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SOLUBILITIES OF HIGH MOLECULAR WEIGHT NORMAL ALIPHATIC PRIMARY AMINES

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The solubility curves of long-chain aliphatic compounds in organic solvents show a characteristic deviation from a linear relationship between concentration and temperature. In low concentrations the solubility of these compounds increases relatively little with considerable increase in temperature, while at higher concentrations their solubility increases markedly with relatively little rise in temperature. Hence, the initial slope of a typical solubility curve is very steep, while at moderate dilutions the slope changes abruptly, giving a relatively flat curve at higher concentrations. This behavior is exhibited by the higher fatty acids (1, 2), ketones (3), nitriles (4), amine salts (5), and amides, anilides, and N,N-diphenylamides (6). In order to obtain more complete data concerning the effects of various polar groups upon the solubilities of aliphatic compounds, the previous investigations in this Laboratory have been extended to the normal aliphatic primary amines. This paper presents the solubilities of decylamine, dodecylamine, tetradecylamine, hexadecylamine, and octadecylamine in fourteen organic solvents.

EXPERIMENTAL

The amines were obtained by hydrogenation of the highly purified nitriles used in the previous solubility investigations (4). They were purified by two distillations *in vacuo* to remove all secondary amine. The freezing points of these amines are listed in Table I.

The solvents were those used for the previous solubility studies. They were freshly distilled and cooled without access to the atmosphere, to prevent contamination with carbon dioxide.

The solubilities of the amines were determined with the equipment and in the manner described in previous reports (4, 10). Precautions were taken to prevent exposure of the amines to carbon dioxide.

RESULTS AND DISCUSSION

The solubility curves of the primary amines are similar to those of the fatty acids, ketones, and nitriles. The amines, however, do not exhibit the marked correlation between solubility and polarity of the solvent which is so striking with the other compounds.

The primary amines form simple eutectics with the non-polar solvents benzene, cyclohexane, and tetrachloromethane. These eutectic systems are illustrated graphically by the benzene (Fig. 1) and tetrachloromethane (Fig. 2) diagrams. The compositions and freezing points of the eutectics are listed in Table II.

The solubilities of the amines in these non-polar solvents are listed in Tables III–V. In these solvents, the amines are most soluble in benzene and least soluble in tetrachloromethane.

The solubilities of the amines in the slightly polar solvents trichloromethane,

ethyl ether, ethyl acetate, and butyl acetate are listed in Tables VI–IX, respectively, and the solubility curves for the amines in trichloromethane are shown graphically in Fig. 3.

TABLE I

FREEZING POINTS OF PURIFIED AMINES

AMINE	NO. OF C ATOMS	F.P., °C.	LIT. M.P., °C.
Decylamine	10	16.11	—
Dodecylamine	12	28.32	25 (7) 27–28 (8, 9) 28.0 (F.P.) (10)
Tetradecylamine	14	38.19	37 (8, 9)
Hexadecylamine	16	46.77	45–46 (9, 11) 46 (12) 47 (13)
Octadecylamine	18	53.06	54–55 (9) 47 (13) 55–56 (14)

TABLE II

EUTECTICS FORMED BY THE AMINES

SOLVENT		NO. OF C ATOMS				
		10	12	14	16	18
Benzene	Wt. % amine	31.7	18.0	10.8	6.1	2.2
	F.P., °C.	−5.6	+0.2	3.0	4.6	5.2
Cyclohexane	Wt. % amine	12.8	8.3	5.5	2.7	1.0
	F.P., °C.	−10.5	−3.5	+0.8	4.0	5.6
Tetrachloro-methane	Wt. % amine	7.2	4.4	1.9	0.4	<0.1
	F.P., °C.	−25.8	−24.4	−23.4	−23.0	—

TABLE III

SOLUBILITIES OF AMINES IN BENZENE

NO. OF C ATOMS	G. PER 100 G. BENZENE				
	10.0°	20.0°	30.0°	40.0°	50.0°
10	395	∞	∞	∞	∞
12	72	277	∞	∞	∞
14	26.4	83	302	∞	∞
16	10.0	30.7	98	388	∞
18	4.2	14.8	52	173	1000

