TECHNICAL

Thermal Behavior of Prospective Hydroxy Acid Grease Thickeners

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Melting points and heats of fusion were determined for 13 hydroxy acids and their lithium salts with chain lengths ranging from 14 to 24 carbons. Included were hydroxy acids prepared from two unusual plant sources, *Lesquerella* sp. and *Crambe abyssinica*. Upper melting point temperatures, transition entropies, and heat capacity changes of the lithium salts on heating and cooling suggest that many of the salts, particularly those of 14-hydroxyeicosanoic and 9(10)-hydroxystearic acids, would perform satisfactorily as gelling agents in the production of lubricating greases.

KEY WORDS: Differential scanning calorimetry, entropy, heat capacity, hydroxy acids, lithium salts, lubricating grease, melting point.

Each year nearly 50,000 metric tons (MT) of ricinoleic acid enter U.S. commerce as castor oil, which is generally imported at prices higher than those for common domestic vegetable oils. This statistic seems an extraordinary tribute to the chemical functionality of a hydroxy fatty acid. The fact that such utility is stymied from time to time by market vagaries that distort the price/supply of castor oil would seem sufficient reason to consider more dependable domestic alternatives that can deliver cost-performance advantages comparable to those provided by ricinoleic acid.

Chemical hydroxylation and microbial modification (1) of unsaturated fatty acids or development of other hydroxy acid-bearing plants (2) are possible, though currently less than fully exploited, routes to hydroxy acids. Much information on alternative hydroxy acids and knowledge of their effectiveness is needed to identify competitive chemical preparations or new crops and justify development of economical large scale production.

Accordingly, our studies focused on the thermal behavior of hydroxy acids and their lithium salts because this property is critical to the major use of hydroxy acid salts as thickening agents in gelled lubricants. For practical reasons, we intentionally examined isomeric mixtures that result from chemical hydroxylation of specific acids, and we have compared the properties of these mixtures with those of 12-hydroxystearic acid, one of the most widely used grease thickeners (3).

In addition, our studies included a comparison of hydroxy acids derived from the oil of *Crambe abyssinica* (4) with 14-hydroxyeicosanoic acid made by reducing a 20-carbon ricinoleic acid homolog that occurs in the oil of *Lesquerella* (5). These two unusual seed oils are of interest because they represent potential domestic replacements for materials that are obtained largely through imports. Others (6–8) have characterized alkali metal salts of unsubstituted fatty acids, which also can serve as grease thickeners.

EXPERIMENTAL PROCEDURES

Hydroxy acids were obtained from Nu-Chek-Prep (Elysian, MN) with the exception of 12-hydroxystearic acid (Eastman Kodak, Rochester, NY), the 14-hydroxyeicosanoic acid, and the hydroxylated *Crambe abyssinica* acids. The hydroxylated crambe acids and one of the 13(14)-hydroxydocosanoic acid samples, identified by (M), were prepared in this laboratory by Miwa and co-workers (unpublished information). The 12-hydroxystearic acid, recrystallized from n-hexane, was more than 99% pure by gas chromatography (GC). Other commercial acids, 99% pure with respect to chain length, were purified no further. Stearic acid was from the Hormel Institute (Austin, MN).

14-Hydroxyeicosanoic acid was prepared by hydrazine reduction (9,10) of the unsaturated hydroxy acid, lesquerolic acid (5), and the saturated acid was purified by preparative thin-layer chromatography of the methyl ester on Silica Gel 60 F-254 precoated plates (EM Laboratories, Inc., Elmsford, NY) in hexane/ether (70:30).

Lithium salts were prepared by dissolving approximately 25 mg of acid in 0.5 mL of 95% ethanol and adding a 30% excess of LiOH and 4 mL of water. Warming the mixture on a steam bath for several minutes facilitated salt formation. Salts of acids containing more than 18 carbon atoms were isolated by filtration and washed with hexane and water. The 14 and 16 carbon salts were extracted into hot ethanol after the reaction mixture was evaporated to dryness.

Several samples were analyzed by GC-MS (mass spectrometry) through a Packard 7401 gas chromatograph equipped with a 1.22 m × 3.2 mm glass column packed with 3% Silar 5CP, 80-100 mesh, and attached to a CEC 21-492-1 mass spectrometer (Dupont Instruments Corp., Boston, MA).

