discrepancies in dyes 26, 27 and 28 have already been discussed. The case of no. 58 (phenolindophenol) cannot be interpreted until the cause of the great difference in absorption of the water and methanol solutions is found. Some of the remaining large discrepancies are doubtless due to experimental error. If we arbitrarily exclude the eight cases with the largest Δ, the average value of Δ becomes 3 mμ. It may therefore be reasonably predicted that when new members of these five great classes of dyes are investigated, the average difference between calculated and observed values will not be over 3 mμ. Indeed, if we should consider the various factors that we have noted but not used, this difference would probably be reduced to 2 mμ.

Summary

Six great classes of dyes are brought together into one family. The wave length, λ, of the main absorption band of any member of the family is determined by two rules. The first, theoretical, states that λ is always greater, the greater the fraction of the characteristic positive charge that is on the auxochromes. The second, empirical, states that the effect upon λ of various groups is additive. Thus a number of additive constants are obtained, from which λ can be calculated, and which are all qualitatively consistent with the theoretical rule.

However, in the acridine dyes the calculation applies, not to the first (x) band, but to the second (y) band. With this proviso, the table shows that with new dyes of the family λ can be predicted with an average error of not more than 3 mμ.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

The System Octadecylamine–Acetic Acid

BY W. O. POOL, H. J. HARWOOD AND A. W. RALSTON

The present investigation is a continuation of work dealing with the properties of high molecular weight aliphatic compounds and reports the behavior of binary mixtures of octadecylamine and acetic acid.

Method

Preparation of Materials.—Anhydrous acetic acid was prepared by partially freezing 99.5% glacial acetic acid and allowing the liquid portion to drain from the crystals. The freezing point of the acid used was 16.63°.

Fatty acid from hydrogenated soybean oil was converted to nitrile which was then hydrogenated to amine. After a preliminary distillation the octadecylamine was fractionated in a Stedman-packed column. The freezing point (53.02°) of the fraction used was in good agreement with the best literature value[1] (53.06°).

The octadecylammonium acetate was prepared in benzene and after several crystallizations had a freezing point of 84.4°.

Determination of Equilibrium Temperatures.—Mixtures containing more than 55 mole % of acetic acid were prepared by weighing octadecylammonium acetate and acetic acid into small glass tubes which were then sealed. Octadecylamine and acetic acid were used to prepare samples containing 3 to 53 mole % of acetic acid. Mixtures having less than 3 mole % of acetic acid were prepared from octadecylamine and octadecylammonium acetate. Equilibrium temperatures were obtained by observation of the tubes as they were rotated vertically about their short axes in a water-bath. The temperature of the bath was electrically controlled and was subject to very nice adjustment. A condition of equilibrium was proved by noting the temperature at which a solid phase disappeared as the sample was warmed slowly and comparing this temperature with that at which a trace of crystals definitely exhibited growth as the sample was cooled slowly. These two temperatures were always within a few tenths of a degree of each other. The filled circles in Fig. 1 represent the upper or solution temperatures. In some cases unstable crystals transformed to the stable modifications with such speed that true solution temperatures could not be obtained. To secure an approximate solution temperature, the tube was warmed in hot water until the contents were entirely liquid. The tube was then placed in the bath which had a fixed temperature slightly below the melting point of the most stable modification. The mixture would generally supercool and remain liquid. The tube was then removed from the bath, immersed momentarily in cold water and replaced immediately in the bath. If the crystals, which had formed by the rapid cooling, went into solution, the fixed temperature of the bath was lowered, and the entire procedure was repeated. In this way two temperatures were obtained, an upper at which the unstable crystals remelted, and a lower at which the unstable crystals remained or underwent a transformation to a more stable modification. The upper of these two temperatures, which were usually within 0.5° of each

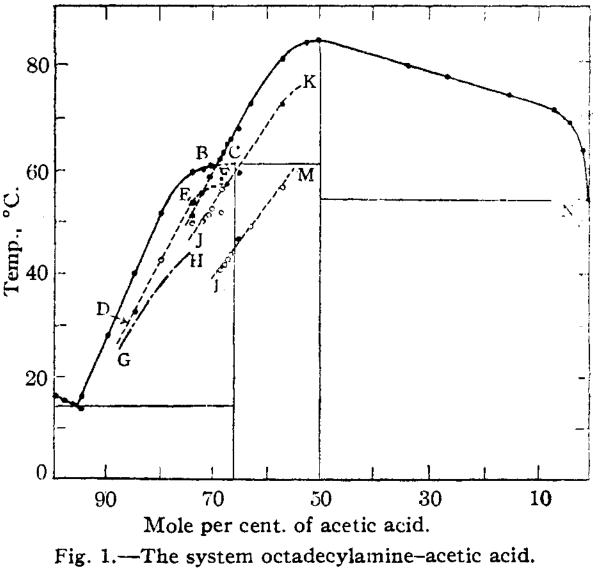

Fig. 1.—The system octadecylamine–acetic acid.

