A Comparative Study of the X-ray Diffraction Patterns and Thermal Transitions of Metal Soaps[1,2]

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X-RAY diffraction patterns at room temperature and differential heating curves between room temperature and about 200-250° C. have been obtained for a number of metal soaps of barium, calcium, and lithium. The purpose of this paper, besides reporting these data, is to point out the extent to which different soaps of the same cation behave similarly, in contrast with the highly individual behavior of soaps of different cations.

Some information as to the extent to which sodium soaps of different fatty acids exhibit similar polymorphic behavior, and also similar phase behavior with water is available. The present authors concluded on the basis of binary phase diagrams of anhydrous sodium soaps (8) and heats of transition (11) that at least some of the phases of sodium soaps from C_{12} to C_{26}, including saturated soaps and oleate, were isomorphous. Buerger, Smith, Ryer, and Spike (1), Mills (7), and Ferguson, Rosevear, and Stillman (2) have used x-ray diffraction patterns at room temperature to identify similar phases in different soap systems. McBain, Vold, and Jameson (6), and McBain, Elford, and Vold (5) have achieved a measure of success in correlating the phase behavior of mixed sodium soaps in water with that of the same soaps taken separately. The labor entailed in achieving an understanding of the phase behavior of soaps in oil would obviously be substantially lessened if a similar situation prevails with soaps of other cations.

It has been found already (3, 13) that the stearates and palmitates of the same metal exhibit very similar behavior. The present work extends these ideas to unsaturated soaps and soap mixtures, and lithium 12 hydroxy stearate. Two calcium resinates (abietic acids) were also investigated.

Experimental Part

Materials and Techniques: The soaps employed, and their origin or mode of preparation, are summarized in Table I. X-ray diffraction patterns were obtained at room temperature (ca. 25°C.) with a North American Philips Co. recording x-ray spectrometer as previously described (12). Differential heating curves were obtained using white mineral oil as a reference material in the calorimeter, also described elsewhere (9). The heating rate normally employed was 1.5 degrees per minute. Lack of perfect performance of the control system occasionally led to rates as high as 2 degrees per minute over portions of a run. A few runs were made at 0.5 degrees per minute, which rate leads to a lower sensitivity but assists in resolving successive close-lying transitions.

Results: X-ray diffraction patterns for the several soaps are presented in Figs. 1-5. Numerical values of the positions of the principal peaks and their rela-

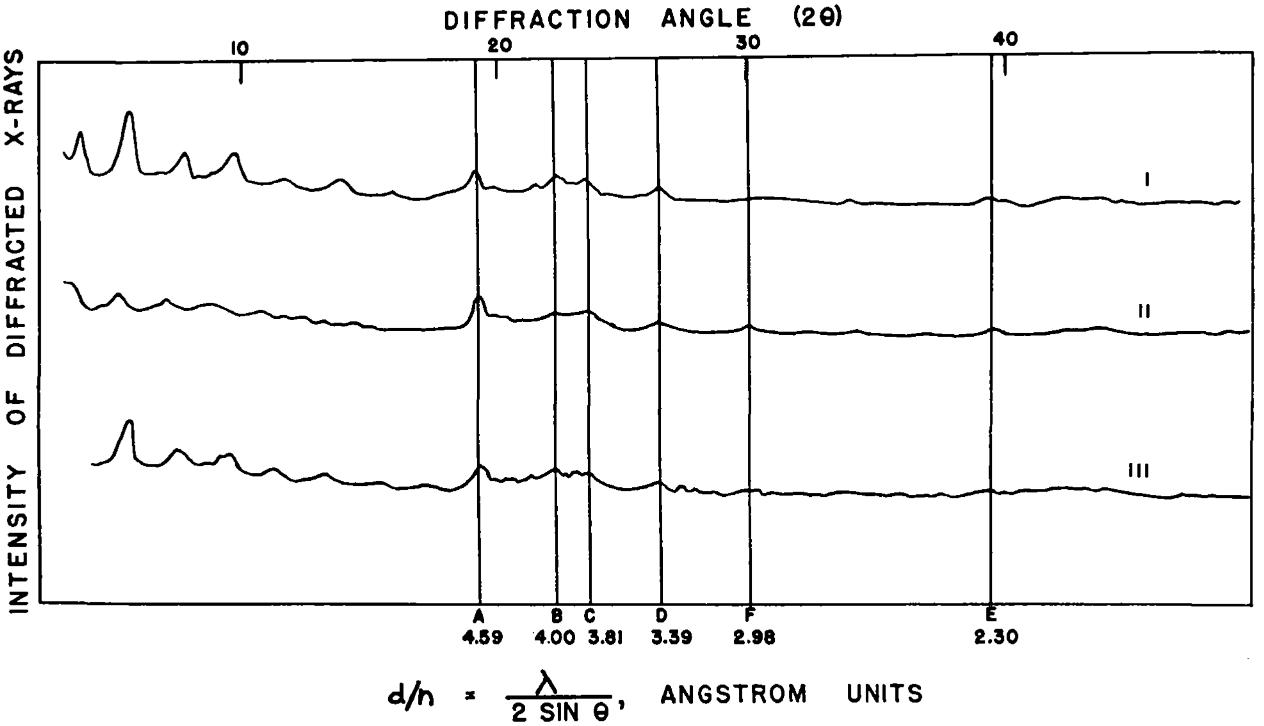

FIG. 1. X-ray Diffraction Patterns of Barium Soaps. I, Barium Palmitate; II, Barium Stearate; III, Barium "Tallowate." Lines A, B, C, D, E, and F are used to characterize the patterns and help distinguish them from those of other soaps.