In general, the amines are more soluble in trichloromethane than in any other solvent investigated. It is apparent from the wide divergence of the solubilities in tetrachloromethane and in trichloromethane that further halogenation of the

TABLE IV

SOLUBILITIES OF AMINES IN CYCLOHEXANE

NO. OF C ATOMS	G. PER 100 G. CYCLOHEXANE				
	10.0°	20.0°	30.0°	40.0°	50.0°
10	318	∞	∞	∞	∞
12	57	230	∞	∞	∞
14	19.9	68	268	∞	∞
16	7.4	26.6	86	360	∞
18	2.8	13.2	42.9	144	940

TABLE V

SOLUBILITIES OF AMINES IN TETRACHLOROMETHANE

NO. OF C ATOMS	G. PER 100 G. TETRACHLOROMETHANE					
	−20.0°	0.0°	20.0°	30.0°	40.0°	50.0°
10	10.5	57	∞	∞	∞	∞
12	5.5	19.8	148	∞	∞	∞
14	2.3	7.7	56	235	∞	∞
16	0.5	3.2	21.2	73	335	∞
18	<0.1	0.6	7.7	27.9	120	835

TABLE VI

SOLUBILITIES OF AMINES IN TRICHLOROMETHANE

NO. OF C ATOMS	G. PER 100 G. TRICHLOROMETHANE						
	−40.0°	−20.0°	0.0°	20.0°	30.0°	40.0°	50.0°
10	17.7	43.0	148	∞	∞	∞	∞
12	9.2	20.0	56	315	∞	∞	∞
14	4.5	11.2	29.5	110	308	∞	∞
16	2.4	6.6	17.0	56	117	378	∞
18	1.2	3.3	9.4	31.9	63	149	845

TABLE VII

SOLUBILITIES OF AMINES IN ETHYL ETHER

NO. OF C ATOMS	G. PER 100 G. ETHYL ETHER					
	−40.0°	−20.0°	0.0°	20.0°	30.0°	34.5°
10	1.4	12.1	86	∞	∞	∞
12	0.2	3.4	22.6	275	∞	∞
14	—	0.2	5.8	71	273	705
16	—	—	0.2	18.5	72	135
18	—	—	—	4.4	22.7	46.8

hydrocarbon results in a loss of solvent action. The behavior of the amines in ethyl acetate and in butyl acetate is unusual in that the solubilities are practically identical in these two solvents.

TABLE VIII

SOLUBILITIES OF AMINES IN ETHYL ACETATE

NO. OF C ATOMS	G. PER 100 G. ETHYL ACETATE					
	−20.0°	0.0°	20.0°	30.0°	40.0°	50.0°
10	14.8	69	∞	∞	∞	∞
12	4.7	18.6	221	∞	∞	∞
14	1.7	7.8	57	233	∞	∞
16	0.3	3.2	19.7	63	295	∞
18	—	0.9	9.5	27.0	100	845

TABLE IX

SOLUBILITIES OF AMINES IN BUTYL ACETATE

NO. OF C ATOMS	G. PER 100 G. BUTYL ACETATE					
	−20.0°	0.0°	20.0°	30.0°	40.0°	50.0°
10	13.3	69	∞	∞	∞	∞
12	4.4	23.0	221	∞	∞	∞
14	1.4	9.7	62	233	∞	∞
16	0.2	3.5	23.9	64	295	∞
18	—	1.0	11.4	30.4	100	845

TABLE X

SOLUBILITIES OF AMINES IN ACETONE

NO. OF C ATOMS	G. PER 100 G. ACETONE					
	−20.0°	0.0°	20.0°	30.0°	40.0°	50.0°
10	6.6	54	∞	∞	∞	∞
12	0.3	8.1	266	∞	∞	∞
14	—	0.1	15.5	228	∞	∞
16	—	—	<0.1	4.7	445	∞
18	—	—	—	<0.1	3.7	17.0

