

46. The Instability of Ammonium Salts of Higher Fatty Acids.

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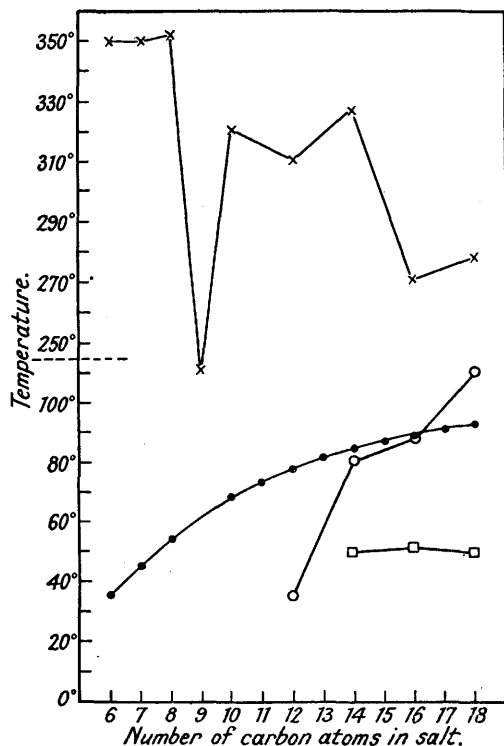
The stability of ammonium soaps of a series of fatty acids from heptic to stearic has been investigated by means of chemical and X-ray analysis. Neutral soaps are found to lose ammonia readily and pass into the more stable acid soaps. "Long spacings" of neutral and acid ammonium salts and m. p.'s of acid ammonium salts are recorded.

LAWRENCE (*Trans. Faraday Soc.*, 1933, **29**, 1008), who considered that the irregular m. p.'s of sodium salts of fatty acids (Vorländer, *Ber.*, 1910, **43**, 3120) (Fig. 1) might be due to thermal decomposition or to the presence of traces of water, examined the lower-melting ammonium salts, and finding that these exhibited similar irregularities (Fig. 1), concluded that some other explanation was required.

This conclusion implies that the irregularities in the above two cases have a similar origin; but whereas the high temperatures involved and the difficulties surrounding the purification of sodium soaps (cf. Malkin, *Ber.*, 1930, **63**, 1810) are sufficient explanation of Vorländer's results, those of Lawrence appeared to us to be due to the instability of ammonium salts, many of which are known to lose ammonia and pass into the more stable acid salts, $R \cdot CO_2NH_4, R \cdot CO_2H$ (Currie, *J. Agric. Res.*, 1914, **2**, 8; McMaster and Magill, *J. Amer. Chem. Soc.*, 1916, **38**, 1796).

In order to test this view we have submitted a series of ammonium salts of acids ranging from heptic to stearic to chemical and X-ray analysis. Most of the salts were made by treating a slightly warm alcoholic solution of the fatty acid with excess of a concentrated solution of ammonia in alcohol, and cooling (ice if necessary), but this method was found unsuitable for the more soluble salts of the lower fatty acids (C_{10} downwards) which were made by passing dry ammonia into an ethereal solution of the acid. After the colourless crystalline salts had been dried rapidly in a vacuum or on porous tile, m. p., X-ray, and

FIG. 1.
M. p.'s of sodium and ammonium salts of fatty acids.



- × = Sodium salts (Vorländer).
- = Ammonium salts (Lawrence).
- = Ammonium salts (Lawrence): transition to mesomorph.
- = Acid ammonium salts (Kench and Malkin).

analytical data were determined (ammonia by the final stage of the Kjeldahl method).

We found the salts made by the above two methods to be quite different. Those from alcohol, when freshly prepared, had an ammonia content approaching that of the neutral salt and lost ammonia fairly rapidly on standing. M. p.'s were not easy to determine owing to sintering over a wide range of temperature. Salts from ether, however, were comparatively stable, and melted as a rule quite sharply. Analysis showed that they were almost

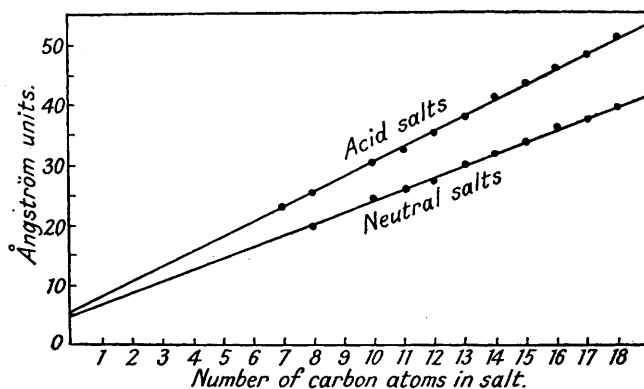
* The results of Escales and Koepke (*J. pr. Chem.*, 1913, **87**, 258) indicate that neutral ammonium formate and acetate are stable.

entirely acid salts. In view of this difference, we also prepared salts of the higher acids by the ether method, and found that acid salt formation is general, the much smaller solubility of the acid salt in ether than in alcohol apparently being the deciding factor in the different behaviour.