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[2] Contribution from the Department of Chemistry, University of Southern California.

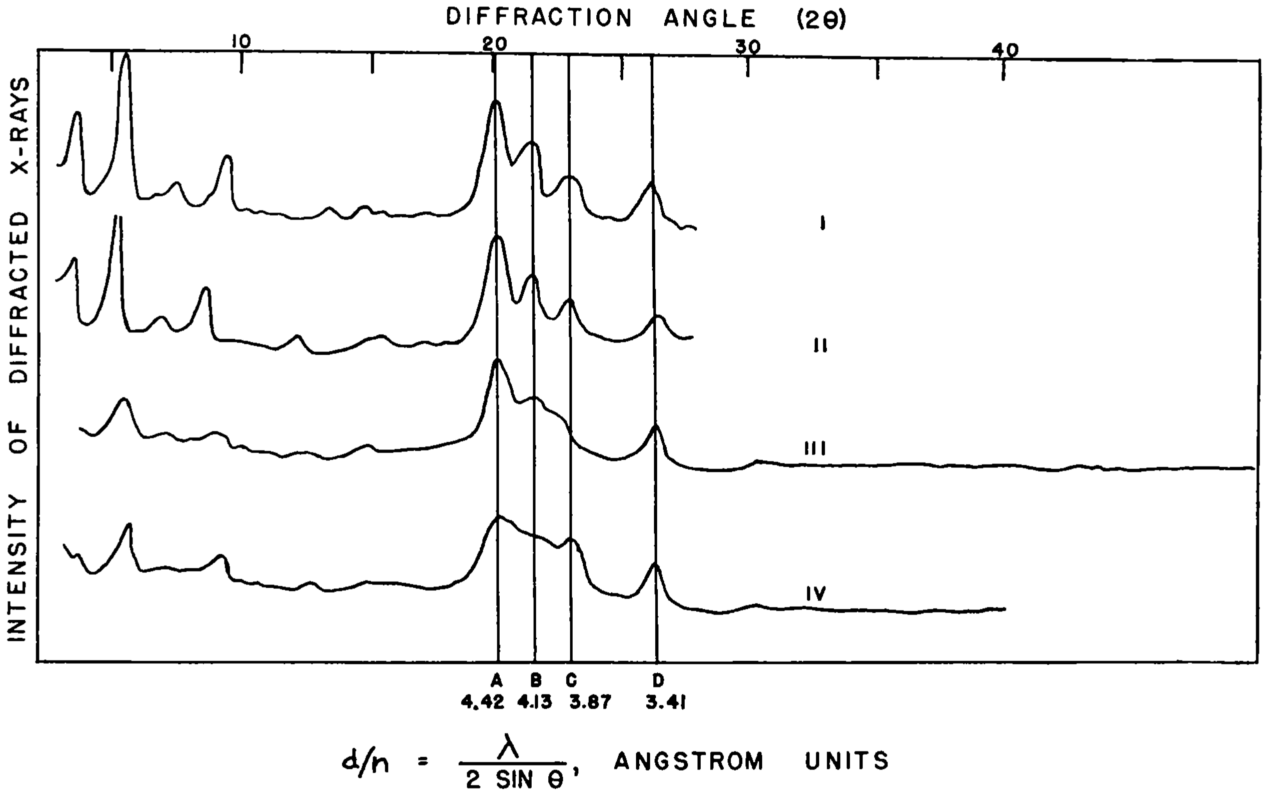

FIG. 2. X-ray Diffraction Patterns of Calcium Soap Hydrates. I, Calcium palmitate monohydrate; II, calcium stearate monohydrate; III, calcium "tallowate" monohydrate; IV, hydrated calcium oleate. Lines A, B, C, and D are used to characterize the patterns and help distinguish them from those of other groups.

tive intensities are summarized in Tables II and III. Repeated evaluations of the accuracy of the diffraction measurements have shown that for different samples of the same stock of soap, reproducibility is about ± 0.02° (in 2θ; the precision in Å varies with 2θ) in line position and about 5% in relative intensities. Data for independent preparations of soap are available for calcium and lithium stearates. The long spacings are more sensitive to purity of the stearic acid than are the short spacings. Variations up to 1-2 Å in position have been found in samples between whose short spacings differences of at most 0.02-0.03 Å occurred. The relative intensities vary enormously as between the long spacings and the short spacings. The effects are believed due to orientation of the crystallites in the sample mount of the instrument. Within the group of short spacings, however, the maximum variation in intensity in four independent samples was less than 10%.

Transition temperatures as obtained from differential heating curves are summarized in Table IV. Differential heating curves for the remainder are given in Fig. 6. The transition temperatures reported are derived from the experimental curves by backwards extrapolation of the steeply rising portion of a peak to its intersection with the (substantially) constant steady state differential temperature or base line. This procedure has been justified empirically by results obtained on materials of known melting point (9). The values given are probably correct to within ± 2-3°.

