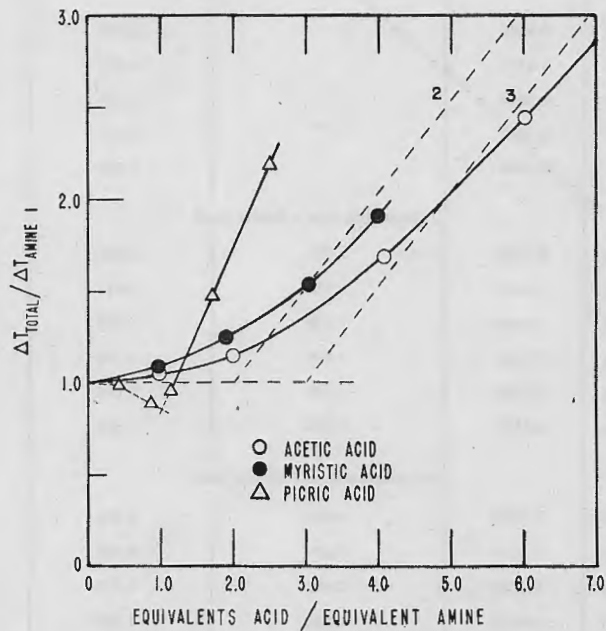


Figure 4 - Relative cryoscopic effects produced by additions of various acids to solutions of triisoamylamine

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 TABLE 6  
 Cryoscopic Effects Resulting From the Addition of Acids to Amines in Benzene

Increment Symbol	$\Delta T_{\text{total}}$ (°C)	Solute Added * (equivalents kg solvent)	Relative Cryoscopic Effect $\left(\frac{\Delta T_{\text{total}}}{\Delta T_{\text{amine 1}}}\right)$	Acid-Amine Ratio $\left(\frac{\text{equivalents acid}}{\text{equivalents amine}}\right)$	Relative Cryoscopic Effect $1 + \frac{\Delta T_{\text{acid}}}{[N_1] \times K_f}$
Cetyldimethylamine + Myristic Acid					
Amine 1 <sub>a</sub>	0.205	0.0393	1.000	0.000	
Acid 1 <sub>a</sub>	0.217	0.0337	1.059	0.858	
Acid 2 <sub>a</sub>	0.243	0.0723	1.185	1.840	
Acid 3 <sub>a</sub>	0.293	0.1127	1.429	2.868	
Acid 4 <sub>a</sub>	0.363	0.1514	1.771	3.852	
Triisoamylamine + Myristic Acid					
Amine 1 <sub>b</sub>	0.182	0.0350	1.000	0.000	
Acid 1 <sub>b</sub>	0.199	0.0338	1.093	0.964	
Acid 2 <sub>b</sub>	0.227	0.0665	1.247	1.899	
Acid 3 <sub>b</sub>	0.281	0.1062	1.544	3.034	
Acid 4 <sub>b</sub>	0.347	0.1395	1.907	3.985	
Dimethylaniline + Myristic Acid					
Amine 1 <sub>c</sub>	0.212	0.0403	1.000	0.000	
Acid 1 <sub>c</sub>	0.330	0.0425	1.557	1.055	
Acid 2 <sub>c</sub>	0.449	0.0866	2.118	2.149	
Acid 3 <sub>c</sub>	0.558	0.1288	2.632	3.196	
Acid 4 <sub>c</sub>	0.671	0.1717	3.165	4.261	
Pyridine + Myristic Acid					
Amine 1 <sub>d</sub>	0.180	0.0393		0.000	1.000
Acid 1 <sub>d</sub>	0.270	0.0437		1.112	1.441
Acid 2 <sub>d</sub>	0.370	0.0843		2.145	1.931
Acid 3 <sub>d</sub>	0.475	0.1243		3.163	2.446
Acid 4 <sub>d</sub>	0.572	0.1629		4.145	2.930
Triisoamylamine + Acetic Acid					
Amine 1 <sub>e</sub>	0.200	0.0380	1.000	0.000	
Acid 1 <sub>e</sub>	0.210	0.0372	1.050	0.978	
Acid 2 <sub>e</sub>	0.229	0.0759	1.145	1.998	
Acid 3 <sub>e</sub>	0.337	0.1546	1.685	4.069	
Acid 4 <sub>e</sub>	0.488	0.2286	2.440	6.016	
Acid 5 <sub>e</sub>	0.658	0.3026	3.290	7.963	
Triisoamylamine + Picric Acid					
Amine 1 <sub>f</sub>	0.200	0.0384	1.000	0.000	
Acid 1 <sub>f</sub>	0.198	0.0170	0.990	0.443	
Acid 2 <sub>f</sub>	0.178	0.0334	0.890	0.870	
Acid 3 <sub>f</sub>	0.192	0.0434	0.960	1.130	
Acid 4 <sub>f</sub>	0.296	0.0655	1.480	1.706	
Acid 5 <sub>f</sub>	0.438	0.0959	2.190	2.497	

