Thermophysics of metal alkanoates
V. Heat capacities and thermodynamic properties of lithium *n*-butanoate and *n*-hexanoate [a]

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The heat capacities of solid lithium *n*-butanoate and *n*-hexanoate have been investigated by adiabatic calorimetry between 5 and 350 K. The values at $T = 298.15$ K of $C_{p,m}/R$, $\{S_m^0(T) - S_m^0(0)\}/R$, $\{H_m^0(T) - H_m^0(0)\}/R$, and $\{G_m^0(T) - H_m^0(0)\}/RT$ are 18.45, 20.85, 3071.0 K, and -10.546 for *n*-CH$_3$(CH$_2$)$_2$CO$_2$Li, and 25.98, 27.48, 4200.8 K, and -13.387 for *n*-CH$_3$(CH$_2$)$_4$CO$_2$Li. No evidence was obtained for the occurrence in either salt of subambient discontinuous (first-order) phase transitions. Both alkanoates, however, undergo gradual (higher-order) thermodynamic transformations in the temperature region explored: possible origins of these are discussed qualitatively. Analysis of the expected "lattice" heat capacities for members of the homologous series in terms of CH$_2$ contributions has been performed.

1. Introduction

We recently provided by equilibrium adiabatic calorimetry[1,2] a complete picture, in terms of $C_{p,m}/R$, $\{S_m^0(T) - S_m^0(0)\}/R$, $\{H_m^0(T) - H_m^0(0)\}/R$, and $\{G_m^0(T) - H_m^0(0)\}/RT$, of the thermophysics of lithium, sodium, and potassium propanoates in the temperature range 5 to 350 K.

Investigation has been extended to the next higher homologs for which, in general, different thermal behavior, and, in particular, changes in the fusion mechanisms are to be expected. It is known[3] for example that, when Na or K is the cation, the so-called "chain fusion process"—associated with the transformation of the anion from its extended configuration into a (more or less) spheroidal one—starts with $n_C = 4$ (n_C: number of carbon atoms) giving rise (in this instance) to a mesomorphic liquid of the smectic type and subsequently an isotropic liquid.

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[a] The first paper in this series is reference 7.
† Died 24 January 1986.

In the lithium n-alkanoate family, to which belong the four homologs studied in the present (n-butanoate and n-hexanoate) and next (n-pentanoate and n-heptanoate) papers of this series, changes in thermal behavior are less drastic, and the presently available information (consisting mainly of $\Delta_{fus}S_m/R$ and $\Delta_{trs}S_m/R$ obtained by one of us from d.s.c. traces recorded at $T/K \geqslant 110$)[3,4] is summarized here.

The fusion temperatures increase from methanoate ($n_C = 1$) to propanoate ($n_C = 3$), then decrease smoothly from n-butanoate ($n_C = 4$) to n-hendecanoate ($n_C = 11$), and finally remain almost constant from n-dodecanoate ($n_C = 12$) to n-eicosanoate ($n_C = 20$). Propanoate also exhibits fusion of a metastable form. A plot of the corresponding $\Delta_{fus}S_m/R$ values in figure 1 shows no correlation apparent among the entropies of fusion in the three lowest homologs, whereas linear correlations exist among the entropies of fusion for the homologs for which $4 \leqslant n_C \leqslant 11$ ($\Delta_{fus}S_m/R = 2.681 + 0.388n_C$; compare curve A in figure 1), and among the entropies of fusion for those for which $12 \leqslant n_C \leqslant 20$ ($\Delta_{fus}S_m/R = 4.372 + 0.004n_C$; compare curve B in figure 1). The $\Delta_{fus(M)}S_m/R$ value which pertains to fusion of the metastable propanoate[3] also falls on curve A, extrapolated to $n_C = 3$. In conclusion, it can be reasonably asserted that the high-temperature stable form (Crystal I) of each of the three lowest homologs has its own mechanism of fusion, whereas metastable propanoate and homologs for which $4 \leqslant n_C \leqslant 11$ have related fusion processes, and homologs for which $12 \leqslant n_C \leqslant 20$ also have similar mechanisms but differ from those of the previous set.

Plastic crystals form at $400 < T_{trs} < T_{fus}$ for $n_C \geqslant 12$, but a discussion of them is unnecessary here.

