Preparation and Characterization of a Number of Amine Salts of Long-Chain Fatty Acids

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THE DIFFICULTY encountered in the purification of the long-chain fatty acids by solvent recrystallization, especially from nonpolar solvents, has been attributed to the formation of solid solutions between fatty acids of approximately the same chain length (15), which probably results from hydrogen bonding between carboxyl groups (16). It would be expected that this difficulty could be overcome by using a derivative of the acids in which the carboxyl groups would be blocked.

Several successful applications of this principle have been reported, which involve the solvent recrystallization of molecular compounds formed by fatty acids with organic nitrogen compounds and subsequent regeneration of the pure acid (7, 8, 10, 18). In this connection the present investigation was carried out to obtain information regarding the tendency of various types of amines to form readily crystallizable salts with long-chain fatty acids. A number of aliphatic, aromatic, and heterocyclic amines, including primary, secondary, and tertiary amines and a few diamines, were investigated from this point of view with one or more fatty acids. The amine salts obtained were identified and characterized.

Experimental

Materials. The fatty acids used were the highest grade of Eastman Kodak products with the following exceptions. The 12-hydroxystearic acid was a technical commercial grade obtained from Emery Industries Inc. The oleic acid (f.p., 16.3°) and the elaidic acid (f.p., 43.6°) were prepared as previously described (11). Most of the amines were Eastman Kodak products. Those not available from this source were 1-cyclohexylamino-2-propanol and hydroxylalkylamines from Commercial Solvents Corporation, Dow Chemical Company, or American Cyanamid; 2,4,4-trimethyl-2-aminopentane were from Rohm and Haas; and pyridine derivatives were from Reilly Tar and Chemical Corporation or Delta Chemical Works. With the exception of U.S.P. 95% and absolute ethanol all the solvents were of analytical or reagent grade.

Procedure. The amine-fatty acid compounds were prepared by solvent recrystallization in a centrifugal filtration tube (17), starting with the appropriate mixture of acid and amine. An equimolar ratio of acid and amine was used unless otherwise mentioned. When it was known from binary freezing-point data that more than one compound could be formed, all the acid-amine ratios indicated for the system were usually investigated. Acetone usually proved to be a satisfactory solvent. In some cases however a discoloration gradually developed in the acetone solutions, and benzene was used instead. Since the amine salts dissociate in solution, special solvents such as ethanol, 1,4-dioxane, or mixtures of ethanol and acetone, ethanol and benzene, or acetone and benzene sometimes had to be used to obtain crystals of the salt uncontaminated by the acid or the amine. After a total usually of at least three crystallizations, the crystals were freed from solvent in an intermittent partial vacuum (over fresh paraffin shavings when benzene was the solvent) and finally dried in a vacuum desiccator over sodium hydroxide pellets.

The crystalline products isolated can be identified as amine salts of the acids. They were formed under extremely mild conditions by simple recrystallization of the mixture of the acids and amines from a solvent in which the amine was usually infinitely soluble. The acid can be regenerated by stirring with aqueous mineral acid at the melting point of the salt. The salt structure of the compounds with 2-aminopyridine and its derivatives is also proved by the complete binary freezing point diagrams already published. The acid-amine compounds had well-defined characteristic x-ray long spacings and infrared spectra in the solid state (14). Duplicate nitrogen analyses afforded further confirmation of their structure.

Unless otherwise indicated, freezing-point determinations were made by the sealed tube, thermostatic method (9), which involves taking the average of two temperatures a few tenths of a degree apart, at one of which all the crystals disappear and at the other of which a few crystals persist during prolonged agitation at constant temperature. When the freezing point was found to drift downward during the freezing-point measurement, because of slight decomposition, capillary melting points were obtained.

Surface and interfacial tensions were measured with a Du Noüy tensiometer at 27° on aqueous solutions prepared from CO_2-free distilled water and between these aqueous solutions and Nujol, respectively. The readings were corrected by the methods of Harkins and Jordan (3) and Zuidema and Waters (21), respectively.