Calcium resinates were heated from room temperature to 250°C. without any transitions being discovered.

TABLE I

Source and Composition [a] of Metal Soaps

Soap	Source	Fatty Acid Composition
Barium Palmitate	Lab. Prep.[c]	Kahlbaum-Schering HP
Barium Stearate	Metasap Chem. Co.	Tech. Stearic Acid
Barium Tallowate	Lab. Prep.[b]	50% Tech. HOl; 30% HStr (Armour Neo-fat 1-65); 20% HP (Neo-fat 1-56)
Calcium Palmitate	Lab. Prep.[c]	Eastman HP (No. 1213)
Calcium Stearate	Lab. Prep.[c]	Eastman HStr (No. 402)
Calcium Oleate	Lab. Prep.[c]	Lab. prep. from Hormel Foundation 99½% pure methyl oleate
Calcium Tallowate	Lab. Prep.[c]	50% Tech. HOl; 30% HStr (Neo-fat 1-65); 20% HP (Neo fat 1-56)
Calcium Resinate(1)	Lab. Prep.[c]	Hercules Rosin "Staybelite"; di- and tetrahydro abietic acids
Calcium Resinate(2)	Lab. Prep.[c]	Hercules Resin 731, largely dehydro abietic acid; balance di- and tetrahydro abietic acid
Lithium Palmitate	Lab. Prep.[b]	Eastman HP (No. 1213)
Lithium Stearate	Lab. Prep.[b]	Lab. purified HStr from Neo-fat 1-65 by recrystallization from acetonitrile (10)
Lithium Tallowate	Lab. Prep.[b]	50% Tech. HOl; 30% HStr (Neo fat 1-65); 30% HP (Neo-fat 1-56)
Lithium 12-hydroxy-stearate	...............[d]	12-hydroxy-stearic acid

[a] The soaps were dried to constant weight at 110° before use, except for calcium oleate which was dried at 90° in vacuo and for calcium soap hydrates which were air dried at 50°C.

[b] Prepared as precipitates by neutralization of an ethanol solution of the fatty acids with an aqueous solution of the metallic hydroxide under carbonate-free conditions.

[c] Prepared by metathesis in aqueous alcohol from the corresponding sodium soap and calcium chloride (or barium chloride for BaP_2).

[d] Recovered from a commercial grease stated to contain this soap, by extraction of the oil with n-heptane.

TABLE II

X-ray Diffraction Patterns of Metal Soaps

A. Barium Soaps

Palmitate		Stearate		Tallowate		Oleate	
d/n, Å	(I/26)[a]	d/n, Å	(I/12)[a]	d/n, Å	(I/17)[a]		
43.5	(1.00)[b]	49.7	(.67)[b]	46.0	(1.00)[b]		
4.58	(0.39)	4.59	(1.0)	4.59	(.53)		
......	......	4.47	(.42)	4.41	(.18)		
4.42	(0.15)	4.40	(.42)	4.31	(.18)		
4.07	(0.19)	......	......	4.14	(.18)		
3.92	(0.27)	4.00	(.25)	3.99	(.24)		
......	......	3.81	(.50)	3.84	(.24)		
3.78	(.23)	......	......	3.78	(.18)		
3.38	(.19)	3.39	(.33)	3.39	(.18)		
......	......	......	......	3.28	(.12)		
2.93	(0.12)	2.98	(.17)	2.98	(.12)		
......	......	......	......	2.89	(.12)		
2.30	(0.12)	2.30	(.25)	2.30	(.12)		
2.14	(.08)	2.15	(.17)	......[e]	......		
......	......	2.09	(.17)	......[e]	......		

B. Calcium Soap Hydrates

d/n, Å	(I/55)	d/n, Å	(I/45)	d/n, Å	(I/31)	d/n, Å	(I/21)
45.8	(1.00)[b]	49.5	(1.00)[b]	47.0	(.48)[c]	47.0	(.95)
4.41	(.80)	4.41	(.87)	4.41	(1.00)	4.42	(1.00)
4.13	(.49)	4.14	(.53)	4.14	(.39)	4.23	(.71)
3.87	(.31)	3.88	(.31)	3.96	(.16)	4.05	(.67)
......	......	3.74	(.04)	......	......	3.86	(.90)
3.41	(.27)	3.41	(.22)	3.41	(.45)	3.43	(.81)
not run	......	not run	......	2.94	(.10)	2.98	(.10)
not run	......	not run	......	2.85	(.07)	......	......

C. Anhydrous Calcium Soaps

d/n, Å	(I/67)[a]	d/n, Å	(I/25)[a]	d/n, Å	(I/38)[a]	d/n, Å	(I/21)[a]
45.5	(.51)[b]	50.4	(.38)[b]	47.5	(.42)[b]	46.6	(.43)[b]
......	......	......	......	4.45	(1.00)	4.51	(.43)
4.10	(1.00)	4.13	(1.00)	4.18	(.58)	{ 4.28[d]	(1.00)
3.92	(.13)	3.96	(.16)	3.98	(.37)	{ 4.16	......
3.67	(.31)	3.73	(.24)	......	......	......	......
3.37	(.06)	3.55	(.08)	3.42	(.37)	3.44	(.29)
2.92	(.03)	......	......	2.94	(.05)	2.98	(.10)
2.49	(.07)	2.48	(.08)	......	......	......	......
2.37	(.03)	2.35	(.08)	......	......	......	......
......	......	2.22	(.12)	......	......	......	......
......	......	2.13	(.12)	......	......	......	......