TABLE XI

SOLUBILITIES OF AMINES IN 2-BUTANONE

NO. OF C ATOMS	G. PER 100 G. 2-BUTANONE					
	−20.0°	0.0°	20.0°	30.0°	40.0°	50.0°
10	10.0	65	∞	∞	∞	∞
12	3.6	18.6	290	∞	∞	∞
14	0.2	2.8	48	285	∞	∞
16	—	—	8.3	48	580	∞
18	—	—	0.2	6.3	85	1975

The solubilities of the amines in acetone and in 2-butanone are listed in Tables X and XI, respectively, and the acetone curves are shown in Fig. 4.

TABLE XII

Solubilities of Amines in Methanol

No. of C atoms	g. per 100 g. methanol						
	−40.0°	−20.0°	0.0°	20.0°	30.0°	40.0°	50.0°
10	31.0	172	550	∞	∞	∞	∞
12	4.8	29.7	196	930	∞	∞	∞
14	≈0.2	2.8	62	292	770	∞	∞
16	—	0.2	6.1	116	256	785	∞
18	—	—	0.6	15.6	95	256	1440

TABLE XIII

Solubilities of Amines in 95% Ethanol

No. of C atoms	g. per 100 g. 95% ethanol						
	−40.0°	−20.0°	0.0°	20.0°	30.0°	40.0°	50.0°
10	8.5	91	350	∞	∞	∞	∞
12	2.0	14.1	115	660	∞	∞	∞
14	—	1.5	30.2	218	660	∞	∞
16	—	—	3.0	83	239	770	∞
18	—	—	0.1	7.2	75	280	1630

TABLE XIV

Solubilities of Amines in Isopropanol

No. of C atoms	g. per 100 g. isopropanol						
	−40.0°	−20.0°	0.0°	20.0°	30.0°	40.0°	50.0°
10	11.1	49.0	228	∞	∞	∞	∞
12	4.7	15.0	75	492	∞	∞	∞
14	0.6	3.7	25.1	154	458	∞	∞
16	—	0.4	7.3	68	169	580	∞
18	—	—	0.5	30.0	86	228	1330

TABLE XV

Solubilities of Amines in *n*-Butanol

No. of C atoms	g. per 100 g. *n*-butanol						
	−40.0°	−20.0°	0.0°	20.0°	30.0°	40.0°	50.0°
10	9.5	30.8	182	∞	∞	∞	∞
12	2.4	8.5	57	430	∞	∞	∞
14	0.2	2.4	16.5	130	405	∞	∞
16	—	<0.1	3.9	55	148	515	∞
18	—	—	0.4	22.7	75	208	1240

TABLE XVI

Solubilities of Amines in Acetonitrile

No. of C atoms	g. per 100 g. acetonitrile					
	−20.0°	0.0°	20.0°	30.0°	40.0°	50.0°
10	2.8	12.7	∞	∞	∞	∞
12	—	0.2	27.7	∞	∞	∞
14	—	—	1.8	14.9	∞	∞
16	—	—	0.2	1.3	14.8	∞
18	—	—	—	0.3	1.9	10.5