Differential scanning calorimetry (DSC) was as described (11). Indium, tin (Perkin Elmer Co., Norwalk, CT), and standards melting at 217 and 244°C (Arthur H. Thomas Co., Swedesboro, NJ) were used to extend the upper range of the melting point calibration curves. Heats of fusion (ΔH_f) of lithium salts were determined (11) on fused and resolidified samples and, when possible, on solvent crystallized material, but they were not determined for scans showing unusual baseline shifts at the melting transition. Where baseline shifts were not excessive or unusual, the procedure of Guttman and Glynn (12) was used for baseline interpretation. For acids, ΔH_fs were determined on samples as received or after crystallization from hexane; endotherm areas were combined in calculating ΔH_fs for samples exhibiting multiple endotherms. Scan speeds for ΔH_f runs were either 2.5 or 10°C/min. Before measuring ΔH_f, attempts were made to trap each sample in a single form by conditioning at various temperatures. Where this was not possible, scans that had the least number of forms were used for ΔH_f

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[1] The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

measurements. The major form contributing to a measurement, therefore, was not always the highest melting.

Baseline shifts reflecting heat capacity changes upon melting or freezing were determined as the difference between extrapolated baselines at the transition. These shifts were measured in millicalories/sec. using range 8, and were converted subsequently to cal/deg mole.

RESULTS

Nomenclature. For convenience, sample nomenclature was abbreviated according to the acid's most distinguishing features; i.e., position of hydroxyl group and chain length. For example, 12-hydroxystearic acid is identified as 12-OH-18 and its lithium salt as Li-12-OH-18.

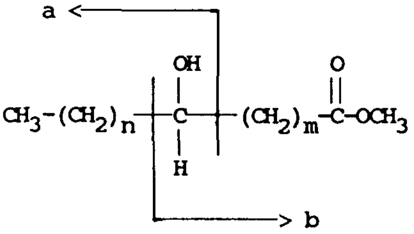
Examples of GC-MS data for the hydroxy acids used in this study are given in Table 1. Similar ion masses allowed comparisons of intensities to estimate concentrations of components. Results for four of the samples show approximately the same intensity for ion pairs that arise from hydroxyl groups on adjacent carbon atoms. The commercial acids generally were essentially 50:50 or 60:40 mixtures of isomers and are so identified by including both hydroxyl positions in the name—i.e., 9(10)-OH-14. The data for 12-OH-18, however, show only 0.5% of 11-OH-18. The 12-OH-18, as well as the 14-OH-20 from *Lesquerella* (13), were relatively pure positional isomers.

Melting points. Melting point data on the hydroxy acids and their lithium salts are summarized in Table 2. Representative DSC scans for six of the lithium salts appear in Figure 1. The highest melting endotherm for each sample is designated as Form I and each successive form represents a lower melting temperature. The multiple forms of the commercial samples possibly reflect the fact that these acids and their salts are mixtures. The 12-OH-18 and 14-OH-20 acids, which represent single positional and stereochemical structures, each had one form and their lithium salts three or less forms. It is surprising, however, that the 9(10)-OH-18 and 6(7)-OH-18 acids, known mixtures, also gave relatively simple melting curves. Similarly, the 9(10),12(13)-diOH-18 acid, theoretically 16 different isomers, and the OH-crambe acids, a mixture of chain lengths as well as positional isomers, exhibited only six endotherms, no more than the 11(12)-OH-20 and even fewer than the 15(16)-OH-24 acids. The 13(14)-OH-22 samples provide an equally interesting contrast, but in this instance melting points and thermodynamic properties are consistent with the fact that 13(14)-OH-22 (M) contained a slightly different ratio of isomers than the commercial sample (Table 1).

Some thermograms of the lithium salts contained more endotherms than did those of the acids, others were less complex (Table 2). Nine of the salts, however, exhibited at least one form that appeared only in melt scans of solvent crystallized material. Only one acid, the OH-crambe, behaved this way.