Results and Discussion

Most of the amines investigated gave crystallizable fatty acid compounds. These are listed in Table I, which shows the solvent used, the weight percentage of solute in the crystallizing solution, and the mole ratio of acid to amine in the compound isolated as indicated by the nitrogen analysis. The last two columns give the freezing point of the compound and, when available, its freezing point obtained from the binary freezing-point data (12, 13, 14) or other literature sources (4, 5, 6).

N-Methylmorpholine, 1,2,3,4-tetrahydroquinoline, and *alpha-*, *beta-*, and *gamma*-picoline gave no fatty acid compound on acetone recrystallization of an equimolar mixture with palmitic acid. The crystallized products proved to be palmitic acid containing only a trace of nitrogen.

Other amines investigated, not included in Table I, were those which showed an intermediate behavior

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when equimolar mixtures with palmitic acid were recrystallized from acetone. Though the nitrogen contents of the crystallized products obtained were appreciable, they did not correspond to any simple assignable amine-acid ratio. Since each of these products had been subjected to at least three recrystallizations, a definite tendency toward compound formation between these pairs is indicated. The observed nitrogen contents and, in parentheses, the theoretical values for the 1:1 amine-acid compound are as follows: tribenzylamine, 0.69% (2.58%); 3-aminoquinoline, 0.78, 0.70% (6.99%); 2-aminobenzothiazole, 0.92, 0.83% (6.89%), 8-aminoquinoline, 1.30% (6.99%); nicotine, 1.79, 1.92% (6.69%); 2-methylpiperidine, 2.83, 2.95% (3.94%); and 2-amino-3-methylpyridine, 5.33, 5.44% (7.68%). These results may possibly be accounted for by a marked difference in the solubilities of the acid and the amine in the solvent used (2). They might, on the other hand, be caused by the fact that the 1:1 compound melts incongruently. For example, the binary freezing-point diagram for palmitic acid with 2-amino-3-methylpyridine (13) indicates that incongruent melting might be involved in this instance when crystallizing from a solvent.

Of the large variety of primary mono-amines investigated, the few which failed to give well-defined equimolar compounds on repeated recrystallization, starting with an equimolar acid-amine mixture, all showed a definite tendency to form such compounds. Primary amines not included in this study were aromatic amines such as aniline, *para*-toluidine, and *ortho*-phenylenediamine, for which the binary freezing-point diagrams with palmitic acid show no signs of compound formation (14).

By the same procedure, starting with equimolar mixtures, the symmetrical alkyl, substituted alkyl, and aralkyl secondary amines investigated all gave compounds containing two molecules of fatty acid and one of amine. This suggests that if a crystalline 1:1 compound exists, it probably has an incongruent melting-point. A 1:1 compound was obtained however when the > NH group was in a saturated ring, as in morpholine, piperidine, and pyrollidine. Dicyclohexylamine and 2,2′-dipyridylamine likewise gave 1:1 compounds. The binary freezing-point diagram for palmitic acid with 2-2′-dipyridylamine (13) shows that a crystallizable 2:1 compound does not exist in this system. The binary diagram for palmitic acid with morpholine (14), on the other hand, indicates a 2:1 compound which melts incongruently.

Other amines which gave a 2:1 compound by recrystallization of the equimolar acid-amine mixture were ethylenediamine and piperazine.

Of the tertiary amines investigated triethanolamine gave a 1:1 compound, N-diethylcyclohexylamine gave a 2:1 compound, and N-methylmorpholine, 1,2,3,4-tetrahydroquinoline, and *alpha*-, *beta*-, and *gamma*-picoline showed no tendency to form a crystallizable compound. Binary freezing-point data for the system palmitic acid—*alpha*-picoline (14) confirm the nonexistence of any crystallizable compound in this system.