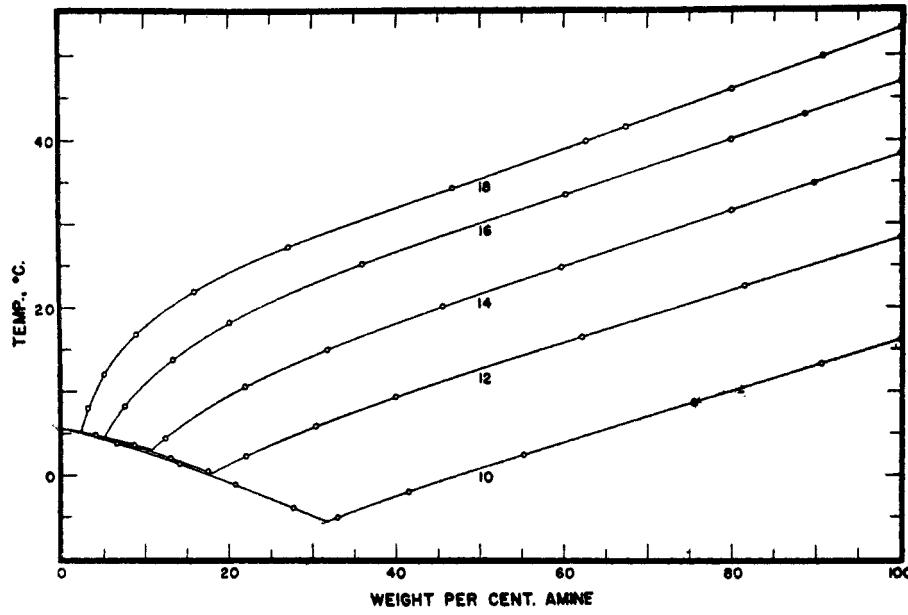

FIG. 1. SOLUBILITIES OF THE PRIMARY AMINES IN BENZENE
The numbers of the curves refer to the number of carbon atoms in the compounds

