152. *An Infrared Spectroscopic Examination of Some Anhydrous Sodium Soaps.*

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The infrared spectra of a series of sodium soaps have been obtained in the range 1800—650 cm.$^{-1}$ and various features of the spectra from acetate to stearate are discussed. The effect of heat on anhydrous sodium stearate and palmitate has been investigated. The liquid-crystalline form of these soaps is discussed.

Childers and Struthers[1] showed that the infrared spectra of the sodium soaps from the acetate to the hexanoate are useful in characterising the corresponding fatty acids. Recently, Meikeljohn *et al.*[2] extended this work, using barium soaps up to C_{36}, and point out an empirical relationship between the number of bands in the 1250 cm.$^{-1}$ region and the number of carbon atoms in the chain.

Experimental

The sodium soaps from C_8 to C_{18} were prepared by standard methods from aqueous sodium hydroxide and an ethanolic solution of the acid; the acids were very pure. The even-numbered acids were presented by Dr. S. Paul, and the odd-numbered acids by Dr. J. Devine, of these laboratories. The soaps of fatty acids of shorter chain-length were similarly prepared from commercial acids of B.D.H. quality.* To obtain the anhydrous forms, each soap was heated to 140° in a vacuum oven for several hours in the presence of phosphoric oxide. All spectra shown were obtained by means of potassium chloride discs (several additional spectra were obtained with Nujol mulls).

A Grubb-Parsons S.3 double-beam infrared spectrometer was used, with a heated cell for the investigation of the effects of temperature on the anhydrous soaps.

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* The physical characteristics of most of the acids used have been previously described.[11] The setting points or m. p.s of the remaining acids are as follows: C_{13}, m. p. 41—41·5°; C_{14}, s. p. 53·9°; C_{16}, s. p. 62·25°; C_{17}, m. p. 57·5—58°; C_{18}, s. p. 69·3°.

[1] Childers and Struthers, *Analyt. Chem.*, 1955, **27**, 737.

[2] Meikeljohn, Meyer, Aronovic, Schuette. and Meloche, *ibid.*, 1957, **29**, 329.

RESULTS AND DISCUSSION.

The spectra of the anhydrous sodium soaps are shown in Figs. 1 and 2 over the range 1800—650 cm.$^{-1}$. For a detailed analysis of the spectra we can first consider the bands which arise from vibrations of the carboxylate group and then those of the paraffinic chain.

In relation to the bands arising from vibrations of the carboxylate group Lecomte and his co-workers[3] have shown that when ionisation occurs giving rise to the $CO{\cdot}O^-$ group, resonance is possible between the two C–O bonds, and that the usual carbonyl absorption vanishes and is replaced by two bands, approximately between 1610 and 1550 cm.$^{-1}$ and between 1400 and 1300 cm.$^{-1}$. These bands correspond to the antisymmetrical and symmetrical vibrations of the $CO{\cdot}O^-$ structure.

Ito and Bernstein,[4] dealing with the spectrum of solid sodium acetate, assigned bands at 1578 cm.$^{-1}$ and 1414 cm.$^{-1}$ to C–O stretching vibrations and a band at 646 cm.$^{-1}$ to a $CO{\cdot}O^-$ deformation frequency. The spectra of all the anhydrous sodium soaps examined here exhibit bands near 1560 and 1415, and at 695 cm.$^{-1}$, which can be similarly assigned. (Both the acetate and the propionate have the last band at a lower frequency, but the band remains constant in frequency with further increase of chain length.)

A fairly complete assignment of long-chain paraffins is now available[5] and this enables us to discuss the remaining bands in the spectra of the sodium soaps.

Two constant sets of bands at 1460 and 1380 cm.$^{-1}$ are observed in all the spectra; they arise from CH_2 and CH_3 symmetrical bending deformation modes. These frequencies are well known and are observed in the infrared spectra of all long-chain compounds. The relative intensity of the 1380 cm.$^{-1}$ band decreases as the length of chain increases. A band at 1440 cm.$^{-1}$ may be tentatively assigned to the vibration of the CH_2 group adjacent to the carboxylate group by analogy with a similar assignment in carboxylic acids.[6] A very prominent feature of the spectra of the soaps is a set of absorption bands marked by the intensity and regularity of its members in the 1200—1350 cm.$^{-1}$ region. Analogous regular series of bands have been observed in this region of the spectrum of many long-chain compounds including paraffins,[5] bromides,[7] fatty acids,[8] and glycerides.[9] In the alkyl bromides Brown and Sheppard[7] have shown clearly that the bands arise from CH_2 wagging modes and originate near 1250 cm.$^{-1}$. In the monocarboxylic acids Jones *et al.*[8] assign the bands generally to CH_2 wagging and twisting modes. Meikeljohn *et al.*[2] noted a similar series in the spectra of some barium soaps and point out an empirical relationship between the number of bands and the number of carbon atoms in the chain. (The number of bands for even numbers of carbon atoms is equal to half the number of carbon atoms, whilst for odd numbers of carbon atoms it is half the number of carbon atoms + 1.) Certain anomalies to this relationship were observed for the soaps below C_{16} owing to weaker intermediate bands which had to be disregarded. Our spectra of the anhydrous sodium soaps show no such anomalies and the empirical rule rigidly holds.