These results are at variance with those of McMaster (*loc. cit.*; *J. Amer. Chem. Soc.*, 1914, 36, 1916), who claims to obtain neutral salts from ether, but in spite of his remarkably accurate analyses, considerable doubt may be expressed regarding the purity of his materials: for instance, ammonium palmitate quickly became yellow, *i.e.*, probably contained unsaturated acids; ammonium caprylate (octoate) is described as a cheese-like mass, and ammonium caprate (decoate) as an amorphous substance greasy to the touch.

X-Ray examination confirmed our analytical results. Salts obtained from alcohol yielded two distinct long spacings, the lines corresponding with the shorter spacing being the more intense, and salts from ether yielded only the longer of the above two spacings, with an occasional faint indication of the shorter. From the analytical data and the intensities of the lines, the shorter and the longer spacings were identified with the neutral and the acid soaps respectively. The progress of the change neutral \rightarrow acid soap was well shown by the alteration in intensity of the two sets of lines of the X-ray spectrum.

FIG. 2.



Long spacings of neutral and acid ammonium salts of fatty acids.

The observed spacings for acid and neutral ammonium salts are given in Table I and plotted in Fig. 2. The experimental error is greater than usual with such measurements owing to the heterogeneity of the crystals, but the curves probably represent the true values to ± 0.2 Å. The spacings correspond with double molecules with carboxyl groups

TABLE I.

Long X-ray spacings of neutral and acid ammonium salts (in Å.).

Carbon atoms in acid	7	8	10	11	12	13	14	15	16	17	18	
Neutral salt	19.6	24.2	25.4	27.1	29.6	31.5	33.0	36.1	36.4	38.4	
Acid salt	22.8	25.1	30.2	32.2	35.0	37.7	40.9	43.2	45.8	47.9	50.8

(Salts of acids from propionic to hexoic rapidly become liquid and lose ammonia beyond the acid salt stage. They are consequently unsuitable for X-ray investigation.)

in juxtaposition. The hydrocarbon chains in neutral salts are inclined to the reflecting planes at an angle of $45^{\circ}40'$ (increase in length per carbon atom, 0.9 Å.), and those of acid salts are vertical (increase per carbon atom, 1.27 Å.). Piper (J., 1929, 234) obtained similar results for neutral and acid potassium salts of fatty acids, and showed that these possessed tilted and vertical chains respectively.

The difference in melting behaviour of neutral and acid salts affords a good indication of the composition of any particular ammonium salt. The curve in Fig. 1 gives to within 1° the comparatively sharp m. p.'s of acid salts (Table II), and the range of sintering above

this temperature is roughly proportional to the amount of neutral salts present; m. p.'s lower than the curve indicate impurity, or a higher percentage of free acid due to

TABLE II.

M. p.'s of acid ammonium salts of fatty acids.

Carbon atoms in acid	7	8	10	11	12	13	14	15	16	17	18
M. p.....	45°	54°	68°	72°	77°	81°	84°	86°	89°	91°	93°

further dissociation. It was clear from our m. p. determinations that, could the m. p.'s of neutral salts be taken without decomposition, they would be considerably higher than those of the acid salts, and with a view to obtain some idea of this temperature, we sealed a little ammonium laurate in the bottom of a capillary tube, in order to minimise dissociation, and found the m. p. to be in the neighbourhood of 130° (acid ammonium laurate, m. p. 77°). Comparison of Lawrence's m. p. values with the curve in Fig. 1 indicates that the irregularities found by him were, in fact, due to loss of ammonia from his neutral salts. His myristate and palmitate appear to have been mainly acid salts, but the stearate probably contained a certain amount of neutral salt. It is difficult to offer any explanation for the abnormally low m. p. of the laurate, but it is quite unacceptable that a salt should melt at a lower temperature than the pure parent acid.

During our m. p. determinations we were unable to observe the "transitions to mesomorphs" stated by Lawrence to occur in the neighbourhood of 50°.

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