D. Lithium Soaps

						(12-hydroxy-stearate)	
d/n, Å	(I/114)[a]	d/n, Å	(I/69)[a]	d/n, Å	(I/63)[a]	d/n, Å	(I/114)[a]
36.5	(1.00)[b]	41.8	(1.00)[b]	41.25	(.38)[b]	46.52	(.28)[b]
4.27	(.11)	4.26	(.25)	4.27	(1.0)	4.24	(1.00)
4.14	(.08)	4.19	(.22)	......	......[f]	......	......[f]
4.01	(.12)	4.04	(.70)	4.04	(.14)	......	......[g]
3.82	(ca.0)	3.86	(.07)	3.95	(.16)	3.96	(.09)[g]
3.61	(.12)	3.63	(.51)	3.76	(.37)	3.77	(.28)
......	......	......	......	3.58	(.35)	......	......
......	......[h]	3.42	(.03)	3.38	(.06)	3.57	(.07)
3.22	(.02)	3.24	(.07)	3.25	(.03)	......	......
......	......	......	......	2.98	(.05)	......	......
......	......	2.49	(.10)	2.87	(.03)	2.48	(.06)
......	......	......	......	2.60	(.05)	......	......
2.37	(.03)	2.35	(.07)	2.49	(.11)	......	......
......	......	......	......	2.37	(.03)	......	......
2.26	(.07)	2.27	(.19)	2.28	(.08)	2.28	(.07)
......	......	2.19	(.04)	2.19	(.03)	......	......
2.13	(.22)	2.13	(.03)	2.12	(.03)	2.24	(.02)
......	......	2.10	(.09)	......	......	......	......
2.08	(.16)	2.04	(.04)	2.10	(.03)	......	......
2.01	(.10)	2.01	(.07)	2.03	(.05)	......	......
1.96	(.06)	......	......	......	......	......	......

[a] Values shown are ratios of the height of the given peak above the background scattering to the height of the most intense peak in the given pattern expressed in scale units where 100 corresponds to full scale deflection on the recorder.

[b] The value of the long spacing is calculated as a mean of several orders. I/I_0 is that of the third order peak.

[c] An additional weak long spacing of 51.00 Å was present, possibly due to separate crystallization of different components of the soap.

[d] The two halos could not be well resolved. I/I_0 is given for the unresolved pair, to which each is contributing about 1/2.

[e] Barium tallowate exhibits unresolved lines in the region of d/n 2.01-2.25 Å.

[f] These two lithium soaps may well have a diffraction maximum near 4.15-4.18 Å but it is not resolvable from the intense peak at 4.27 Å.

[g] The line at 3.96 may be more closely related to those of the other soaps at 4.01-4.04 than to those at 3.82-3.95, on the basis of intensity relations.

[h] Lithium palmitate may well have a diffraction maximum near 3.4 Å, but it is too weak to report positively.

TABLE III

X-ray Diffraction Patterns[a] of Rosin and Calcium Resinates

Staybelite Rosin		Resin 731		Calcium Resinate (from Staybelite)		Calcium Resinate (from Resin 731)	
d/n, Å	(I/84)[b]	d/n, Å	(I/36)[b]	d/n, Å	(I/12)[b]	d/n, Å	(I/18)[b]
8.82	(.47)	......	......	20.22	(.33)	19.21	(.61)
7.35	(.20)	......	......	14.47	(.50)	16.93	(.22)
6.43	(.95)	......	......	6.29	(1.00)	5.96	(1.00)[d]
5.69	(.56)	5.72	(1.00)[c]	5.51	(.75)	......	......
5.32	(1.00)	......	......	......	......	......	......
4.78	(.56)	......	......	......	......	......	......
4.33	(.35)	......	......	......	......	......	......
4.11	(.36)	......	......	......	......	......	......
3.84	(.24)	......	......	......	......	......	......

[a] Only lines of $I/I_0 > 0.2$ have been tabulated. Additional lines, particularly for Staybelite Rosin, can be seen from Fig. 5.

[b] Reported as the ratio of the height of the given peak above the background intensity to that of the most intense peak in the given pattern expressed in scale units.

[c] Very wide halo. An additional composite of unresolved lines is evident in the region of 2θ between 4 and 10°.

[d] Very wide halo.

Discussion

X-ray Diffraction Patterns: Vold and Hattiangdi (13) suggested that the diffraction patterns of metal palmitates and stearates were sufficiently characteristic to permit identification of the cation without necessarily having information as to the nature of the anion. For barium soaps and calcium soap hydrates the inclusion of 50% oleate to form a mixed soap approximating the composition of tallow soaps in no way vitiates this scheme. Even pure hydrated calcium oleate[3] yields a rather similar pattern.

Calcium soap hydrates undergo an appreciable change in crystal form upon dehydration (cf. curves I and II of Figs. 2 and 3) only when extremely pure (10). When it occurs, this change appears to be identical for palmitates and stearates.