Since in the liquid state the amine salts of the fatty acids dissociate to form an equilibrium mixture of amine, acid, and amine salt, their crystallization from an organic solvent involves the principles described by Dimroth (2) for the solvent crystallization of molecular compounds. Thus, in choosing a solvent, special consideration must be given to the relative solubilities of the amine, acid, and salt in order that pure salt crystals be obtained. This is illustrated by the behavior of the various salts of tris(hydroxymethyl)aminomethane. Starting with an equimolar acid-amine mixture, the pure palmitic acid salt was obtained with no difficulty from absolute ethanol. Under the same conditions the crystals obtained with stearic acid had a very low nitrogen value and those with lauric acid were high in nitrogen content. By using solvent mixtures in which the solubilities of the amine and the specific acid were more nearly alike (Table I), it was possible to obtain pure salt crystals with a number of fatty acids.

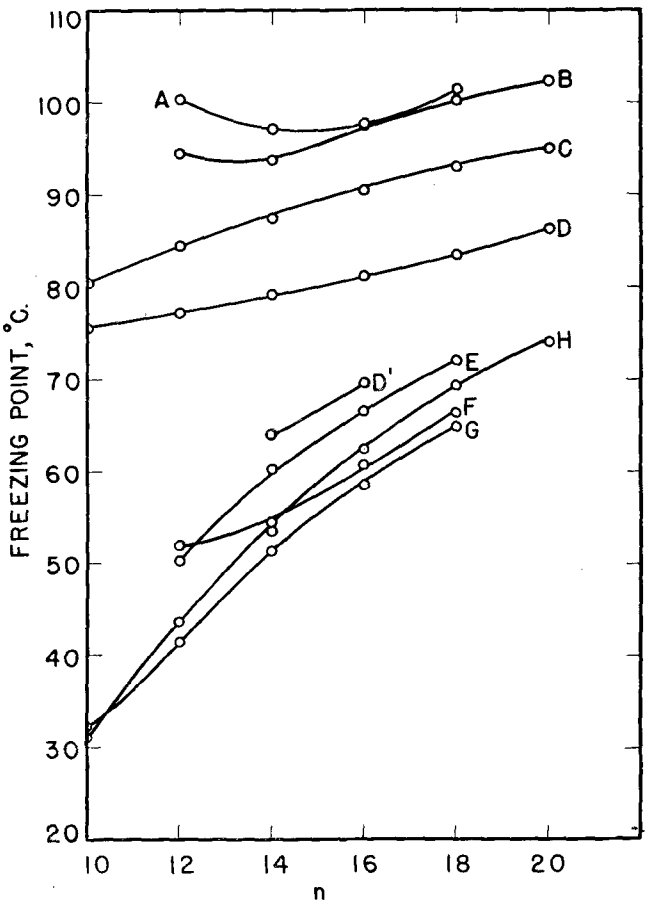

FIG. 1. Freezing points *vs.* *n*, the number of carbon atoms in the fatty acid moiety, for salts of the following amines: A, tris (hydroxymethyl)aminomethane; B, piperazine; C, cyclohexylamine; D and D′, benzylamine (2 forms); E, morpholine; F, 2,2′-dipyridylamine; and G, 2-aminopyridine. H is curve for corresponding normal saturated fatty acids.

Ethanolamine gave the 1:1 compound with palmitic acid when the crystallization of the equimolar mixture was carried out from a concentrated benzene solution. The 2:1 compound was obtained however by two crystallizations from dioxane, followed by two crystallizations from acetone.

Two polymorphic forms of the 1:1 compound of benzylamine with myristic and palmitic acids were obtained, depending upon the solvent used. The high-melting form was obtained from benzene and the low-melting modification from acetone. Attempts to isolate low-melting forms of the stearic and lauric acid compounds were not successful.