TABLE 1

GC-MS Data on Selected Hydroxy Fatty Acid Methyl Esters



		Mass		Intensity			
n	m	a	b	a	b	b-32	Compound
4	7	101	187	2556	851	5558	9-OH-14
3	8	87	201	10000	568	4426	10-OH-14
6	7	129	187	1793	686	4959	9-OH-16
5	8	115	201	2121	543	2531	10-OH-16
6	9	129	215	952	28	47	11-OH-18
5	10	115	229	1192	3825	10000	12-OH-18
8	11	157	243	635	678	1534	13-OH-22
7	12	143	257	1976	321	1070	14-OH-22
8	11	157	243	1873	3263	7533	13-OH-22 (M)
7	12	143	257	5438	2241	6158	14-OH-22 (M)

TABLE 2

Melting Data on Hydroxy Acids and Their Lithium Salts

	Acid (C)							Salt (C)					
Compound	VII	VI	V	IV	III	II	I	VI	V	IV	III	II	I
9(10)-OH-14				42	49	56	62^{a}		195	206	213	218^{a}	228^{b}
9(10)-OH-16			43	52	56	64	69^{a}			187	195	207^{a}	209^{b}
6(7)-OH-18					60	67	74^{a}	187	191	195	197^{a}	201^{a}	208^{b}
9(10)-OH-18						78	82^{a}				202	209^{a}	218^{a}
11(12)-OH-18			56	62	68	74	78^{a}		186	195	200	205	216^{a}
12-OH-18							84					218^{a}	220^{a}
9(10),12(13)-diOH-18		48	56	59	64^{a}	68	72			205	210	217^{a}	222^{a}
11(12)-OH-20		56	64	69	72	75	78^{a}		185	191^{a}	200^{b}	205	214^{a}
14-OH-20							89				174^{a,b}	209^{a}	215^{a}
13(14)-OH-22	52	63	69	76	79	84	89			186	192^{a}	202^{b}	213^{a}
13(14)-OH-22 (M)					81	87	92^{a}				197^{a}	208^{b}	217^{a}
15(16)-OH-24	69	74	77	80	84	88^{a}	91			176	185^{a}	195^{b}	210^{a}
OH-crambe		56^{a}	60^{b}	63	67^{a}	70^{a}	74^{b}			187	193^{a}	203^{b}	213^{a}
18							71			119^{a}	122^{a}	204^{a}	228^{a}

[a] Major form(s) in ΔH_f determination, minor amounts of others may be present.

[b] Form observed only with solvent crystallized material.

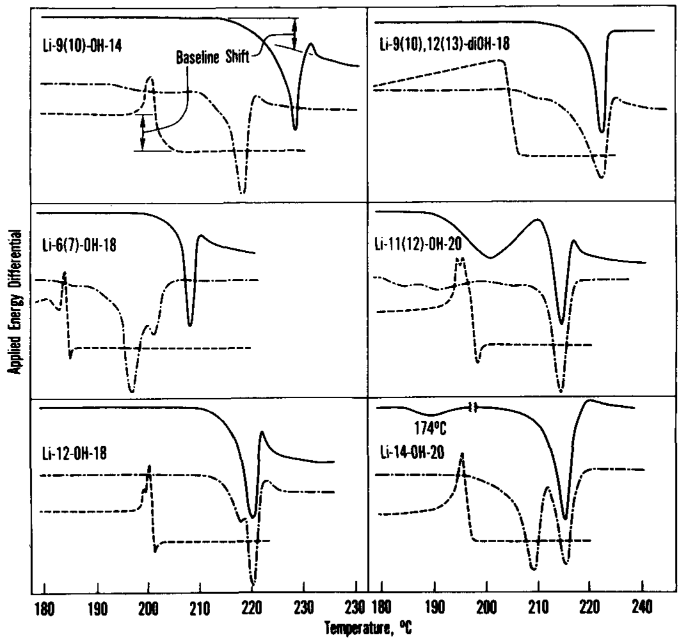


FIG. 1. Typical DSC heating and cooling scans of lithium salts with endotherms shown as negative peaks; ——, 10°C/min heating scans of solvent crystallized material; – – –, 0.624 °C/min cooling scans; –·–, 10°C/min heating scans after slow cooling except for Li-12-OH-18, 2.5°C/min.

With the acids, Form I melting points were distributed over a range from 62 to 92°C, and as expected they tended to increase with increasing molecular weight. Most of the salts, however, melted within a narrower range, around 210°C, regardless of molecular weight.

Although literature data are sparse on the thermal behavior of hydroxy acids and their alkali salts (14), several publications describe the behavior of alkali salts of saturated fatty acids (6–8). Lithium stearate was included in the present study to relate to such work on simple alkyl gel-forming salts. Our data corroborate those of Sakurai *et al.* (15), who reported three phase transitions in Li-18 at 112, 202, and 228°C; but we found the lowest melting transition from the original melt scan to be broad and flat-topped, suggesting the presence of two forms. On reheating after solidification, the endotherm again appeared in the same temperature region but was symmetrical, as is typical of a single form. Four polymorphic forms of Li-16 have been identified by microscopic observation, DSC and X-ray diffraction as a function of temperature (16).