\* Values for "Amine" increments are those for solutions of amine before additions of acid.  
 Values for "Acid" increments represent total acid added.

## DISCUSSION OF RESULTS

Any attempt to interpret cryoscopic data of the type reported here requires some assumption concerning the extent to which the solutes present conform to Raoult's law in their effects on the freezing point of benzene. It will be assumed as a first approximation that the individual kinetic units present at the concentrations studied have substantially ideal effects on the activity of benzene, and that they do not form solid solutions with the solvent which is frozen out. This is in agreement with the observed behavior of picric acid and three of the four amines, whose deviations from ideal behavior in these dilute solutions lie essentially within the limits of experimental error of the method. Furthermore, applications of the same assumptions to the data for myristic and acetic acids lead to constants for the dissociation of the acid dimer which are consistent with those derived from measurement of the dielectric properties of fatty acids in benzene (16).

The validity of Raoult's law for benzene solutions containing less than 0.07 moles of solute per kilogram of solvent, even when the solute is distinctly polar, can be demonstrated by an analysis of the very precise cryoscopic data reported by Batson and Kraus (6) for triisoamylammonium picrate in this solvent. These authors noted that the depressions reported are considerably less than those obtained for corresponding concentrations of triphenylmethane, and attributed the discrepancy to association into double or more complex aggregates. If we assume that triisoamylammonium picrate does not dissociate appreciably into free ions or into free acid and amine, and that in these dilute solutions the association of ion pairs is preponderantly to double units only, according to the equilibrium



where N represents the amine, and A the acid, and further that for the solute species actually present the solvent obeys Raoult's law exactly, we can compute the constant,

$$K_{\text{N}_2\text{A}_2} = \frac{[\text{N}_2\text{A}_2]}{[\text{NA}]^2},$$

for the association process. The results of this computation are presented in Table 7.

The computation of  $K_{\text{N}_2\text{A}_2}$  for determinations B1 and B2 produced negative and therefore impossible values. The values of  $K_{\text{N}_2\text{A}_2}$  computed for determinations A1, A2, B1, and B2 cannot be expected to be reliable. The uncertainty assigned by Batson and Kraus to their measurements in this dilute range is comparable to the difference to be expected between the cryoscopic behavior of this picrate ( $K_{\text{N}_2\text{A}_2} \sim 10$ ) and an unassociated solute such as triphenylmethane. However, in the concentration range 0.01718 to 0.06941 formula weights of solute per kilogram of benzene inclusive,  $K_{\text{N}_2\text{A}_2}$  is sufficiently constant to justify the initial assumptions. In this range the mean for  $K_{\text{N}_2\text{A}_2}$  is 8.7. If it is supposed that the precision of their  $\Delta T$  measurements is uniform, the high computed values of  $K_{\text{N}_2\text{A}_2}$  for their determinations C1 and G1 indicate that a more complex association equilibrium begins to exert appreciable effects at these higher concentrations. Hence, in the low concentration range we can conclude that Raoult's law is valid for this system. The departure of pyridine solutions from ideal behavior has been reported previously (8), and is attributed to the formation of a solid solution of pyridine in benzene. Given the basic assumptions indicated, some interesting deductions can be made from the data presented here concerning the interaction of acids and amines in dilute benzene solutions.