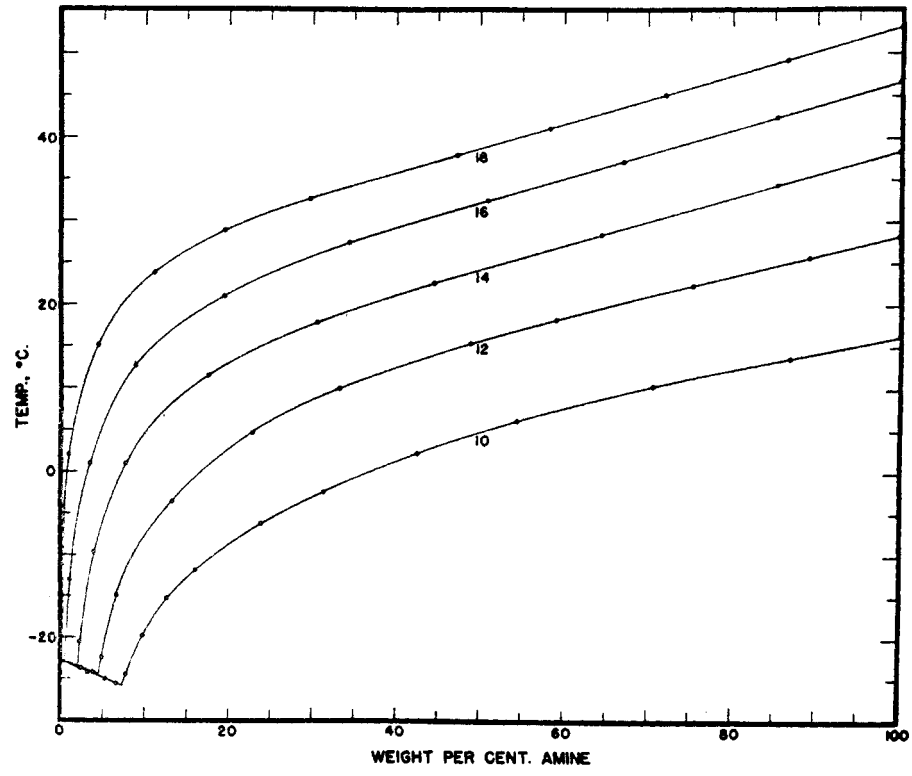

FIG. 2. SOLUBILITIES OF THE PRIMARY AMINES IN TETRACHLOROMETHANE

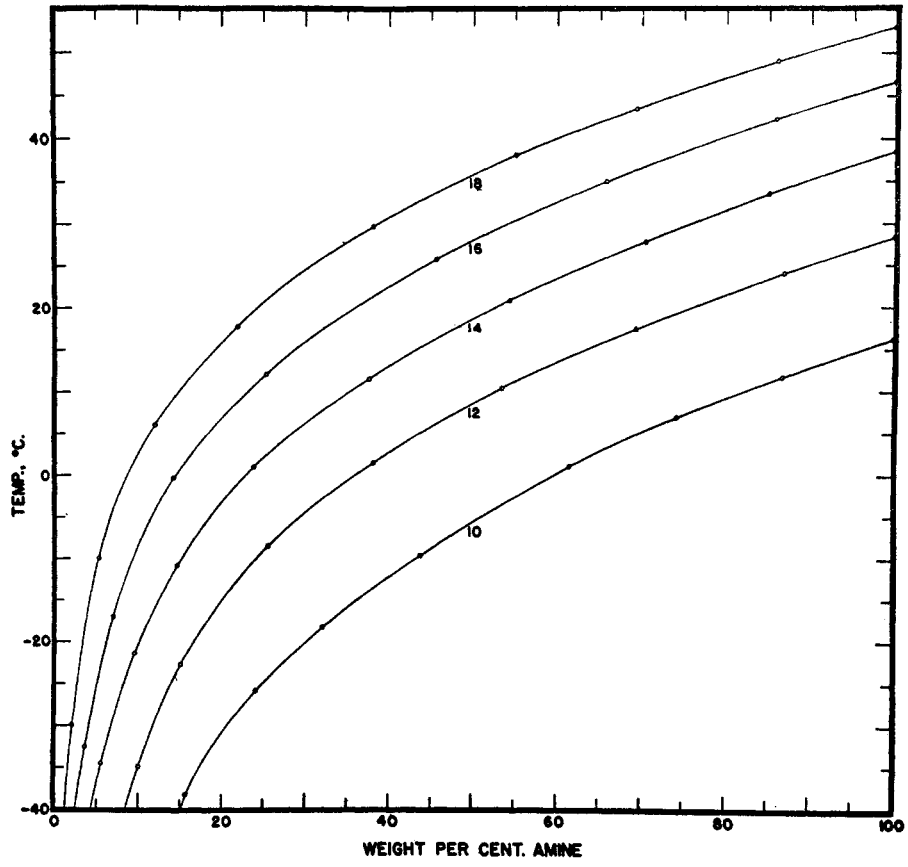

FIG. 3. SOLUBILITIES OF THE PRIMARY AMINES IN TRICHLOROMETHANE

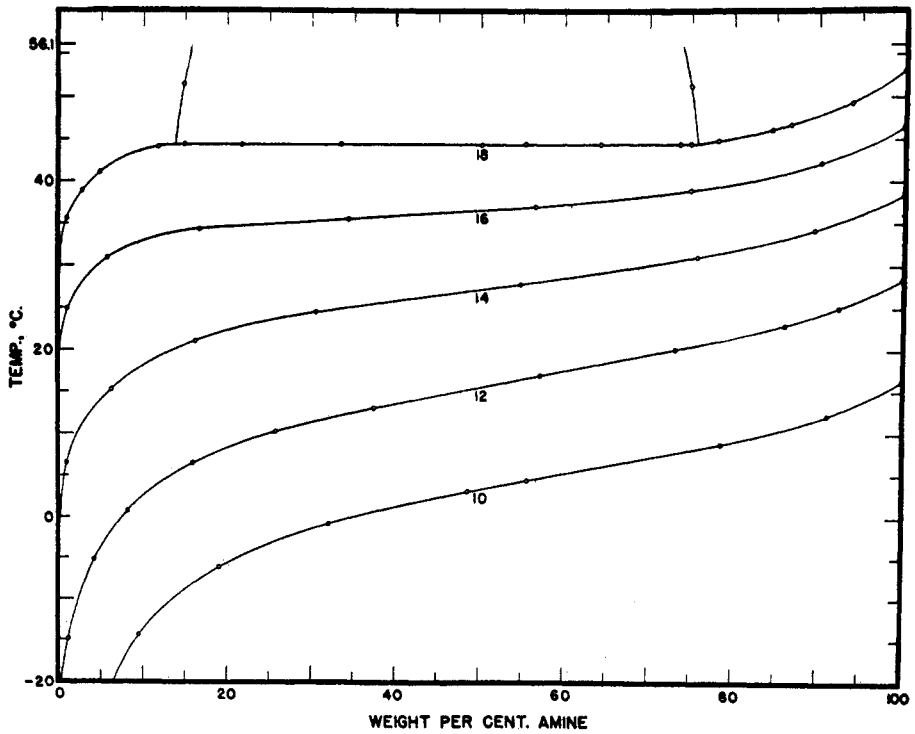

FIG. 4. SOLUBILITIES OF THE PRIMARY AMINES IN ACETONE

The amines are somewhat more soluble in 2-butanone than in acetone. It can be seen in Fig. 4 that the solubility of octadecylamine in acetone becomes so limited that a considerable region consisting of two immiscible solutions