TABLE I

Preparation and Characterization of Various Fatty Acid-Amine Compounds

Amine	Acid	Original proportions[a]	Solvent[b]	Concentration[c]	% Nitrogen		Moles acid to amine in compound	Freezing point, °C.[d]	
					Found	Calculated		Found	Literature
Ethylamine	Palmitic	1:1	B	65	4.39	4.65	1:1	67.0	
Diethylamine	Palmitic	1:1	E_a	75	2.33, 2.37	2.39	2:1	61.3	
Dibutylamine	Palmitic	1:1	A	75	2.18, 2.19	2.18	2:1	48.5	
Diisobutylamine	Palmitic	1:1	A	75	2.23, 2.18	2.18	2:1	46.5	
Di-*sec*-butylamine	Palmitic	1:1	A	80	2.17, 2.19	2.18	2:1	41.3– 43.2	
ter-Butylamine[e]	Palmitic	1:1	B	50	4.26, 4.26	4.25	1:1	87.3	
n-Amylamine	Palmitic	1:1	A	90	3.77, 3.73	4.07	1:1	37.2	
Di-*n*-amylamine	Palmitic	1:1	A	80	2.13, 2.16	2.09	2:1	48.4	
Isoamylamine	Palmitic	1:1	B	80	4.04, 4.04	4.07	1:1	51.6	
ter-Octylamine[f]	Palmitic	1:1	A	50	3.63, 3.62	3.63	1:1	71.4	
Stearylamine	Palmitic	1:1	B	40	2.94, 2.94	2.66	1:1	82.5– 82.9	85–85.5[g]
Ethylenediamine	Palmitic	1:1	2A:E_a	30	4.82, 4.83	4.89	2:1	100.7–101.4[h]	
	Oleic	1:1	D	25	4.44, 4.49	4.48	2:1	56.8– 63.0[h]	
Ethanolamine	Palmitic	1:1	B	65	4.61, 4.53	4.41	1:1	71.5– 74.4[h]	
	Palmitic	1:1	C, A	[i]	2.36, 2.39	2.41	2:1	68 – 69.5[h]	
Diethanolamine	Palmitic	1:1	B	40	4.05, 4.12	3.87	2:1	59.4– 60.2[h]	
Triethanolamine	Palmitic	1:1	B	50	3.66, 3.65	3.45	1:1	67.2– 68.0[h]	
2-Amino-2-methyl-1-propanol	Palmitic	1:1	B	50	4.12, 4.14	4.05	1:1	90.3– 90.6[h]	
2-Amino-2-methyl-1,3-propanediol	Palmitic	1:1	B	50	3.92, 3.92	3.87	1:1	95.8– 96.4[h]	
2-Amino-1-butanol	Palmitic	1:1	A	60	3.95, 4.04	4.05	1:1	71.3	
2-Amino-2-ethyl-1,3-propanediol	Palmitic	1:1	B	50	3.73, 3.65	3.73	1:1	92.3– 93.0	
Tris(hydroxymethyl)aminomethane	Lauric	1:1	E_{90}[j]	30	4.36, 4.35	4.36	1:1	100.2–101.2	
	Myristic	1:1	E_{95}[j]	30	4.41, 4.43	4.01	1:1	96.6– 98.2	
	Palmitic	1:1	E_a[k]	30	3.70, 3.69	3.71	1:1	97.5– 98.6	
	Stearic	1:1	E_a:B[j]	10	3.43, 3.46	3.45	1:1	101.0–101.9	
	Oleic	1:1	E_a:A	50	3.65, 3.49	3.47	1:1	78 – 80	
	Elaidic	1:1	E_{95}[k]	50	3.46, 3.47	3.47	1:1	74.6– 75.6	
N-Methyl glucamine	Palmitic	1:1	E_a	30	3.44, 3.39	3.10	1:1	70.0– 71.8	
Cyclohexylamine	Capric	1:1	B	65	5.32, 5.10	5.16	1:1	80.5	
	Lauric	1:1	A	65	4.71, 4.69	4.69	1:1	84.5	
	Myristic	1:1	A	35	4.29, 4.28	4.28	1:1	87.6	
	Palmitic	1:1	B	55	3.93, 3.92	3.94	1:1	90.6	
	Stearic	1:1	B	55	3.74, 3.63	3.65	1:1	93.0	
	Elaidic	1:1	A	65	3.65, 3.66	3.67	1:1	62.6	
	Arachidic	1:1	B	35	3.38, 3.38	3.41	1:1	94.6– 95.6	
Dicyclohexylamine	Palmitic	1:1	B	60	3.23, 3.20	3.20	1:1	70.4	
1-Cyclohexylamino-2-propanol	Palmitic	1:1	A	50	3.76, 3.81	3.39	1:1	66.5	
N,N-Diethyl cyclohexylamine	Palmitic	1:1	B	80	2.07, 2.09	2.10	2:1	35.2	
Benzylamine	Capric	1:1	B	65	4.96, 4.97	5.02	1:1	75.7	
	Lauric	1:1	B	60	4.55, 4.54	4.56	1:1	77.3	70–73.5[l]