Heats of fusion. Significant base line shifts at phase transitions often occurred in melt scans of the hydroxy acids and their lithium salts. With the acids, these shifts generally indicated a simple change in heat capacity like that shown in the original melt scan for Li-9(10),12(13)-diOH-18 (Fig. 1). Values for ΔH_f in such scans were easily corrected according to Guttman and Flynn (12) and then converted to molar heats of fusion given in Table 3 for the acids. Similar treatment of data from initial scans of solvent crystallized lithium salts was often precluded, however, by small exothermic peaks that followed the melt endotherms. For example, see scans for Li-9(10)-OH-14 and others in Figure 1. Values reported for the salts (Table 3) were, therefore, taken from heating scans on cooled melts, which usually evidenced shifts between stable heat capacities even though they generally showed more than one polymorphic form.

Specific heats of fusion for the mono-hydroxy fatty acids fell within a rather narrow range, 34–43 cal/g, with a single exception, 13(14)-OH-22 (M), which fell near 50 cal/g. Without exception, those for the salts distributed only a little more broadly, at 18–30 cal/g. Major structural variants or mixture (e.g., stearic acid, 9(10),12(13)-diOH-18, and OH-crambe) exhibited specific heats of

TABLE 3

Heats and Entropies of Fusion of Hydroxy Acids and Their Lithium Salts

Compound	ΔH_f		ΔS_f[a]	Compound	ΔH_f		ΔS_f[a]
	cal/mole	cal/g	cal/deg mole		cal/mole	cal/g	cal/deg mole
13(14)-OH-22 (M)	17,800	49.9	48.7	Li-14-OH-20	9200	27.4	18.8
13(14)-OH-22	15,400	43.3	42.6	Li-12-OH-18	9200	29.9	18.6
15(16)-OH-24	15,300	39.8	42.4	Li-18	9200[b]	31.8[b]	18.4
18	14,300	50.4	41.7	Li-9(10)-OH-18	8700	28.4	17.7
11(12)-OH-20	13,600	41.3	38.7	Li-6(7)-OH-18	8000	26.0	16.8
14-OH-20	13,600	41.4	37.6	Li-13(14)-OH-22 (M)	8000	22.2	16.4
9(10)-OH-18	12,700	42.3	35.8	Li-13(14)-OH-22	7500	20.6	15.4
6(7)-OH-18	12,400	41.2	35.7	Li-15(16)-OH-24	7000	18.0	14.5
11(12)-OH-18	11,000	36.9	31.6	Li-OH-crambe	7000[c]	19.4[d]	14.4
9(10)-OH-16	10,700	39.4	31.4	Li-11(12)-OH-20	6900	20.6	14.1
12-OH-18	10,300	34.2	28.8	Li-11(12)-OH-18	6700	21.8	13.7
9(10)-OH-14	8,800	38.6	26.3	Li-9(10)-OH-16	6500	23.3	13.5
9(10),12(13)-diOH-18	8,300	26.1	24.5	Li-9(10)-OH-14	5500	23.4	11.2
OH-crambe	6,400[c]	18.1[e,f]	18.8	Li-9(10),12(13)-diOH-18	4400	13.6	8.9

[a] Calculated using temperature of major endotherm (Table 2).

[b] ΔH_f = 12,023 cal/mole (41.4 cal/g) from four endotherms of solvent crystallized material.

[c] Based on average molecular weight of 340 for crambe fatty acids (17).

[d] ΔH_f (203 and 213 C forms) = 10,400 cal/mole (30.7 cal/g).

[e] No difference in ΔH_f whether major peak at 67 or 70 C (Table 2).

[f] ΔH_f (60 and 74 C forms) = 10,800 cal/mole (31.8 cal/g).

fusion that were either higher or much lower than those for the other samples.

Forms I and V of the OH-crambe, seen only during the original melt scan, had a combined ΔH_f of 32 cal/g, which was 14 cal/g higher than Forms II, III, or VI and more typical of the hydroxy acids. OH-Crambe was the only sample that exhibited transient endotherms characteristic of solvent crystallized material. Such behavior, however, occurred more often with the salts. For example, the combined ΔH_f of Forms I and II for Li-OH-crambe was about 31 cal/g, almost 12 cal/g higher than Forms I and III. Form I, however, was also observed during successive runs and was therefore prominent in both ΔH_f values.