appears. Of the fatty acid derivatives investigated in the present series, octadecylamine is the only one which forms conjugate solutions with a solvent of a polarity as low as that of acetone.

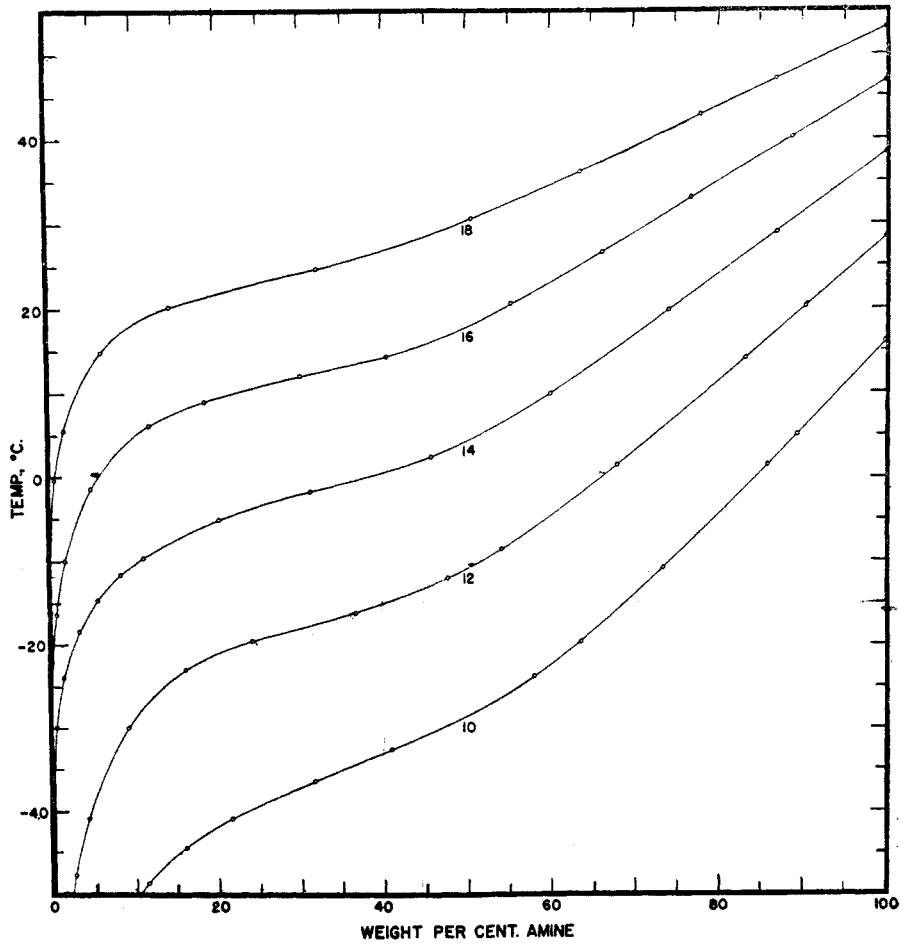

FIG. 5. SOLUBILITIES OF THE PRIMARY AMINES IN METHANOL

The solubilities of the amines in methanol, 95% ethanol, isopropanol, and *n*-butanol are listed in Tables XII–XV, respectively. The behavior of the amines in the alcohols is illustrated by the methanol curves (Fig. 5) and the *n*-butanol curves (Fig. 6).