Intercrystalline discontinuous (first-order)[5] transitions occur in most homologs with $n_C > 3$ at $110 \leqslant T_{trs} \leqslant 400$. The remarkable alternation in T_{trs}, shown in the upper part of figure 2 with odd-even values of n_C, is not apparent in the fusion temperatures. By extrapolation, Sanesi et al.[6] considered that an analogous transition might also occur at least in lithium n-hexanoate, although at a temperature (lower than 110 K) inaccessible to their d.s.c. analysis. However, if d.s.c. $\Delta_{trs}S_m/R$ values are plotted against n_C, as in the lower part of figure 2, two distinct sets of points are obtained, relevant to the odd (curve A) and even (curve B) homologs, respectively.
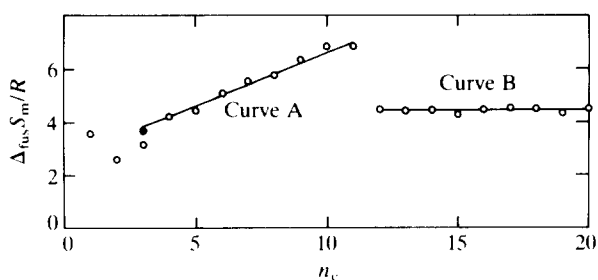

FIGURE 1. Entropies of fusion for lithium n-alkanoates through eicosanoate. ●, Fusion of metastable propanoate. See text for equations.
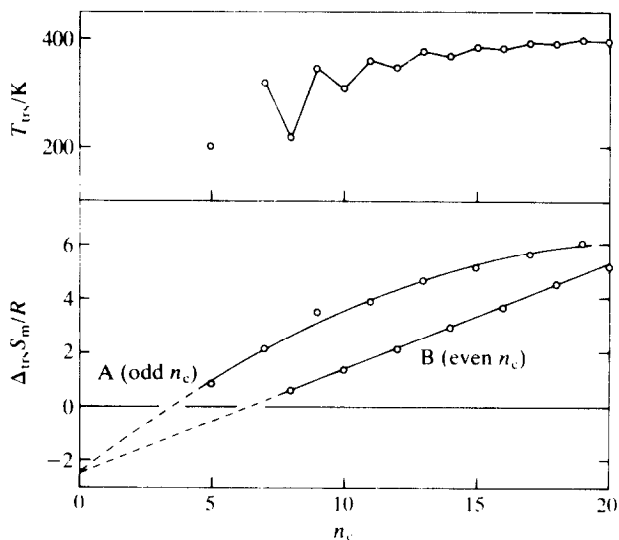
FIGURE 2. Upper part: intercrystalline transition temperatures at $T/K > 110$ in lithium n-alkanoates with $n_C > 3$. Lower part: related entropies of transition. (See text for equations and identification of even and odd n_C values).

Curve B is satisfactorily interpolated by the linear equation: $\Delta_{trs}S_m/R = -2.460 + 0.383(n_C)_{even}$. For $(n_C)_{even} < 8$, the extrapolated $\Delta_{trs}S_m/R$ values are negative, which leads to the conclusion that no intercrystalline discontinuous (first-order) transition is to be expected for either n-hexanoate or n-butanoate (studied in the present paper), although nothing can be said about the possible occurrence of gradual (higher-order) transformations in these salts. Curve A can in turn be interpolated with the parabolic equation $\Delta_{trs}S_m/R = -2.499 + 0.790(n_C)_{odd} - 0.018(n_C)^2_{odd}$. Both curves are seen to have a common origin at $-(2.48 \pm 0.02)$.

2. Experimental

Lithium n-butanoate and n-hexanoate were prepared by reacting Fluka puriss ($\geqslant 99.5$ moles per cent) Li_2CO_3 suspended in anhydrous methanol with a moderate excess (10 per cent) of Fluka puriss n-butanoic ($\geqslant 99.5$) and n-hexanoic ($\geqslant 99$; tested by g.c. at the origin) acids, respectively. After refluxing under stirring for about 6 h. cooling to room temperature, and separating of some unreacted carbonate by filtration, the solutions were concentrated to incipient crystallization in a Rotavapor device under reduced pressure. The solid alkanoates recovered after standing overnight were further purified by repeated dissolution in methanol and fractional precipitation with propan-2-ol. Both salts were finally dried to constant mass at about 380 K under vacuum and tested by d.s.c. analysis.