TABLE 7  
Association Constant For Triisoamylammonium Picrate\*

Determination No.	Concentration (formula wt) (kg solvent)	$K_{N_2A_2}$
A1	0.00442	43.7
A2	0.00882	13.8
A3	0.01882	9.2
A4	0.03012	9.4
A5	0.04264	8.9
A6	0.05513	8.8
A7	0.06941	9.0
B1	0.00362	---
B2	0.00835	---
B3	0.01718	7.3
B4	0.02965	8.0
B5	0.04082	8.0
B6	0.05323	8.0
C1	0.09013	23.6
D1	0.04805	10.6
E1	0.02547	8.4
F1	0.03348	8.6
G1	0.07798	17.3
		avg 8.7 †

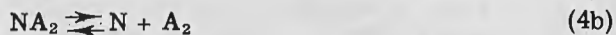
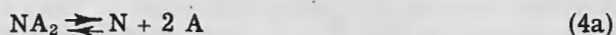
\* Computed from the data of Batson and Kraus

† Excluding A1, A2, B1, B2, C1, and G1

It is clear that the compounds resulting from the reaction between amines and carboxylic acids in these dilute solutions are in equilibrium with substantial amounts of free acid, even in the presence of an excess of amine. Indeed, dimethylaniline gives no indication of reaction with myristic acid; the points for the freezing point depression after the addition of acid lie quite precisely on the dotted line 0 (Figure 3), that corresponds to the independent cryoscopic effect of the acid. This behavior is in accord with that observed by O'Connor (19) for the same amine with acetic acid. There is evidently some interaction between pyridine and myristic acid, but the compound formed must be highly unstable. Even in the case of the two aliphatic amines the minimum amount of uncombined acid that must be assumed to explain the data is so considerable that such amines can not be depended upon for complete suppression of carboxylic acids in nonpolar solvents such as benzene, or in lubricating oils or fuels which are highly aromatic. However, it is reasonable to expect that in lubricating oils that are less aromatic in character and of lower polarizability, the amine-acid complexes will be less dissociated into free acid and amine than in equally concentrated benzene solution. Such a smaller dissociation is suggested by the work of Pohl, Hobbs, and Gross (21) who found that dimeric acetic acid was more readily dissociated in an aromatic than in a paraffinic solvent. They reported a dissociation constant for acetic acid in heptane which is about 1.7 percent of that for the same acid in benzene. The very small concentrations of free carboxylic acid which this may imply in the case of the amine-acid compounds could still be effective for rust inhibition because the supply of acid would be replaced by dissociation of the complex as soon as it was withdrawn by adsorption on metal surfaces. The rust inhibition obtained from amine complexes with long-chain acids (3, 4, 5) may well result from the free acid supplied by this dissociation.

The data for triisoamylamine plus picric acid indicate the formation of a stable amine picrate having the composition of one equivalent of acid to one of amine. No significant dissociation can be inferred from the data in this case. The abnormally small depressions produced by the compositions approximating stoichiometric proportions of the amine and acid indicate an appreciable interaction between the amine picrate molecules which is not reflected in the dielectric measurements of Maryott (15), but which is supported by the data of Batson and Kraus (6). Graphical interpolation of their published results indicates an abnormality of 16 percent in a 0.0384 molal solution as compared with the 14 percent abnormality estimated from our data at the same concentration. This concentration corresponds to the intersection of the extrapolated branches of a plot of  $\Delta T$  vs. total picric acid added to triisoamylamine. The intersection falls within one percent of the abscissa corresponding to a 1:1 ratio of acid to amine. Computations of  $\Delta T_{\text{total}}$ , using  $K_{N_2A_2}$  derived from the measurements of Batson and Kraus, predicted depressions corresponding to the first two additions of picric acid which were  $0.006^\circ$  and  $0.003^\circ\text{C}$  less, respectively, than the observed depressions of Table 6. The course of the curve beyond the stoichiometric point is very nearly that to be expected from the independent action of the excess picric acid. It has a slope corresponding to  $K_f = 4.7$  as compared with  $K_f = 5.1$  for a benzene solution of picric acid alone. The difference is in excess of the experimental error, and may indicate a slight tendency of the picric acid molecule to associate with the amine picrate. Strong acids such as hydrogen chloride may be expected to react as completely with aliphatic tertiary amines as does picric acid. Davis (9) has interpreted the data (18) for dimethylaniline plus hydrogen chloride to indicate a dissociation constant for the reaction  $C_6H_5N(CH_3)_2HCl \rightleftharpoons C_6H_5N(CH_3)_2 + HCl$  of about  $1.5 \times 10^{-6}$ , if concentrations are expressed in the molarity system. The aliphatic amine hydrochlorides should be even less dissociated.