The amines differ from the other fatty acid derivatives studied in this Laboratory in that they are considerably more soluble in the lower alcohols than in any of the other solvents investigated except trichloromethane. Most of other the

compounds are less soluble in the alcohols than in the other solvents except the highly polar solvents such as acetonitrile. The amines differ widely in their solubilities in the various alcohols, while the solubilities of other long-chain compounds do not differ greatly in these solvents.

The solubilities of the amines in acetonitrile are listed in Table XVI, and are shown graphically in Fig. 7.

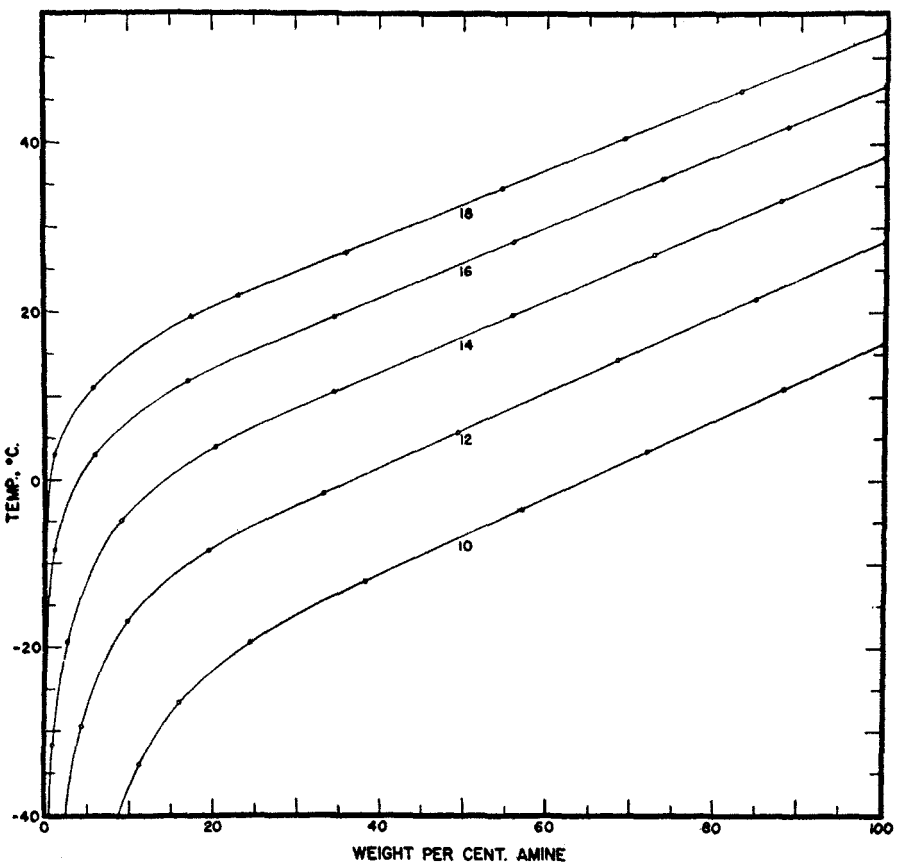

FIG. 6. SOLUBILITIES OF THE PRIMARY AMINES IN *n*-BUTANOL

The amines are less soluble in this highly polar solvent than in any other solvent studied and octadecylamine shows a region of immiscibility similar to that found in the octadecylamine-acetone system. In the acetonitrile system the entire immiscible region exists below the boiling point of the solvent and the upper limit of the region of conjugate solutions can, therefore, be located.