Lithium palmitate and stearate have almost identical diffraction patterns at room temperature. However both lithium tallowate and lithium hydroxy stearate exhibit larger variations. The position of the most intense short spacing (line B, Fig. 4) is nearly

TABLE IV

Transition Temperatures of Metal Soaps[a] (°C.)

Cation	Anion			
Barium	Palmitate 130[3]	Stearate 136[3]	Tallowate 102[e]	Oleate not studied
Calcium (Soap hydrate)	not studied	123[10, 12, c]	96[c, e]	60 83
Calcium (Dry soap)	106[3, b] (147)[d]	86[12] 123 (150)[d] 195	75(?)[e]	49
Lithium	101[14] 191 223	113 185 224	88 155 196	12-hydroxy-stearate[f] absent 179 218

[a] Where indicated by reference numbers, data to fill out this table have been taken from prior publications of the authors.

[b] The palmitic acid from which this sample was prepared is of poor quality. Comparable overlapping of the transitions at 86 and 123° has been found for technical calcium stearates (3).

[c] Very large heat effect. Some samples of calcium stearate hydrate also exhibit a transition of the second kind at 48°, as do samples of dry soap prepared therefrom (but at 65°).

[d] Very small heat effect.

[e] In all the tallowates, heat absorption occurs at this transition over a wide temperature range, as is evident from Fig. 6 on which the temperatures, where the transition begins, is marked as well as the temperatures at which heat absorption has become rapid. The latter are the temperatures reported in the table.

[f] The small inflection (not designated by an arrow) on Fig. 6 for this soap occurs at 129°. It appears to be an artifact arising from a departure of the heating rate from its controlled value.

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[3] Reports differ (4, 10) as to whether calcium oleate forms a monohydrate or a dihydrate. This sample contained 2.23% H_2O, not quite sufficient for the monohydrate.

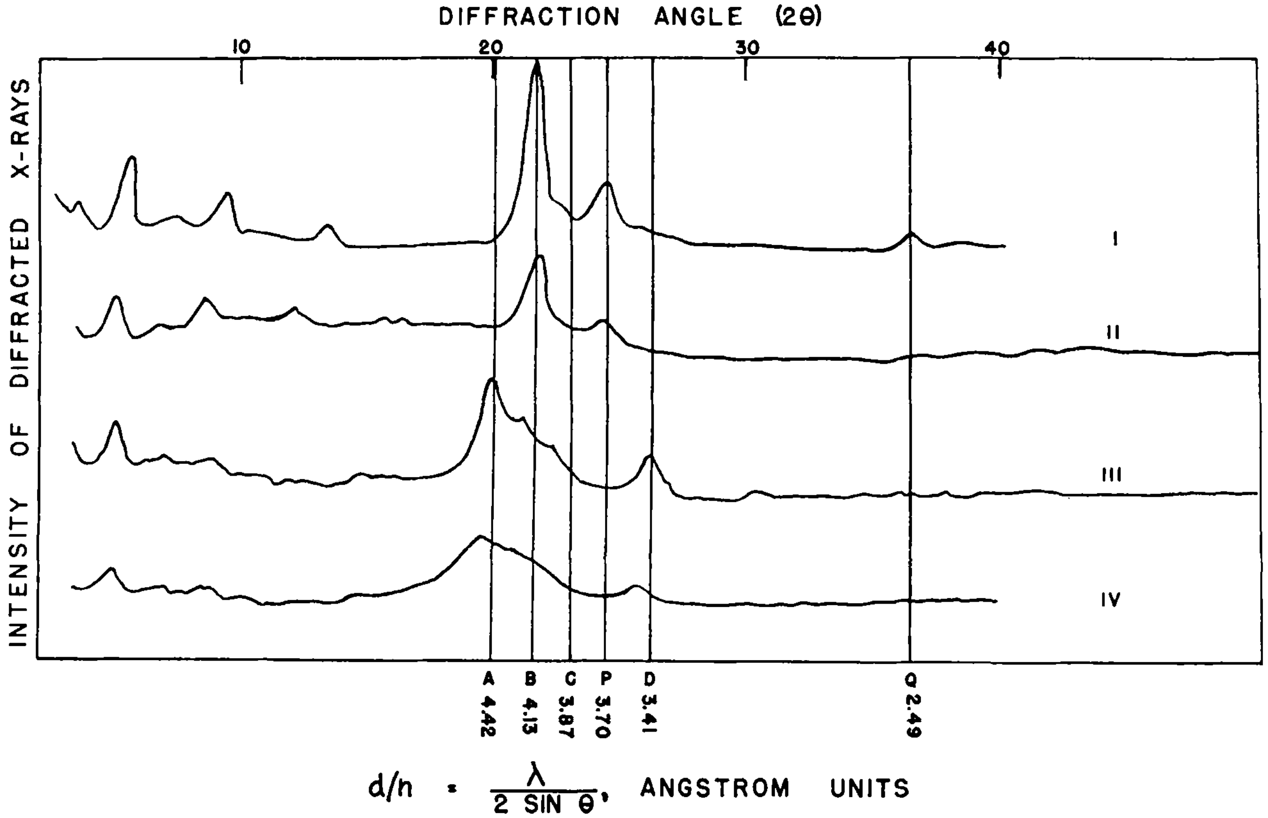


FIG. 3. X-ray Diffraction Patterns of Anhydrous Calcium Soaps. I. Calcium palmitate; II, calcium stearate; III, calcium "tallowate," IV, calcium oleate. Lines B, P, and Q serve to emphasize the close similarity of curves I and II. Lines A, B, C, and D are those used to characterize the patterns of calcium soap hydrates. It is seen that calcium tallowate and oleate retain the structure of the hydrate after drying but with slight displacement and appreciable broadening of the lines.