A satisfactory explanation of the data for the reaction of triisoamylamine or cetyldimethylamine with myristic acid appears to require that one equivalent of a tertiary aliphatic amine combine with two equivalents of myristic acid monomer (or directly with one unit of the acid dimer) to form a molecular complex that is considerably dissociated in dilute solutions. An attempt was made to compute equilibrium constants for some possible reactions between cetyldimethylamine and myristic acid by a method that took account of the relative concentrations of the monomer and dimer forms of the acid required by the constants of Table 5. Not one of the equilibrium expressions corresponding to the reactions



was satisfactorily constant, although in the range between 0 and  $1\frac{1}{2}$  formula weights of acid per formula weight amine, the expression

$$K_{NA_2} = \frac{[N] [A_2]}{[NA_2]}$$

corresponding to equilibrium (4b), varied less rapidly with varying acid to amine ratio than did those for equilibria (3) and (5). (Equilibrium (4a) could be used as an alternative for (4b) because  $[A_2]$  and  $[A]$  are mutually dependent upon  $K_{A_2}$  and equilibrium (1).)

If the only equilibria to be considered were (1) and (4b),  $\Delta T_{\text{total}}$  should approach the dotted line 2 (Figure 3) asymptotically as the excess of the acid becomes sufficient to suppress the dissociation of the complex. The curves for both cetyldimethylamine and triisoamylamine with myristic acid, however, cross this line. The same is true for the system triisoamylamine plus acetic acid. The fact that the observed cryoscopic effects are substantially less than can be accounted for by equilibria (1) and (4b) indicates the occurrence of some further interaction between the solutes present.

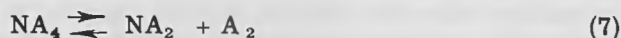
By analogy to the behavior of triisoamylammonium picrate, the equilibrium



was postulated, which should conform to the expression

$$K_{\text{N}_2\text{A}_4} = \frac{[\text{N}_2\text{A}_4]}{[\text{NA}_2]^2}$$

As an alternative, the equilibrium



was proposed, for which the expression

$$K_{\text{NA}_4} = \frac{[\text{A}_2][\text{NA}_2]}{[\text{NA}_4]}$$

would hold.

For the case in which an interaction represented by equilibrium (6) or (7) leads to a complex having a stability at least an order of magnitude less than that of  $\text{NA}_2$ , it is possible to determine the approximate value of  $K_{\text{NA}_2}$  without reference to these interactions. This is done by computing apparent values of  $K_{\text{NA}_2}$  from the experimental data with the assumption that only equilibria (1) and (4b) apply, and extrapolating the resulting plot of  $K_{\text{NA}_2}$  vs. acid-amine ratio to zero acid-amine ratio. The extrapolation is somewhat uncertain because of the curvature in the plot. A more precise extrapolation is possible if a reasonable value of  $K_{\text{N}_2\text{A}_4}$  or  $K_{\text{NA}_4}$  is introduced into the computations for  $K_{\text{NA}_2}$ . The resulting plot of  $K_{\text{NA}_2}$  has less curvature. For the conditions specified (i.e.,  $\text{NA}_2$  is much more stable than  $\text{N}_2\text{A}_4$  or  $\text{NA}_4$ ) the effect of  $K_{\text{N}_2\text{A}_4}$  or  $K_{\text{NA}_4}$  on  $K_{\text{NA}_2}$  decreases with decreasing acid-amine ratio; the extrapolated value of  $K_{\text{NA}_2}$  is not found to be significantly altered by as much as a two-fold variation in  $K_{\text{N}_2\text{A}_4}$  or  $K_{\text{NA}_4}$ . By considering only equilibria (1) and (4b),  $K_{\text{NA}_2}$  was estimated to be  $3 \times 10^{-3}$  for the system containing triisoamylamine plus myristic acid.