The distribution clearly originates in the spectrum of sodium propionate near 1300 cm.$^{-1}$. One would expect the number of bands observed to be related to the number of methylene groups present rather than to the total number of carbon atoms; *e.g.*, Brown *et al.*[5] discussed the selection rules for methylene wagging modes for odd-numbered hydrocarbons and stated that one band should be observed for every methylene group. With the anhydrous sodium soaps this is true, however, for only the first few members (Table 1).

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[3] Duval, Lecomte, and Douville, *Ann. Phys.*, 1942, **17**, 5; *Bull. Soc. chim. France*, 1942, **9**, 263.

[4] Ito and Bernstein, *Canad. J. Chem.*, 1956, **34**, 170.

[5] Brown, Sheppard, and Simpson, *Phil. Trans.*, 1954, *A*, **247**, 35.

[6] Francis, *J. Chem. Phys.*, 1951, **19**, 942.

[7] Brown and Sheppard, *Trans. Faraday Soc.*, 1954, **50**, 535.

[8] Jones, McKay, and Sinclair, *J. Amer. Chem. Soc.*, 1952, **74**, 2575; Von Sydow, *Acta Chem. Scand.*, 1955, **9**, 1119.

[9] Chapman, *J.*, 1956, 2522.

The distribution is very similar to that for *n*-alkyl bromides.[7] In terms of the methylene groups the number of bands for the even-numbered soaps is $\frac{1}{2}n + 1$ and for odd-numbered, excluding sodium propionate $\frac{1}{2}(n + 1) + 1$ (where n is the number of methylene groups). An interesting feature of the distribution is that for the odd-numbered soaps the highest-frequency band is always at a higher frequency than that of the even-numbered soaps, *i.e.*, the frequency of the band alternates from even- to odd-numbered soap; furthermore, whilst the same number of bands are observed in the spectra of an odd-numbered soap as in the spectra of the next higher even-numbered soap, yet all the bands are shifted in frequency. This could be useful in distinguishing odd- and even-numbered soaps.

FIG. 1. *Infrared spectra of anhydrous sodium soaps (acetate to octanoate).*

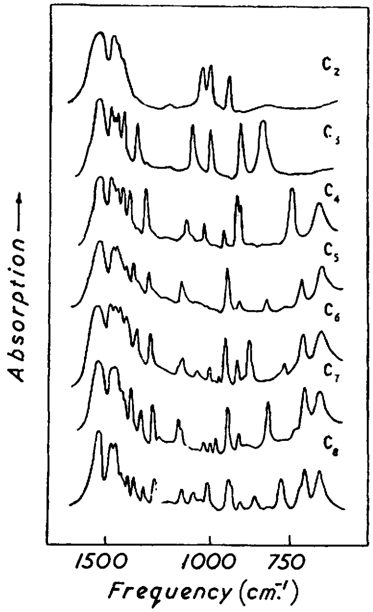
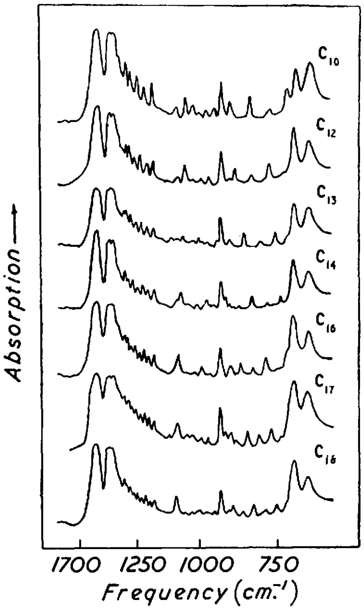


FIG. 2. *Infrared spectra of anhydrous sodium soaps (decanoate to stearate).*



The frequency difference between the highest-frequency band and the next band of lower frequency is always less than the frequency difference between the other bands. This was also observed with the barium soaps [2] and related tentatively to the presence of the α-methylene group. (The C–H distances in this group are probably greater than in the other methylene groups.) The high-frequency band, in contradistinction to the other bands in the distribution, which tend to spread out in frequency, moves gradually to lower frequencies as the chain length increases.