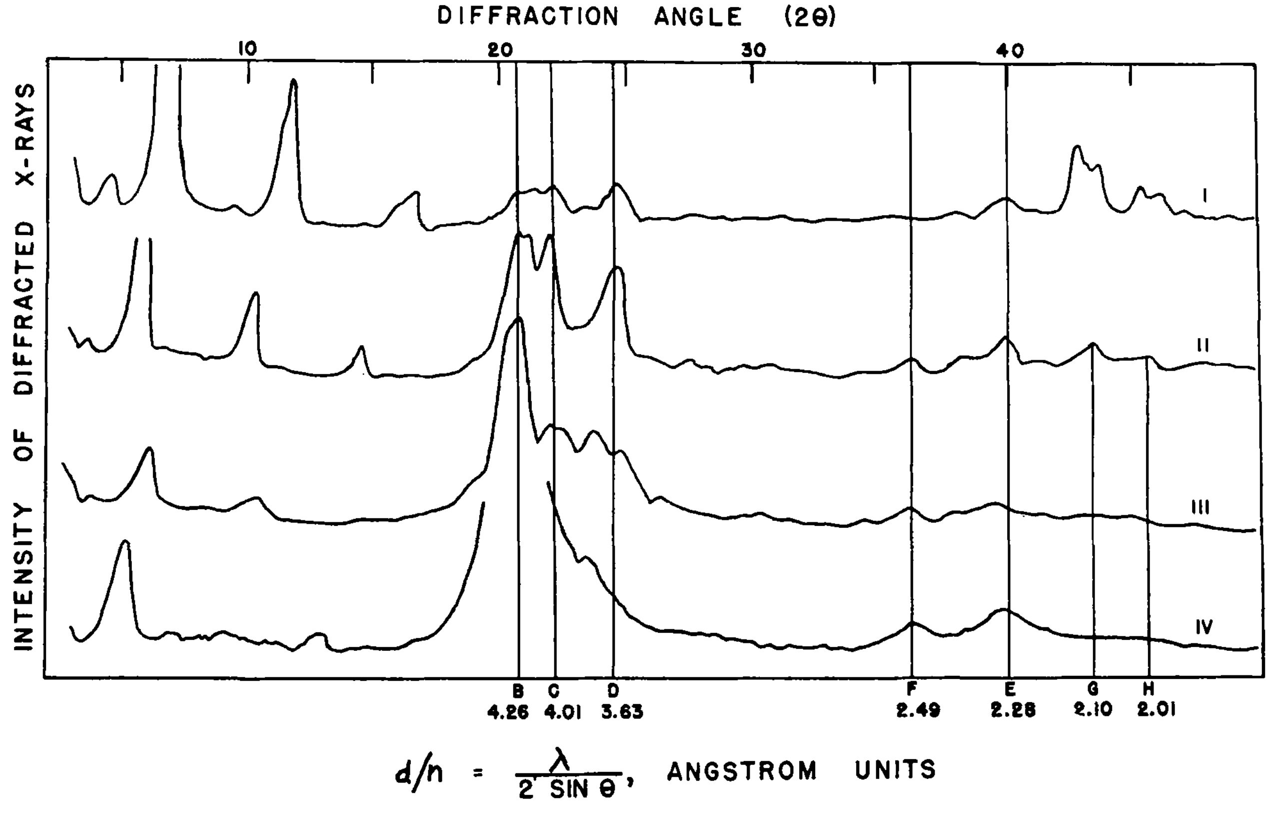


FIG. 4. X-ray Diffraction Patterns of Lithium Soaps. I, Lithium palmitate; II, lithium stearate; III, lithium "tallowate"; IV, lithium 12-hydroxy-stearate. Lines B, C, D, E, F, G, and H are used to characterize the patterns and help distinguish them from those of other soaps.