By assuming equilibria (1), (4b), and (6), an attempt was made to fit a value of  $K_{\text{N}_2\text{A}_4}$  to the data for this same system. No assignable value of  $K_{\text{N}_2\text{A}_4}$  was consistent with a constant value of  $K_{\text{NA}_2}$ . However, a value of  $K_{\text{N}_2\text{A}_4}$  was chosen which led to only a moderate variation in  $K_{\text{NA}_2}$ . The corresponding values of  $K_{\text{NA}_2}$  were plotted and extrapolated to zero acid-amine ratio, yielding  $K_{\text{NA}_2} = 3.0 \times 10^{-3}$ . The agreement of the values of  $K_{\text{NA}_2}$  deduced with and without considerations of a secondary interaction is evidence that the evaluation of this constant is independent of the assumption concerning the secondary equilibrium, either postulated or existing.

If the only equilibria to be considered were (1) and (4b),  $\Delta T_{\text{total}}$  should approach the dotted line 2 (Figure 3) asymptotically as the excess of the acid becomes sufficient to suppress the dissociation of the complex. The curves for both cetyldimethylamine and triisoamylamine with myristic acid, however, cross this line. The same is true for the system triisoamylamine plus acetic acid. The fact that the observed cryoscopic effects are substantially less than can be accounted for by equilibria (1) and (4b) indicates the occurrence of some further interaction between the solutes present.

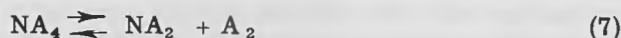
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By assuming equilibria (1), (4b), and (6), an attempt was made to fit a value of  $K_{\text{N}_2\text{A}_4}$  to the data for this same system. No assignable value of  $K_{\text{N}_2\text{A}_4}$  was consistent with a constant value of  $K_{\text{NA}_2}$ . However, a value of  $K_{\text{N}_2\text{A}_4}$  was chosen which led to only a moderate variation in  $K_{\text{NA}_2}$ . The corresponding values of  $K_{\text{NA}_2}$  were plotted and extrapolated to zero acid-amine ratio, yielding  $K_{\text{NA}_2} = 3.0 \times 10^{-3}$ . The agreement of the values of  $K_{\text{NA}_2}$  deduced with and without considerations of a secondary interaction is evidence that the evaluation of this constant is independent of the assumption concerning the secondary equilibrium, either postulated or existing.

By a system of simultaneous equations which assumed equilibria (1), (4b), and (7) to be valid,  $K_{NA_4}$  was computed from the experimental data and the previously established values of  $K_{A_2}$  and  $K_{NA_2}$ . The computed values of  $K_{NA_4}$  corresponding to increasing total acid content were, respectively, 0.71, 0.110, 0.0714 and 0.0855. The first of these was discarded as unreliable because the value of  $[NA_4]$  used in its computation must be obtained as the difference of two much larger terms. One of these terms depends upon the difference between two measured freezing points, and is subject to a combined uncertainty which is small percentage-wise, but whose absolute magnitude is comparable with that of  $[NA_4]$  at this very low acid-amine ratio. The representative  $K_{NA_4} = 0.0855$  was chosen as the probable value.

To test the hypothesis that equilibria (1), (4b), and (7) are the controlling equilibria in this system  $\Delta T_{total}$  was computed for each of the benzene solutions of the experimental compositions, using the determined values of  $\Delta T_{amine}$ ,  $K_f$ , and  $K_{A_2}$ , and the tentative values of  $K_{NA_2}$  and  $K_{NA_4}$ . The results of these computations (Table 8 and Figure 5) show excellent agreement between the experimentally measured and theoretically predicted freezing-point depressions.

For comparison, a similar test was made assuming equilibria (1), (4b), and (6). A value of  $K_{N_2A_4} = 0.071$  was chosen, which would produce a fit most favorable to the two uppermost points in Figure 5, since  $\Delta T_{total}$  corresponding to these two points is most sensitive to the variation of  $K_{N_2A_4}$ . Table 8 and Figure 5 present the results of the computations, which demonstrate effectively that the postulated equilibrium (7) is more consistent than (6) with the data for the triisoamylamine-myristic acid system.

Examination of Figure 4 and Table 6 shows that equilibrium (6) is not valid for the triisoamylamine-acetic acid system. The validity of this equilibrium requires that the curve approach the dotted line 3 asymptotically, whereas it very definitely crosses this line.