In the spectrum of sodium oleate, there are only five bands in this region and the

TABLE 1.

No. of C atoms in soap	No. of CH_2 groups	No. of bands observed in 1250 cm.$^{-1}$ region	Diff. between cols. 2 and 3	No. of C atoms in soap	No. of CH_2 groups	No. of bands observed in 1250 cm.$^{-1}$ region	Diff. between cols. 2 and 3
3	1	1	0	11 *	9	6	3
4	2	2	0	12	10	6	4
5	3	3	0	13	11	7	4
6	4	3	1	14	12	7	5
7	5	4	1	15 *	13	8	5
8	6	4	2	16	14	8	6
9 *	7	5	2	17	15	9	6
10	8	5	3	18	16	9	7

* It is assumed that the empirical rule observed with the other soaps also holds for these soaps.

empirical rule-of-two relationship is apparently not obeyed. This is to be expected, however, owing to the introduction of a double bond in the chain. There are nine carbon atoms on each side of the double bond (or seven methylene groups). In this case therefore each of the chains on either side of the double bond appears to vibrate separately, and to obey the empirical rule individually.

Two marked series of absorption frequencies can be traced in the spectra, one of which extends from 1075 cm.$^{-1}$ in the spectrum of sodium propionate (1042 cm.$^{-1}$ in sodium acetate) to 1105 cm.$^{-1}$ in that of sodium stearate, and the other which extends from 990 cm.$^{-1}$ in the spectrum of sodium propionate (1009 cm.$^{-1}$ in sodium acetate) to 920 cm.$^{-1}$ in that of sodium stearate. These series are analogous to those observed in the spectra of crystalline paraffins and alkyl bromides and can be broadly assigned to methyl rocking modes. (They are also consistent with the previous assignments of the bands in this region in the spectrum of sodium acetate.[4]) These assignments receive additional confirmation from the fact that in the spectra of the liquid-crystalline form (see Fig. 3) these bands are the least affected by this change of state. This is to be expected for these modes: the skeletal frequencies will be more likely to be affected by such a change. Bands occurring between 1080 and 940 cm.$^{-1}$ probably arise from C–C skeletal vibrations.

A series of bands in the 900—720 cm.$^{-1}$ region are attributed to CH_2 rocking modes. The most characteristic series of bands in this region are listed in Table 2, which also lists the corresponding CH_2 rocking frequencies for the normal paraffins[10] and monocarboxylic acids.[11]

The general similarity of these frequencies in the spectra of the soaps with those of the paraffins (and monocarboxylic acids) suggests that the chains at room temperature are predominantly in the planar *trans*-zigzag configuration similar to the chains in paraffins in the crystalline state.[10]

An important feature about the main CH_2 rocking vibration in the spectra, *e.g.*, of sodium stearate or palmitate, is that this band is single. Many long-chain compounds however show a doublet in this region. Chapman[12] has suggested that the presence of a doublet is indicative of orthorhombic packed hydrocarbon chains, whilst a single band in this region is indicative of triclinic packed chains, so we may deduce that the hydrocarbon chains of the sodium soaps are probably triclinically packed, as observed with silver stearate.[3]

TABLE 2.

n	Paraffins $H{\cdot}[CH_2]_n{\cdot}H$	Monocarboxylic acids $H{\cdot}[CH_2]_n{\cdot}CO_2H$	Sodium soaps $H{\cdot}[CH_2]_n{\cdot}CO_2Na$
2	822	807	812
3	748	750	748
4	732	731	728
5	728	727	726
6	726	724	723
7	723	723	721
8	722	723	720
9	720	721	719

Several other series can be traced in this region but they are not quite so marked as those which occur in the infrared spectra of the crystalline paraffins. One series starts at 850 cm.$^{-1}$ in sodium hexanoate and reaches a limit near 720 cm.$^{-1}$ in sodium laurate.