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[1] Ralston, Hoerr, Pool and Harwood, *J. Org. Chem.*, **9**, 102 (1944).

other, is plotted as an open circle in Fig. 1. Broken lines represent unstable modifications and are drawn in the manner which seemed most logical. The transitory nature of the unstable modifications made positive proof of their composition impossible. Differences in the appearance of the three forms support the interpretation shown. The eutectic formed by octadecylammonium acetate and octadecylamine contained less than 0.1 mole % of the amine and was located by means of a cooling curve of a mixture containing 1.2 mole % of acetic acid. The only observable thermal change occurred at 52.96° and corresponds to the freezing point of the eutectic.

Experimental Results.—The results are given in Table I and are shown graphically in Fig. 1.

TABLE I

OCTADECYLAMINE–ACETIC ACID

AcOH, mole %	Equilibrium temperature, °C. Most stable	Intermediate	Least stable
100.0	16.63	None	None
97.9	15.4	None	None
96.4	14.8	None	None
94.8	16.2	None	13.7
89.9	28.0	Indet.	Indet.
84.8	40.0	32.7	30.5
79.8	51.4	42.6	40.5
74.0	Not detd.	Not detd.	50.8
73.9	59.3	53.6	50.0
72.0	59.8	53.3	49.9
70.8	60.4	58.3	51.1
70.7	60.3	Indet.	51
70.5	60.3	58.3	52
68.8	62.0	51.4	40.5
68.3	63.2	56	41.1
67.5	64.9	Indet.	42.2
67.4	64.8	56.8	Indet.
67.1	65.4	Indet.	43.2
65.2	67.7	59.1	46.2
63.1	72.7	Not detd.	48.7
56.9	80.9	72.5	56.3
52.4	84.0	Indet.	Indet.
50.0	84.4	Indet.	Indet.
33.3	79.5	Indet.	Indet.
26.0	77.1	Indet.	Indet.
14.6	73.5	Indet.	Indet.
6.2	70.4	Indet.	Indet.
3.7	67.9	Indet.	Indet.
1.0	62.6	Indet.	52.9

From Fig. 1 it is evident that only two stable compounds ($C_{18}H_{37}NH_2 \cdot HC_2H_3O_2$ and $C_{18}H_{37}NH_2 \cdot 2HC_2H_3O_2$) are formed between octadecylamine and acetic acid. The first of these compounds has been known and melts at 84.4°. The second compound melts at 60.8° and forms a meritectic system at B having a submerged maximum at C. The eutectic between $C_{18}H_{37}NH_2 \cdot 2HC_2H_3O_2$ and acetic acid occurs at 14.2° and contains 96.6 mole % of acetic acid. Octadecylamine and octadecylammonium acetate appear to form a monotectic system; the eutectic, if any, lies only 0.06° below the freezing point of octadecylamine. The stable compound $C_{18}H_{37}NH_2 \cdot 2HC_2H_3O_2$ has two other modifications indicated by the curves DEF and GH. Octadecylammonium acetate also has two other modifications indicated by the curves JK and LM. The mixture having a composition of 1 mole % of acetic acid exhibits two crystalline forms. The equilibrium temperature shown at N is evidently due to one of the lower melting forms of the ammonium salt. Between 1 and 57 mole % of acetic acid, unstable modifications of octadecylammonium acetate occur, but transformation to the stable crystal takes place so rapidly that equilibrium temperatures cannot be obtained.

Discussion

Davidson, Sisler and Stoenner,[2] in an investigation of the acetic acid–ammonia system, showed the existence of five solid compounds. It is interesting to note that the octadecylamine analogs of $5NH_3 \cdot 4HC_2H_3O_2$, $9NH_3 \cdot HC_2H_3O_2$ and $2NH_3 \cdot HC_2H_3O_2$ do not exist. The absence of bimolecular compounds of octadecylamine and acetic acid containing more than two acetic acid molecules is in keeping with the observation by Ralston, Hoerr and Hoffman[3] that the degree of hydration of octadecylamine is less than that of dodecylamine or octylamine. These authors found that octadecylamine formed only a mono- and a dihydrate, whereas dodecylamine formed a tetrahydrate, and octylamine formed a hexahydrate. It is probable that the ability of amines to form acid salts decreases as the homologous series is ascended.

Summary

1. The temperature–concentration curve for the system octadecylamine–acetic acid has been completed throughout the entire concentration range.

2. The existence of the new solid compound $C_{18}H_{37}NH_2 \cdot 2HC_2H_3O_2$ has been demonstrated.

3. Three modifications of $C_{18}H_{37}NH_2 \cdot 2HC_2H_3O_2$ and $C_{18}H_{37}NH_2 \cdot HC_2H_3O_2$ have been shown to occur.

4. It has been suggested that the formation of the acid salts of the alkyl amine series parallels the formation of the amine hydrates.

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(2) Davidson, Sisler and Stoenner, THIS JOURNAL, **66**, 779 (1944).

(3) Ralston, Hoerr and Hoffman, *ibid.*, **64**, 1516 (1942).