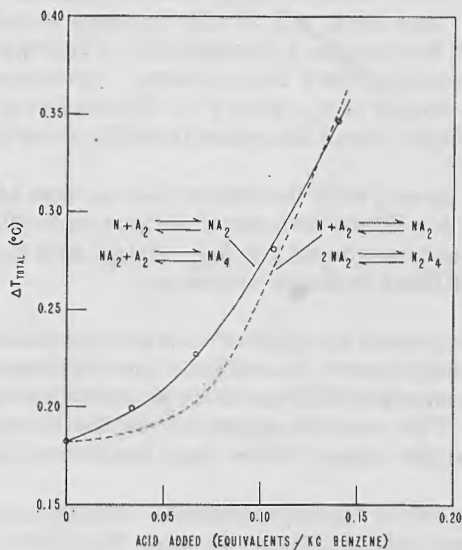


Figure 5 - Test of alternative equilibria in solutions of triisoamylamine plus myristic acid

TABLE 8  
 Test of Alternative Equilibria in Solutions of  
 Triisomyamine Plus Myristic Acid

Amine Content = 0.0350 equivalents/kg;  $K_{A_2} = 7.7 \times 10^{-4}$ ,  $K_{NA_2} = 3.0 \times 10^{-3}$

Total Acid Added  ( $\frac{\text{equivalents}}{\text{kg benzene}}$ )	$\Delta T_{\text{total}}$ Experimental  ( $^{\circ}\text{C}$ )	$\Delta T_{\text{total}}$ Computed $NA_2 + A_2 \rightleftharpoons NA_4$ $K_{NA_4} = 8.55 \times 10^{-2}$  ( $^{\circ}\text{C}$ )	$\Delta T_{\text{total}}$ Computed $2NA_2 \rightleftharpoons N_2A_4$ $K_{N_2A_4} = 7.1 \times 10^{-2}$  ( $^{\circ}\text{C}$ )
0.0338	0.199	0.198	0.187
0.0665	0.227	0.226	0.202
0.1062	0.281	0.284	0.272
0.1395	0.347	0.347	0.353

Computations similar to those described above assuming equilibria (1), (4b), and (7) were made for the system containing acetic acid. Inspection of the curve (Figure 4) suggested that for the acetic acid system  $K_{NA_2}$  and  $K_{NA_4}$  were smaller than the respective constants for the system containing myristic acid. An arbitrary estimate was made for  $K_{NA_4}$  and  $K_{NA_2}$  was computed for each of the experimental mixtures from the data of Table 6.  $K_{NA_2}$  was extrapolated to zero acid-amine ratio as described above. With this value of  $K_{NA_2}$  a more consistent value of  $K_{NA_4}$  was computed. One repetition of this process gave  $K_{NA_2} = 1.02 \times 10^{-3}$  and  $K_{NA_4} = 2.38 \times 10^{-2}$ ; these values were insensitive to further approximations. Table 9 presents a comparison of the theoretically computed and experimentally measured freezing point depressions. Agreement is excellent, except for the mixture of highest acid-amine ratio, where the discrepancy between the observed and computed values is two or three times the experimental uncertainty.

The consistency of the theory with the experimental data is strong evidence that equilibria (4b) and (7) are valid for dilute benzene solutions of tertiary aliphatic amines plus fatty acids, and that the values computed for  $K_{A_2}$ ,  $K_{NA_2}$ , and  $K_{NA_4}$  describe quantitatively the important chemical equilibria in these systems.

The instability of the compounds formed between amines and carboxylic acids in benzene solution, and also the surprising amount of acid bound per equivalent of amine, indicate that the forces between the acid and amine are different in type from those operating in the amine picrates or the amine hydrohalides. The reaction appears to be the formation of a molecular complex between acid dimer and the amine rather than the formation of a true ion pair.

The successful description of the experimental results in terms of one or of a series of equilibrium constants does not, of course, furnish direct information concerning the type of bonds involved, or as to whether the monomeric or dimeric form of the acid is the chemical unit actually reacting with the amine. An analysis employing the constant corresponding to equilibrium (4a) instead of  $K_{NA_2}$  would have given a fit of the data, because the existence of the monomer-dimer equilibrium of the acid makes the two treatments mathematically equivalent.