Effect of Heat on the Anhydrous Soaps.—Several changes of state occur when an anhydrous sodium soap is heated from room temperature to the m. p.;[14-18] *e.g.*, dilatometric measurements[17] over this temperature range show two gross irregularities in the

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[10] Brown, Sheppard, and Simpson, *Discuss. Faraday Soc.*, 1950, **9**, 261.
[11] Corish and Chapman, *J.*, 1957, 1746.
[12] Chapman, Sixth Internat. Spectroscopic Colloquium Symp., Amsterdam, 1956.
[13] Vand, Aitken, and Campbell, *Acta Cryst.*, 1949, **2**, 398.
[14] Vold, Rosevear, and Ferguson, *Oil and Soap*, 1939, **16**, 48.
[15] Vold and Vold, *J. Amer. Chem. Soc.*, 1939, **61**, 808.
[16] Nordsieck, Rosevear, and Ferguson, *J. Chem. Phys.*, 1948, **16**, 175.
[17] Vold, Macomber, and Vold, *J. Amer. Chem. Soc.*, 1941, **63**, 168.
[18] Southam and Puddington, *Canad. J. Res.*, 1947, **25**, 125.

density–temperature curve at about 105—120° and 200°, with minor breaks at other temperatures. With anhydrous sodium palmitate, five phase transitions [15,17] have been observed between the crystalline state and the isotropic melt. An *X*-ray examination of this soap,[16] however, suggests that these phases can be grouped into two basic structures, named the waxy and neat phase, both being thought to be liquid-crystalline.

The infrared spectra of sodium palmitate at different temperatures are shown in Fig. 3. As the temperature approaches 100° the distribution of bands in the 1250 cm.$^{-1}$ region become less well-resolved, particularly the bands at the high-frequency end of the distribution. This is interpreted to mean that the hydrocarbon chains are beginning to flex and twist. (This will produce some rotational isomerism, each isomer having its own frequency in this region, producing a smearing-out of the spectrum.) This interpretation is supported by the fact that the band at 719 cm.$^{-1}$ also decreases slightly in intensity. (This band is associated with the in-phase motion of all the CH_2 groups, so that twisting of parts of the chain will reduce the intensity of this band.) On further heating to about 120—130° this band decreases considerably in intensity, indicating that many more methylene groups are spinning freely about the C–C bonds. All the fine structure in the 1250 cm.$^{-1}$ region vanishes, whilst bands assigned to other CH_2 rocking modes also become diffuse or disappear. Bands assigned to methyl rocking modes decrease in intensity but remain prominent. There is little if any movement in frequency of the carboxylate bands at 1560, 1415, or 695 cm.$^{-1}$ but the intensity of the 695 cm.$^{-1}$ band decreases.

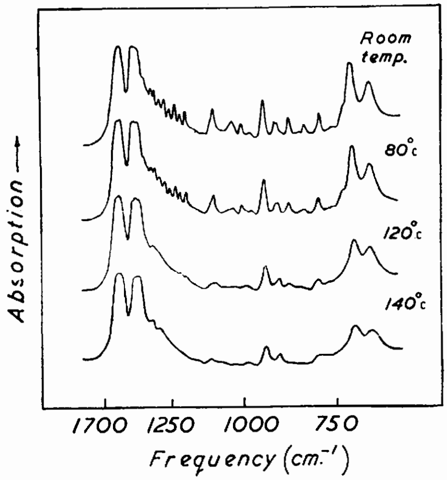

FIG. 3. *Infrared spectra of anhydrous sodium palmitate at different temperatures.*

Above 120—130° the spectrum of the soap is in fact entirely " liquid-like " in character. The changes observed in the spectra are analogous to those observed in the spectra of, *e.g.*, long-chain monocarboxylic acids when the transition from the crystalline to liquid state occurs. Yet this transition occurs some 160° below the " true " m. p. of the soap. It seems clear that at this temperature the methylene groups are spinning freely and the hydrocarbon chains are in a " liquid state." (The large number of rotational isomers produced causes a smearing out of all the fine structure.) We can conclude that the soap is only prevented from completely melting by the strong bond between the highly polar sodium metal and carboxylate groups. The spectra clearly demonstrate the appearance of the " liquid-crystalline " phase of soaps. *X*-Ray data on this phase support this interpretation, since the long spacings are sharp whilst the short spacings are diffuse.

Little change is observed on further heating of the soap up to 200°, except that the bands at 719 and 695 cm.$^{-1}$ decrease further in intensity and the relative intensity of the 1460 and 1415 cm.$^{-1}$ bands alters. The 1415 cm.$^{-1}$ band then becomes of greater intensity.

On cooling of the soap all these spectral changes are observed in reverse order and all the fine detail in the spectra return.

Analogous spectral changes on heating sodium stearate are observed. These changes can obviously be correlated with the variation of other properties of the soaps at these temperatures, such as flow, yield, and mobility.[18] The increased cohesion and plasticity and fibre-forming properties observed above 110° are doubtless due to the fluidity of the hydrocarbon chains at this temperature.

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