The number of forms for Li-18 could not be reduced by pretreatment. Therefore, ΔH_f values, 41.4 cal/g for solvent crystallized sample and 31.8 cal/g for the remelt of melted-cooled material, represent combined forms, which are consistent with known values for Na-18 (6) and Li-18 (18).

Molar heats of fusion and corresponding entropy changes (Table 3) were highest for high molecular weight acids, but with the lithium salts, these thermodynamic quantities were not clearly related to molecular weight. When ranked in terms of ΔH_f (Table 3), Li-14-OH-20, Li-12-OH-18, and Li-18 were highest, but they distributed much differently as acids. In contrast, the relative positions of 9(10)-OH-14 and 9(10),12(13)-diOH-18 were essentially unchanged by slat formation; i.e., both acids remained among those with the lowest molar heats of fusion.

Thermal behavior. Behavior that changed with treatment was the most prominent and consistent feature exhibited by the hydroxy acids and their salts. Baseline shifts, reflecting changing heat capacity during either melting or freezing were, in some instances, quite substantial during initial melts of solvent crystallized samples and during slow cooling from the melt (Fig. 1). Magnitudes of these shifts and their directions, endothermic or exothermic, are listed in Table 4. Two types of baseline behavior found on heating are represented in Figure 1. In the scan for Li-9(10)-OH-14, which exemplified those of the other salts, the base line continues to change rapidly after the melt endotherm, as if the type of associative interaction responsible for the solid and near-solid melt structure were changing rapidly. The other behavior, exemplified by Li-9(10),12(13)-diOH-18, was more typical of that in which molecules in the solid and melt are associated through essentially the same types of interactions. Interestingly, the initial scan for Li-9(10),12(13)-diOH-18 resembled those for the acids more than those for salts, but after slow cooling Li-9(10),12(13)-diOH-18 melted more like the other salts.

In successive heating scans at 10°C/min of the same sample after rapid cooling (20°C/min), baseline shifts were either greatly reduced or not present. When cooled slowly (0.625°C/min) and reheated, however, the lithium salts often again exhibited baseline shifts after the final endotherm (Fig. 1).

Slow cooling from the melt produced curves with simple baseline shifts, generally exothermic, as for Li-9(10)-OH-14 and Li-14-OH-20. Often more than one polymorphic form was suggested by the cooling curve, for example, Li-12-OH-18 and Li-11(12)-OH-20. Li-9(10),12(13)-diOH-18 behaved most unusually during slow cooling. It produced no definite exotherm (Fig. 1). On subsequent heating at 10°C/min, two forms were present, but when the heating rate was 2.5°C/min or less the endotherm was replaced by a large baseline shift similar to the reverse of the slow cooling scan and more like a polymer glass transition.

In general, baseline shifts during heating were greater than those during cooling, and shifts observed with lithium salts were greater than those with acids. These shifts, apparent changes in heat capacity, were most often endothermic during heating and, as expected, exothermic during cooling. With certain samples, however, the shifts during heating and cooling were either both endothermic or both exothermic, as if the initial crystal structures were highly ordered or disordered and well removed from near-equilibrium condition as exhibited, for example, by

TABLE 4

Apparent Heat Capacity Change with Phase Transition[a]

Compound	Baseline shift[b] (cal/deg mole)		Compound	Baseline shift[b] (cal/deg mole)	
	Heating	Cooling		Heating	Cooling
12-OH-18	+65	−24	Li-13(14)-OH-22 M	+139	+12
13(14)-OH-22 (M)	+65	−23	Li-12-OH-18	+98	−39
15(16)-OH-24	+61	−18	Li-11(12)-OH-20	+88	−32
13(14)-OH-22	+40	−17	Li-9(10),12(13)-diOH-18	+85	−62
9(10),12(13)-diOH-18	+35	−8	Li-9(10)-OH-14	+82	−14
9(10)-OH-18	+29	−14	Li-13(14)-OH-22	+78	−41
6(7)-OH	+22	−10	Li-6(7)-OH-18	+73	−49
14-OH-20	0	−13	Li-11(12)-OH-18	+47	−66
11(12)-OH-20	0	−8	Li-9(10)-OH-18	+44	0
9(10)-OH-14	0	+2	Li-9(10)-OH-16	+31	+9
OH-crambe	−8	−3	Li-18	+23	0
9(10)-OH-16	−9	−4	Li-15(16)-OH-24	+19	−31
11(12)-OH-18	−14	−10	Li-OH-crambe	0	−5
18	−16	−5	Li-14-OH-20	−45	−13

[a] After last endotherm on heating solvent crystallized material and after exotherm on slow cooling from the melt.