A description of the computer-operated adiabatic assembly, and of the gold-plated copper calorimeter (designated W-62) employed has already been given.[7] The calorimeter was loaded with 28.488 g of $CH_3(CH_2)_2CO_2Li$ ($\hat{=} 0.30294$ mol, the

relative molar mass being 94.038 g·mol^{-1} on the basis of the IUPAC 1973 relative atomic masses), and with 24.907 g of $CH_3(CH_2)_4CO_2Li$ ($\hat{=}$ 0.20401 mol; 122.086 g·mol^{-1}). Buoyancy corrections were calculated using densities (1.19 ± 0.02) and (1.13 ± 0.02) g·cm^{-3} for n-butanoate and n-hexanoate, respectively, obtained by Spinolo.[8]

3. Results

The experimental $(C_{p,m}/R)$s for lithium n-butanoate and n-hexanoate are plotted in figure 3, and listed in table 1 in chronological sequence by series (designated by I, II, etc.) and within each series. The sequence of the series allows one to deduce the thermal cycles to which the samples were submitted during measurements, and (in most cases) to obtain information on the individual temperature increments.
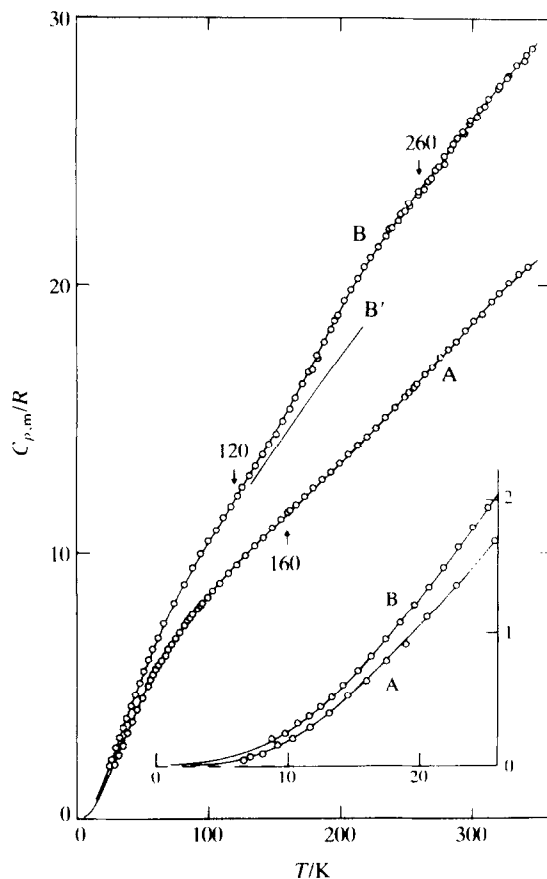

FIGURE 3. Curves A and B: molar heat capacities of lithium n-butanoate and n-hexanoate, respectively, up to 350 K (the region below 26 K is enlarged in the lower right-hand corner). Curve B′: a segment of the calculated (normal) "lattice" curve of lithium n-hexanoate, reported here to emphasize the $C_{p,m}/R$ increment due to the gradual transformations occurring in this salt above 120 K (for details, see text).