The solubility of the amines in nitroethane is indeterminable due to their reaction with this solvent.

The characteristic shape of the solubility curves of long-chain aliphatic compounds has been attributed to intermolecular association (1, 15). The mod-

erately high dipole moments of the amines (16) suggest the probability that these compounds are molecularly associated. Evidence that the amines are associated through hydrogen bonding has been reported (17). It has been observed however, that the amines do not give an abnormal freezing point depression in benzene or boiling point elevation in ethanol, which indicates that they are not associated in these solvents (18). Uutil more complete data concerning the

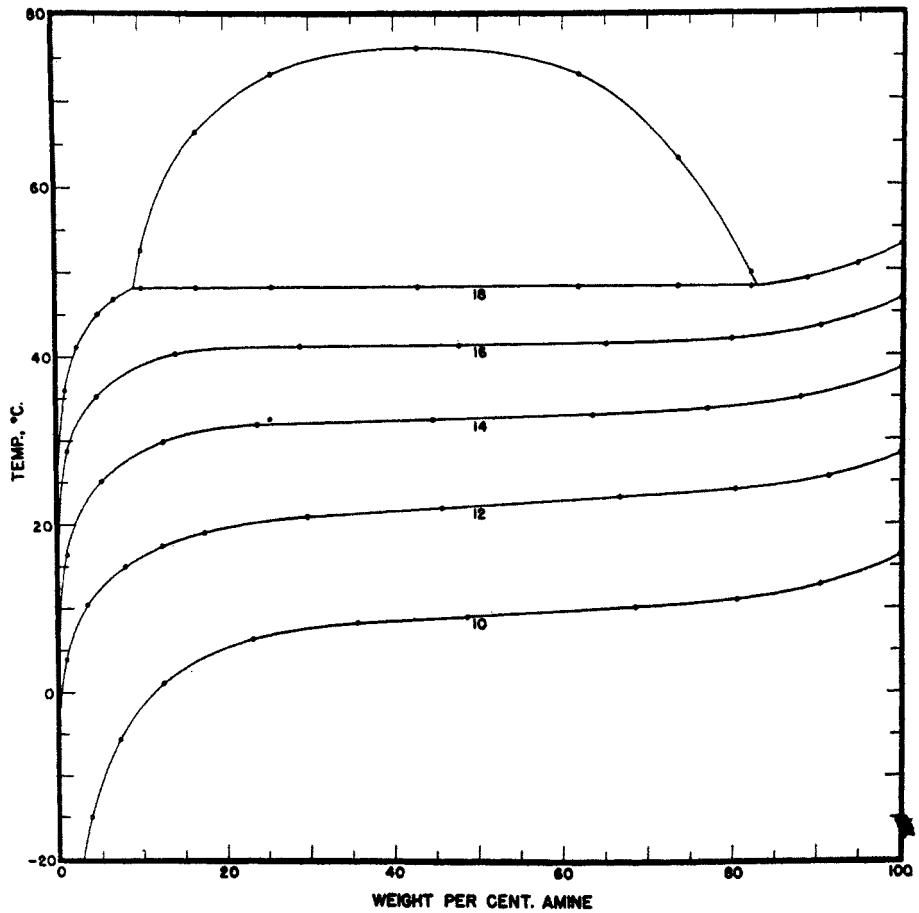

FIG. 7. SOLUBILITIES OF THE PRIMARY AMINES IN ACETONITRILE

behavior of long-chain compounds are available, no conclusions as to the effect of association upon solubility can be drawn.

SUMMARY

The solubilities of decylamine, dodecylamine, tetradecylamine, hexadecylamine, and octadecylamine have been determined in benzene, cyclohexane, tetrachloromethane, trichloromethane, ethyl ether, ethyl acetate, butyl acetate,

acetone, 2-butanone, methanol, 95% ethanol, isopropanol, *n*-butanol, and acetonitrile.

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