	Myristic	1:1	B	60	4.13, 4.14	4.18	1:1	79.2	77–78[l]
	Myristic	1:1	A	60	4.03, 4.08	4.18	1:1	64.1	
	Palmitic	1:1	B	50	3.83, 3.84	3.85	1:1	81.2	79–80[l]
	Palmitic	1:1	A	70	3.86, 3.86	3.85	1:1	69.8	
	Stearic	1:1	B	50	3.55, 3.54	3.58	1:1	83.5	70–70.5[l]
	Arachidic	1:1	B	40	3.28, 3.20	3.34	1:1	86.4	
	Oleic	1:1	T	55	3.54, 3.47	3.60	1:1	33.9	
	12-Hydroxystearic	1:1	A	65	3.40, 3.44	3.44	1:1	78.3	
Dibenzylamine	Palmitic	1:1	A	65	2.03, 2.06	1.97	2:1	57.4	
2-Aminopyridine	Capric	1:1	A	80	10.52, 10.45	10.52	1:1	32.6	
	Lauric	1:1	B	80	9.46, 9.43	9.52	1:1	41.6	41.6[m]
	Lauric	4:1	A	75	2.88, 2.83	3.13	4:1	34.3	33.9[m]
	Myristic	1:1	A	65	8.49, 8.77	8.70	1:1	51.3	51.3[m]
	Myristic	4:1	A	65	2.74, 2.60	2.78	4:1	47.2	47.2[m]
	Palmitic	1:1	A	75	7.95, 8.00	7.99	1:1	58.6	58.8[m]
	Palmitic	4:1	A	50	2.29, 2.40	2.50	4:1	57.2	57.0[m]
	Stearic	1:1	B	60	7.62, 7.68	7.40	1:1	64.9	64.7[m]
	Stearic	4:1	A	20	2.22, 2.21	2.27	4:1	65.0	65.0[m]
	Elaidic	1:1	A	65	7.23, 7.30	7.44	1:1	45.3[p]	40.2[m]
	Elaidic	2:1	A	65	4.21, 4.22	4.25	2:1	36.1	36.7[m]
3-Aminopyridine	Palmitic	1:1	B	65	7.99, 8.12	7.99	1:1	51.4	51.8[n]
2-Amino-4-methylpyridine	Palmitic	1:1	A	50	7.80, 7.83	7.68	1:1	79.3	79.8[o]
	Oleic	1:1	A[j]	60	7.11, 7.14	7.14	1:1	35 – 36	
2-Amino-5-methylpyridine	Palmitic	1:1	A	75	7.74, 7.75	7.68	1:1	61.1	61.2[o]
2-Amino-6-methylpyridine	Palmitic	1:1	A	65	7.74, 7.66	7.68	1:1	65.3	65.3[o]
2-Amino-4,6-dimethylpyridine	Palmitic	1:1	A	65	7.54, 7.53	7.40	1:1	72.7	73.3[o]
	Oleic	1:1	A	50	7.06, 6.86	6.90	1:1	51.4	
2,2′-Dipyridylamine	Lauric	1:1	A	50	11.24, 11.26	11.32	1:1	52.0	
	Myristic	1:1	A	50	10.42, 10.44	10.53	1:1	54.6	
	Palmitic	1:1	A	50	9.87, 9.89	9.82	1:1	60.8	61.0[o]
	Stearic	1:1	A	50	9.19, 9.18	9.22	1:1	66.3	
Pyrollidine	Palmitic	1:1	B	65	4.24, 4.30	4.12	1:1	64.6	
Piperidine	Palmitic	1:1	A	80	3.62, 3.77	4.10	1:1	61.6	
2,6-Dimethylpiperidine	Palmitic	1:1	A	50	3.55, 3.67	3.79	1:1	60.0	
Piperazine	Lauric	2:1	E_{95}	60	5.78, 5.76	5.76	2:1	94.6– 94.8	92–92.5[q]
	Myristic	2:1	E_{95}	50	5.14, 5.18	5.16	2:1	93.8– 94.5	
	Palmitic	2:1	E_{95}	50	4.67, 4.68	4.68	2:1	97.7– 98.3	
	Stearic	2:1	E_{95}	40	4.24, 4.25	4.28	2:1	100.2–100.6	
	Arachidic	2:1	E_{95}	25	4.00, 4.02	3.94	2:1	102.5–102.9	
	Oleic	2:1	1.3E_a:A[j]	50	4.27, 4.31	4.31	2:1	80 – 81.4[h]	
	Elaidic	2:1	1.3A:E_a	50	4.30, 4.30	4.31	2:1	84 – 85	
Morpholine	Lauric	1:1	A	55	4.96, 4.47	4.87	1:1	50.5	
	Myristic	1:1	A	50	4.42, 4.44	4.44	1:1	60.2	
	Palmitic	1:1	A	65	3.96, 4.09	4.08	1:1	66.7	
	Stearic	1:1	A	50	3.78, 3.98	3.77	1:1	72.2	
Furfurylamine	Palmitic	1:1	A	75	3.95, 4.07	3.96	1:1	72.5	
2-Aminothiazole	Palmitic	1:1	4B:A	65	7.91, 7.98	7.85	1:1	53.3	
Phenylhydrazine	Palmitic	1:1	B	60	8.48, 8.45	7.69	1:1	108.4	