TABLE 1. Experimental heat capacities of lithium n-butanoate and n-hexanoate $(R = 8.3144\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
					Lithium n-butanoate						
Series I		335.57	20.402	241.43	15.399	141.35	10.527	88.62	7.730	15.95	0.642
249.22	15.873	342.77	20.690	248.79	15.793	148.02	10.936	94.00	8.025	17.45	0.794
252.34	15.951	Series II		256.13	16.170	154.70	11.210	Series V		19.02	0.911
257.75	16.271	159.90	11.457	Series III		161.40	11.530	56.39	5.192	20.59	1.116
263.90	16.620	165.84	11.746	85.30	7.495	Series IV		58.35	5.383	22.80	1.359
270.06	16.883	172.58	12.077	88.23	7.685	60.32	5.562	62.11	5.751	25.72	1.688
276.20	17.268	179.31	12.370	91.78	7.897	62.19	5.766	Series VI		28.63	2.032
282.35	17.571	186.02	12.701	95.32	8.094	64.40	5.948	6.71	0.036	31.62	2.380
288.49	17.851	192.74	13.008	98.85	8.288	66.61	6.158	7.23	0.069	34.96	2.782
294.85	18.287	199.48	13.316	103.34	8.544	68.82	6.319	8.11	0.092	38.65	3.213
301.52	18.626	206.22	13.652	108.78	8.835	71.52	6.516	9.17	0.155	42.37	3.653
308.19	18.902	212.95	13.977	114.80	9.177	74.71	6.749	10.35	0.207	46.16	4.085
314.82	19.353	219.69	14.305	121.41	9.539	77.91	6.978	11.71	0.294	50.02	4.511
321.47	19.689	226.74	14.636	128.04	9.862	81.11	7.215	13.07	0.394	53.94	4.938
328.39	20.056	234.08	15.023	134.68	10.223	84.32	7.434	14.48	0.516	57.59	5.300
					Lithium n-hexanoate						
Series I		263.83	23.596	81.52	8.837	176.35	16.714	327.05	27.88	22.90	1.635
176.86	16.823	268.66	23.99	88.14	9.478	182.13	17.334	334.05	28.21	24.03	1.786
182.59	17.291	273.64	24.42	94.34	9.966	188.71	17.950	341.06	28.60	25.16	1.941
187.67	17.877	278.79	24.51	100.24	10.427	195.39	18.644	Series IV		26.30	2.098
192.76	18.348	283.90	25.04	105.87	10.871	Series III		8.80	0.02	27.45	2.260
197.86	18.866	289.02	25.47	111.27	11.329	237.15	22.134	9.80	0.244	27.31	2.238
202.96	19.398	294.18	25.66	116.50	11.710	245.39	22.656	10.67	0.316	30.15	2.646
208.07	19.818	299.32	26.04	121.56	12.114	252.03	23.059	11.59	0.371	32.77	3.032
213.18	20.236	304.46	26.28	126.48	12.484	258.80	23.497	12.47	0.438	35.45	3.424
218.29	20.699	309.59	26.68	131.27	12.890	265.58	23.895	13.28	0.514	38.18	3.813
223.42	21.063	321.17	27.45	135.94	13.241	272.37	24.32	14.19	0.600	41.20	4.232
228.54	21.439	327.33	27.77	140.79	13.618	279.14	24.81	15.25	0.710	44.51	4.681
233.65	21.840	333.48	28.22	145.85	14.037	285.92	25.26	16.30	0.823	47.84	5.126
238.79	22.143	339.67	28.39	150.93	14.452	292.69	25.71	17.38	0.945	51.22	5.560
243.93	22.402	345.83	28.84	156.01	14.906	299.47	26.15	18.47	1.070	54.63	5.975
249.00	22.737	Series II		161.09	15.339	306.22	26.53	19.56	1.205	58.07	6.394
254.00	22.940	66.37	7.326	166.17	15.804	313.07	26.97	20.67	1.343	61.54	6.805
258.93	23.381	74.33	8.125	171.26	16.288	320.06	27.40	21.78	1.488		

Moreover, the smoothed $C_{p,m}/R$ values and the values of the relevant molar thermodynamic functions, calculated for a set of selected temperatures as described in reference 7, are summarized in table 2. The standard deviations in the heat capacities begin at 5 per cent at 6 K, and decrease to 0.3 per cent at 20 K and to less than 0.1 per cent above 50 K.

4. Discussion

It is well known[9] that such configurational isomers as

$$\begin{array}{cc} \text{CH}_2\text{---CH}_3 & \text{CH}_3\text{---CH}_2 \\ | & \text{and} \qquad | \\ \text{CH}_2\text{---CH}_3 & \text{CH}_2\text{---CH}_3 \end{array}$$
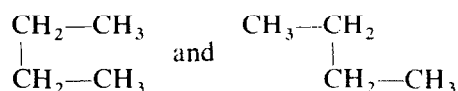
TABLE 2. Molar thermodynamic functions of lithium n-butanoate and n-hexanoate $(R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$