TABLE 9  
 Test of Equilibria in Solutions  
 of Triisomyamine Plus Acetic Acid

Amine Content = 0.0380  $\frac{\text{equivalents}}{\text{kg benzene}}$ ;  $K_{A_2} = 1.6 \times 10^{-3}$

$K_{NA_2} = 1.02 \times 10^{-3}$ ,  $K_{NA_4} = 2.38 \times 10^{-2}$

Total Acid Added $\left(\frac{\text{equivalents}}{\text{kg benzene}}\right)$	$\Delta T_{\text{total}}$ Experimental (°C)	$\Delta T_{\text{total}}$ Computed $NA_2 + A_2 \rightleftharpoons NA_4$ (°C)
0.0372	0.210	0.210
0.0759	0.229	0.229
0.1546	0.337	0.335
0.2286	0.488	0.489
0.3026	0.658	0.665

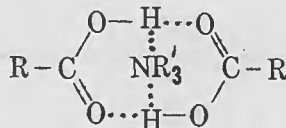
Alternatively, it might be postulated that the observed phenomena were the result of the stepwise reaction of the amine with four successive units of acid monomer. It is true that the equilibria for the first and second steps of such a reaction could be combined to give a constant formally equivalent to  $K_{NA_2}$  and that the third and fourth steps could be combined to obtain a constant equivalent to  $K_{NA_4}$ . It might be concluded from this that the choice of the acid dimer as the reacting unit is an arbitrary one justified by the resulting convenience in the analysis of the data.

The assumptions employed for calculating the concentrations of the various species involved in the equilibria, however, imposes a restriction that does permit a decision between the four-step formulation suggested above on the one hand, and either of the two mathematically equivalent schemes involving the addition of acid to the amine as one dimeric or two monomeric units per step on the other hand. The constants  $K_{NA_2}$  and  $K_{NA_4}$  were computed from concentrations of N,  $NA_2$ , and  $NA_4$  that were derived from the freezing point data on the assumption that neither NA nor  $NA_3$  were present in significant amounts. If appreciable amounts of NA had been present, the true concentrations of N and  $NA_2$  would have been substantially different from those computed, and would have determined a different value for  $K_{NA_2}$ . The same observation also applies to the effect of  $NA_3$  on the concentrations of  $NA_4$  used for determining  $K_{NA_4}$ . The fact that the values derived for these constants by ignoring the possible presence of NA or  $NA_3$  lead to computed depressions of the freezing point in close agreement with experiment supports the idea that the acid dimer is the actual reacting unit.

There is another consideration which supports the choice of the dimeric molecule of the acid as the reacting unit. It is difficult to construct a model for the association of a

single amine molecule with four separate acid monomers that implies an energy of bonding sufficient to compete effectively for monomeric units with the dimerization equilibrium (1).

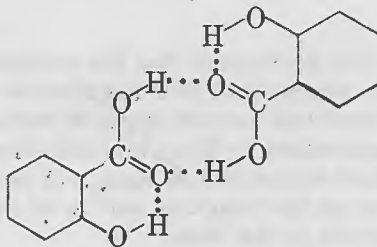
It is, however, possible to suggest a model for the direct bonding of the dimeric acid unit to a tertiary amine for which there would be no difference in the strength of bonding of the two acid molecules. This might be accomplished if the nitrogen of the amine approached one side of the eight-membered ring formed by the hydrogen bridges of the two carboxyl groups with such an orientation that the unshared electron pair of the nitrogen was equally available for dipolar interaction with either of the hydrogens of the dimeric acid, as represented in I.



I

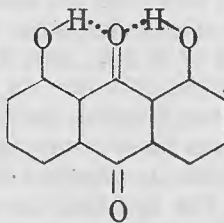
The bonding by a single hydrogen of more than two electronegative atoms at one time is unusual, although Pauling (20) cites the "bifurcated hydrogen bond"  $\text{N-H} \cdots \begin{matrix} \text{O} \\ \vdots \\ \text{O} \end{matrix}$  inferred from the crystal structure of glycine (1).

The simultaneous direction of two hydrogen bridges toward a single oxygen atom has been postulated for the dimeric form of salicylic acid (20)



II

as well as in 1,8-dihydroxyanthraquinone,



III

and some similar compounds.

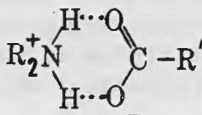
Oxygen differs from nitrogen, it is true, in having two pairs of electrons not involved in covalent bonding, but it must be kept in mind that hydrogen bonding is essentially an electrostatic or dipole effect and not electron sharing.