[a] Mole ratio, acid:amine. [b] A=acetone, B=benzene, C=dioxane, D=diethylether, E_a=absolute ethanol, E_{95}=95% ethanol, E_{90}=90% ethanol, T=toluene. [c] Weight % acid plus amine in solution. [d] Temperature ranges are capillary melting points. [e] Trimethylaminomethane. [f] 2,2,4-Trimethyl-2-aminopentane. [g] Ref. 4. [h] Melted with slight decomposition. [i] Crystallized twice from 25% dioxane solution and twice from 15% acetone solution. [j] One crystallization. [k] Two crystallizations. [l] Ref. 5. [m] From binary f.p. diagram, Ref. 12. [n] From f.p. diagram, Ref. 14. [o] From f.p. diagram, Ref. 13. [p] Difference in f.p. from that obtained from binary f.p. diagram attributed to polymorphism. [q] Ref. 6.

The freezing points of the 1:1 cyclohexylamine, benzylamine (stable and unstable forms), morpholine, 2-aminopyridine, 2,2′-dipyridylamine, and tris(hydroxymethyl)aminomethane salts and the 2:1 piperazine salts have been plotted in Figure 1 as a function of n, the number of carbon atoms in the normal saturated fatty acid moiety. The freezing points of the corresponding fatty acids have also been plotted for comparison. In general, each curve shows a rise in the freezing point as n increases. The tendency to approach a minimum at lower values of n, shown by three of the curves (A, B, and F), is not unusual (19).