[b] Endothermic shift, +; exothermic, −.

9(10)-OH-14 and Li-OH-crambe. The direction or magnitude of shifts were independent of chain length and number of hydroxyl groups. Notably, the commercial grease thickener, Li-12-OH-18, and its parent acid were among samples exhibiting the largest baseline shifts or changes in heat capacity upon melting or freezing.

DISCUSSION

Crystals of long chain fatty acids, and those of their salts, consist of bimolecular double layers in which molecules are associated both head to head (carboxyl to carboxyl) and tail to tail (methyl to methyl) (16,19). Within this general structure identified by X-ray, variations in conformation and packing of polar and nonpolar portions produce differences that are reflected in thermal behavior.

Behavior exhibited by the mixtures of isomeric hydroxy acids and their lithium salts was surprisingly consistent with that exhibited by the analogous pure compounds—i.e., 18, 12-OH-18, 14-OH-20, and corresponding salts.

Among the acids, those with longer uninterrupted methylene chains generally exhibited higher melting points (Table 2), heats of fusion, and greater entropic change upon melting. In Table 3, for example, compare 12-OH-18 with 14-OH-20 and 9(10)-OH-16 with 9(10)-OH-18 and 11(12)-OH-20. Considering all acids except 18 (stearic acid) and OH-crambe, the entropy of fusion was about 2.2 eu/CH_2, as expected of aliphatic materials in which melting correlates with chain rotations and disruption of lateral packing of chains (20). Hydroxylation near the center of the molecule, which would allow for stabilization through hydrogen bonding, also produced higher heats of fusion (Table 3), as can be seen by comparing 9(10)-OH-18 vs. 6(7)-OH-18 and 11(12)-OH-18.

Other self-consistent characteristics are also evident in the data. Foremost is the effect of salt formation on thermodynamic properties and apparent order in the acid crystal structures. Salt formation reduced ΔH_f and ΔS_f substantially and diminished distinguishing differences, as if structure around carboxylate groups no longer contributed to the phase transition. The three homogeneous compounds, Li-14-OH-20, Li-12-OH-18, and Li-18, though quite different as acids, were essentially the same as salts. Entropies of fusion (Table 3) and heat capacity changes that we observed (Table 4) suggest that the melt transition of the salts as a group involved much less change in molecular packing than did the melt transition of the acids. Such facile reversible phase changes at high temperatures (Table 2) are desirable in greases.

Fusion entropies for the hydroxy acid salts correlate better with the length of aliphatic structure distal to the OH-bearing carbon than to the number of CH_2 units between the OH-bearing carbon and the carboxyl group. This importance of methyl end-group structure is compatible with concepts from thermal analysis and X-ray studies on salts of unsubstituted fatty acids (6,16,21). Briefly, salts, unlike acids, retain much of the original crystalling head to head chain association well into the melt. Our data suggest that hydroxy acid salts behave similarly and further imply that order imparted by salt formation is probably enhanced through hydroxyl association. Increased interaction near the carboxyl would enhance the role of distal chain structure in determining a salt's behavior near the melt transition. The general importance of methyl end-group interaction has already been documented for other lipid structures by Larsson (22) and, although Dubleton and Lomer (23) demonstrated no hydrogen bonds in a potassium palmitate, Lunden (24) has described how hydroxyl groups contribute to the fiber structure of 12-OH-18 methyl ester through hydrogen bonding along a two-fold screw axis.

Concerning the utility of hydroxy acid salts as grease thickeners, it is pertinent that electron micrographs of Li-12-OH-18 fibers in greases reveal a twisted-ribbon type structure (25), and that the balance of opinion favors greases thickened with such structures over those thickened with fatty acid salts that lack the spiral structure (26). In view of this tendency of Li-12-OH-18 toward a higher order of crystalline structure, it is not surprising that the salt was among those with high ΔH_f and ΔS_f values (Table 3). Accordingly, Li-14-OH-20, which behaved similarly, appears especially promising among the compounds we examined. By the same criterion, Li-9(10)-OH-18 also shows promise and might even be preferred for its higher-melting forms (Table 2).

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