The two latter cases of chelate-type intramolecular bonding cited illustrate the formation of the six-membered ring observed to be most stable in such cases. Two six-membered chelate rings would also result from the formation of I, and might lead to moderate stability of a type of hydrogen bridging that would otherwise be too weak to detect.

The strength of bonding between the amine and acid is not great; for triisoamylamine with myristic acid, the degree of dissociation of  $NA_2$  estimated for a concentration of 0.01 formula weights per kilogram of benzene is 46 percent as compared, for example, with 13 percent dissociation of the hydrogen-bonded dimer of myristic acid to monomer at the same concentration.

A bond of the type indicated in I implies that the heat of reaction between a tertiary aliphatic amine and a fatty acid should be considerably smaller, per equivalent of acid bound, than the 11.4 kcal estimated by Maryott for the formation of the ion pair in tri-benzylammonium picrate. The resulting compound should have a substantially smaller dipole moment than the 12 Debye units reported by the same author for triisoamylammonium picrate. These implied effects are susceptible to experimental verification, and should permit a decision on the plausibility of structure I as the bonding mechanism in this case.

The type of interaction found for tertiary amines with carboxylic acids will not necessarily be characteristic of the behavior of secondary and primary amines of comparable basicity. Primary and secondary amines may well exhibit hydrogen bonding of the type indicated in IV



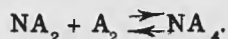
IV

in which the two H atoms of the ammonium ion complete a six-membered chelate ring by forming bridges to the oxygens of the carboxylate ion. The energy of formation of two H-bridges could compensate for that required to dissociate the acid dimer. Experimental work is needed to resolve this point.

The bonding of a second dimer by the  $NA_2$  is more difficult to account for. It is possible that the first dimer unit is sufficiently polarized by the presence of the nitrogen atom so that the loose attachment of a second unit becomes possible; there is insufficient evidence available for useful theorization.

## CONCLUSIONS

1. Tertiary aliphatic amines can react with fatty acids according to the equilibria



It is probable that the dimeric acid molecule reacts directly with such amines through a modified form of hydrogen bridge. This mode of combination is consistent with compositions of solid phases isolated from nonaqueous solvents as well as with the cryoscopic data.

2. The amine-fatty acid complexes are appreciably dissociated into free acid and free amine in dilute benzene solutions.

3. Picric acid reacts with tertiary amines in dilute benzene solution to form amine picrates containing one equivalent of acid per equivalent of amine. These picrates do not dissociate appreciably in benzene, but do associate according to the equilibrium



This behavior, which is in accord with findings previously reported from measurements of cryoscopic and of dielectric properties, indicates that the amines may be expected to behave similarly with hydrogen halides, which are still stronger acids.

4. The less basic aromatic tertiary amines such as dimethylaniline do not react with fatty acids in benzene to a detectable extent. Pyridine reacts with these acids to only a slight extent.

5. There is no evidence in the data presented to indicate micelle formation by tertiary amine-acid complexes of high molecular weight.

6. The tertiary amines of high molecular weight may be expected to act as efficient acid "getters" or neutralizers for hydrobromic and hydrochloric acids in oils but to be much less effective in neutralizing corrosion-promoting short-chain fatty acids formed by the oxidation of the lubricants in service. Amine complexes of long-chain fatty acids may owe their rust inhibiting properties largely to the fact that they provide a reservoir from which the acid is drawn for adsorption on the metal surface, but still prevent a high concentration of the free acid from existing in the oil.

#### RECOMMENDATIONS

1. It is recommended that this study be supplemented by a similar one in an aliphatic solvent such as cyclohexane. The information thus derived would be useful in elucidating the corrosion-inhibiting effectiveness of amine-acid complexes in lubricating oils that are principally paraffinic.

2. It has been indicated that the behavior of primary and secondary amines may not parallel that of tertiary amines of comparable basicity. An investigation of primary and secondary amines would extend the practical value of this study, since these amines are common additives to lubricating compositions.

#### ACKNOWLEDGMENT

Acknowledgment is made to Kenneth L. Temple, formerly of this Laboratory, for the preparation of two compounds of cetyldimethylamine with stearic (b) and lauric (c) acids.

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