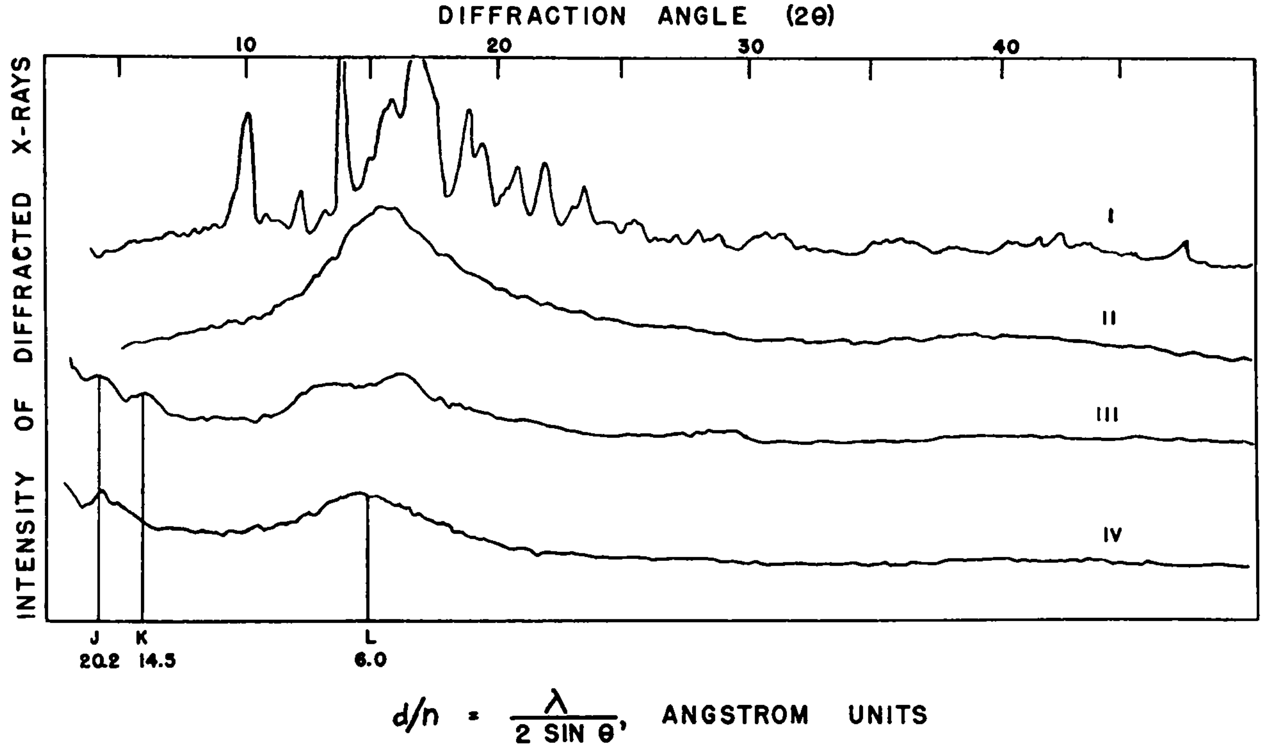


FIG. 5. X-ray Diffraction Patterns of Treated Rosins and of Calcium Resinates. I, Staybelite Rosin (hydrogenated), di- and tetrahydro abietic acids; II, Resin 731 (dehydrogenated, disproportionated), dihydro abietic acid; III, calcium Staybelite resinate; IV, calcium 731 resinate. Lines J and K (for the calcium resinates) correspond to diffraction maxima at much greater values of d/n than any found for the rosins. L, at a value of d/n of 6 Å, corresponds to a region of marked diffraction for all four materials though the degree of resolution is widely variant among them.

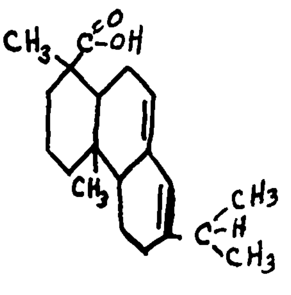
the same for all four, but that of the next most intense (line D) is shifted to an appreciably larger value (3.62→3.77) in going from the normal hydrocarbon chain to the geometrically less uniform unsaturated or hydroxylated chain. Likewise, several prominent diffraction bands in the region of 2 Å in the patterns of the stearate and palmitate are missing from the patterns of the tallowate and hydroxystearate. Nevertheless the points of similarity between the patterns of the four lithium soaps are sufficient to differentiate them as a class distinct from the patterns of soaps of other cations.

The degree of similarity existing between the diffraction patterns of soaps of the same cation in contrast with the differences between patterns of soaps of different cations suggests that the relative orientation of carboxylate groups and metal ions is not markedly affected by the tendency of hydrocarbon chains of varying length or even chemical character (i.e. unsaturated, hydroxylated) to pack together in different ways.

The "long" spacing can be interpreted as the effective length of a repeating unit consisting of two fatty acid ions and associated cations times the sine of the angle of inclination of the chain axis to the planes containing the cations. The difference in chain length between palmitate and stearate is 5.08 Å (for two ions). The differences in long spacing to be expected are less than this by a factor depending on the angle of tilt. Comparison of these values with the observed differences shows that even for palmitates and stearates with otherwise nearly identical patterns the angle of tip of the chains cannot be identical.

The long spacing of the lithium soaps is significantly shorter than for calcium or barium soaps. However it is interesting to observe that this spacing for lithium hydroxy stearate is considerably larger than for other soaps, possibly due to the influence of strong Van der Waal forces between the hydroxyl groups forcing a more nearly perpendicular orientation of the chains.

The apparent absence of a long spacing in either of the rosins (mixed acids of geometry similar to abietic acid):



is not surprising, in view of the fact that the tendency of the carboxyl group to dimerize is opposed by the difficulty of securing an efficient packing of the balance of the molecule on a "head" to "head" basis. However, large values of d/n are found for the calcium resinates which suggests a head to head arrangement. The difficulty of packing the molecules together is possibly the source of the lack of definition in the diffraction patterns of calcium resinates, even the one made from a hydrogenated crystalline rosin. The absence of polymorphic transitions in calcium resinate may also be due to the fact that the irregular abietate ions are interlocked in the solid and cannot readily slip by each other to assume new configurations.