TABLE II

Surface and Interfacial Tensions of Aqueous Solutions of Some Amine Salts of Palmitic Acid at 27°C.[a, b]

Palmitic acid salt of	Concentration in wt. %				
	0.5	0.2	0.1	0.05	0.01
	dynes/cm.	*dynes/cm.*	*dynes/cm.*	*dynes/cm.*	*dynes/cm.*
n-Amylamine	34.9, *0.6*	34.4, *0.8*	33.8, *0.6*	32.9, *0.6*	40.4, *10.9*
Isoamylamine	34.3, *0.6*	34.8, *0.5*	33.7, *0.6*	33.2, *0.6*	42.3, *4.8*
2-Amino-2-methyl-1-propanol	36.8, *3.2*	35.1, *8.2*	35.1, *8.3*	32.5, *13.8*	43.0, *32.8*
2-Amino-2-ethyl-1,3-propanediol	35.4, *6.4*		32.7, *20.2*		48.5, *37.2*
2-Amino-1-butanol	35.3, *2.2*	33.8, *6.8*	33.4, *7.7*	37.9, *12.2*	44.0, *32.5*
Cyclohexylamine[c]			59.9, *37.2*		
1-Cyclohexylamino-2-propanol			35.8, *29.8*		
Morpholine	28.1, *13.9*				43.9, *16.6*

[a] Values printed in italics represent interfacial tensions at Nujol surface.
[b] The surface tensions of water and Nujol and the interfacial tension at water Nujol interface were 72.7, 38.5, and 53.1 dynes/cm., respectively.
[c] Salt of capric acid.

The freezing points of the palmitic acid salts of ethyl, *n*-amyl, and stearylamine (Table I) indicate that a similar minimum occurs in the *n*-alkylamine salt series.

The curves for the morpholine salts and the low-melting form of the benzylamine salts tend to parallel that for the fatty acids so that the difference between the freezing points of the salts and the corresponding fatty acids is more or less uniform for each series over the range investigated. In the homologous series of the piperazine, cyclohexylamine, and high-melting benzylamine salts, on the other hand, this difference becomes markedly greater as *n* decreases. For example, the freezing points of the high-melting benzylamine salts of the C_{10} and C_{20} fatty acids are about 49 and 12 centigrade degrees higher than those of their respective acids. Such information is useful in selecting the amine which will give the optimum yield in separating fatty acids from their homologs by recrystallization of their amine salts (20).

A number of the pure amine salts of palmitic acid and one of capric acid were examined from the point of view of their behavior as surface-active agents. The surface interfacial tensions of aqueous solutions measured at various concentrations are listed in Table II.

The *n*-amylamine and isoamylamine salts were vastly superior in their ability to lower the Nujol/water interfacial tension though they were not appreciably better than most of the others for lowering the aqueous surface tension. A concentration as low as 0.5% of either of these two salts was sufficient to bring the interfacial tension below 1 dyne/cm. In addition, their aqueous solutions had high spreading coefficients (1) on a Nujol surface, of the order of +3 to +5 at concentrations of 0.05% or above, indicating an excellent wetting power.

Summary

Eighty-eight amine salts of long-chain fatty acids have been prepared, purified by solvent crystallization, and characterized. Forty-five of these were salts of palmitic acid. The rest included salts of capric, lauric, myristic, stearic, oleic, elaidic, and 12-hydroxystearic acids. A variety of aliphatic, aromatic, and heterocyclic amines, including primary, secondary, and tertiary amines, were investigated. The majority of these gave 1:1 acid-amine compounds on solvent recrystallization of an equimolar mixture of acid and amine. Some of the amines gave no crystallizable salt, and with others the pure salt could not be obtained by this procedure. Under the same conditions the symmetrical alkyl, substituted alkyl, and aralkyl secondary amines investigated gave crystallizable compounds containing two molecules of fatty acid to one of amine. Molecular compounds of 2-aminopyridine with four molecules of saturated fatty acid were formed by recrystallization starting with a 1 to 4 amine-acid mixture. Surface-tension measurements were made for aqueous solutions of a few of the amine salts.

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