Thermal Transitions: It does not follow that because the crystal structure of different soaps is closely related at room temperature, being pre-determined more cogently within limits by the cation than by the anion, that the different soaps will exhibit similar sets of polymorphic transitions as they are heated.

Although the close similarity in behavior between palmitates and stearates has already been pointed out (3), gross divergence in behavior is found when unsaturated soaps are considered. Calcium oleate absorbs heat at 49°, and only the single transition is observed whereas calcium stearate undergoes a sequence of four transitions in the temperature interval between 25 and 200°C.

The calcium and barium mixed soaps, approximating natural tallowates in composition, show the effect of their 50% content of oleate in that there is but one extremely unsharp transition for each in the range between room temperature and 200°C., and this is at a considerably lower temperature than any of the major transitions of the saturated soaps. The behavior indicates that mixed crystals are formed; otherwise the separate transitions appropriate to the individual components would be found.

It is interesting to note that the transition of lithium palmitate at 101° and lithium stearate at 113° is absent for lithium 12-hydroxy-stearate. Possibly at this temperature the amplitude of thermal motions is insufficient to permit rearrangement of the hydroxylated chains which might be expected to be more firmly bonded to each other through the polar hydroxyl groups. At higher temperatures, where the soaps pass into a soft wax-like state (191° for the palmitate, 185° for the stearate, and 179° for the 12-hydroxy-stearate) the magnitude of the heat absorption for the latter appears from qualitative observation of the differential heating curves to be substantially greater than for the saturated soaps.

In contrast with the calcium and barium soaps, lithium tallowate has a thermal behavior much like that of the palmitate and stearate, but again with markedly lowered temperatures for each of the transitions.

Acknowledgment

The authors wish to thank G. S. Hattiangdi for the determination of some of the x-ray diffraction patterns presented in this paper.

Summary

X-ray diffraction patterns at room temperature for soaps of barium, calcium, and lithium were found to be characteristic for different soaps of the same cation. This is true not only for palmitates and stearates but also (with minor variations) for mixed soaps containing up to at least 50% oleate, for pure calcium oleate, and even for lithium 12-hydroxy-stearate.

Soaps of the same cation in mixtures approximating the composition of natural tallow fatty acids appear to form mixed crystals. The succession of phases formed on heating shows strongly the influence of the oleate in the mixture.

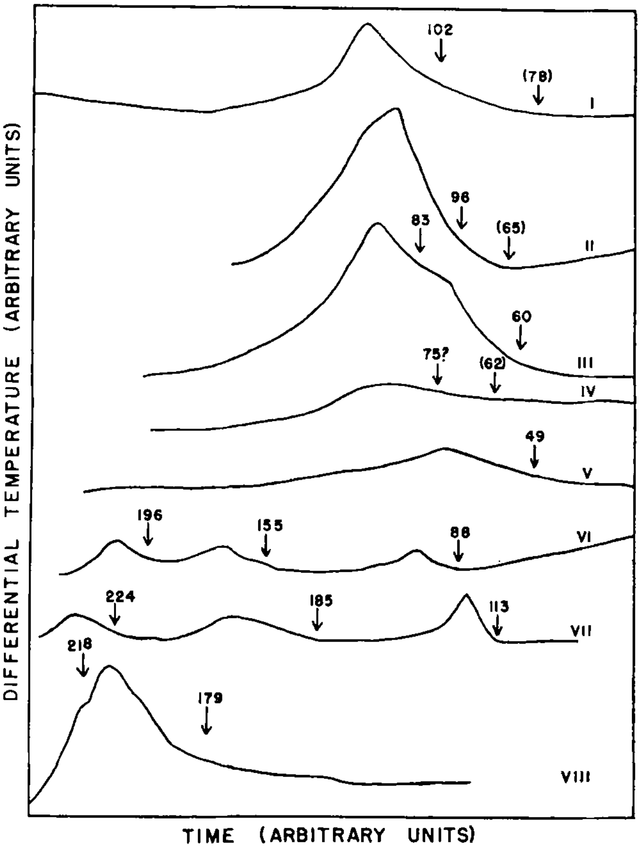


FIG. 6. Differential Heating Curves of Metal Soaps. Numbers on the curves are the temperatures of the sample at the times indicated by the arrows. These are the transition temperatures reported in Table IV, except for those in parentheses which show temperatures where slow heat absorption actually begins in contrast with the extrapolated transition temperatures. Varying rates of heating make it impossible to align the several curves exactly. This is particularly true for curve VII, run at only 0.5 deg./min. I, Barium "tallowate"; II, calcium "tallowate" hydrate; III, hydrated calcium oleate; IV, anhydrous calcium "tallowate"; V, anhydrous calcium oleate; VI, lithium "tallowate"; VII, lithium stearate; VIII, lithium 12-hydroxy-stearate.

Calcium resinates appear to crystallize imperfectly but definitely with a "head to head" arrangement of the abietate radicals in contrast to the acids which give evidence of a head to tail arrangement.

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