$\dfrac{T}{\text{K}}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{S_m^0(T) - S_m^0(0)}{R}$	$\dfrac{H_m^0(T) - H_m^0(0)}{R\,\text{K}}$	$\dfrac{G_m^0(T) - H_m^0(0)}{RT}$
Lithium n-butanoate				
0	0	0	0	0
5	0.025	0.008	0.031	0.002
10	0.188	0.063	0.475	0.016
15	0.559	0.204	2.269	0.053
20	1.054	0.430	6.268	0.117
30	2.191	1.068	22.386	0.322
40	3.374	1.861	50.22	0.606
50	4.512	2.737	89.71	0.943
60	5.540	3.654	140.11	1.318
70	6.407	4.575	199.97	1.718
80	7.139	5.479	267.80	2.132
90	7.780	6.358	342.45	2.553
100	8.364	7.208	423.20	2.976
120	9.451	8.830	601.5	3.818
140	10.482	10.365	800.9	4.644
160	11.467	11.830	1020.5	5.452
180	12.413	13.235	1259.3	6.239
200	13.351	14.591	1516.9	7.007
220	14.314	15.91	1793.5	7.756
240	15.33	17.20	2089.8	8.490
260	16.38	18.47	2406.8	9.208
280	17.46	19.72	2745.2	9.914
298.15	18.45	20.85	3071.0	10.546
300	18.55	20.96	3105.2	10.609
320	19.63	22.19	3487.1	11.295
340	20.59	23.41	3889.5	11.972
350	21.03	24.01	4097.6	12.307
Lithium n-hexanoate				
0	0	0	0	0
5	0.045	0.015	0.056	0.0038
10	0.257	0.099	0.722	0.0269
15	0.683	0.277	2.989	0.0779
20	1.260	0.550	7.802	0.160
30	2.626	1.312	27.064	0.410
40	4.070	2.267	60.60	0.752
50	5.400	3.321	108.06	1.160
60	6.611	4.414	168.21	1.611
70	7.712	5.517	239.92	2.090
80	8.707	6.613	322.10	2.587
90	9.608	7.692	413.75	3.094
100	10.436	8.747	514.02	3.607
120	11.98	10.79	738.3	4.635
140	13.55	12.75	993.3	5.655
160	15.27	14.67	1281.2	6.662
180	17.15	16.58	1605.2	7.658
200	19.04	18.48	1967.1	8.645
220	20.78	20.38	2365.6	9.625
240	22.29	22.25	2796.7	10.600
260	23.59	24.09	3255.7	11.567
280	24.82	25.88	3739.9	12.526
298.15	25.98	27.48	4200.8	13.387
300	26.10	27.64	4249.0	13.475
320	27.40	29.36	4784.1	14.414
340	28.56	31.06	5344.1	15.34
350	29.07	31.90	5632.2	15.80

are present in gaseous n-butane and that the number of possible configurations increases dramatically with increasing n_C. To meet potential energy requirements, however, liquefaction and crystallization do select configurations enabled to enter condensed structures so severely that most often only fully extended zig-zag chains exist in the crystal, particularly at low temperatures.

Although no X-ray diffractometric results are known so far for lithium short-chain n-alkanoates, it can be assumed that condensed phases of the present pair of salts behave in a way somewhat similar to that described above. Thus, for example in the case of n-butanoate at sufficiently low temperatures, chains are expected to fill (tail-to-tail) the space between adjacent ionic layers only in a frozen out (rigid) *anti* configuration:

$$CH_3-CH_2$$
$$|$$
$$CH_2-C \overset{\displaystyle \nearrow O}{\underset{\displaystyle \diagdown O^-}{}}$$
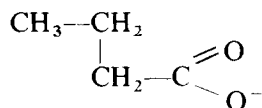
In both salts, it can further be reasonably assumed[10] that, due to the shortness of the chains and to the strength of the electrostatic field, each group of the chain is sunk in a potential well sufficiently deep to hamper any abrupt variation of the tilt angle (*i.e.* the angle between the ionic layer and the axis of the chain), contrary to what occurs in higher even homologs, each of which undergoes a discontinuous (first-order)[5] intercrystalline transition involving this kind of variation. When temperature rises, changes of crystal packing are rather to be expected as a consequence of some kind of intramolecular orientational variation,[11] an example of which is offered by the hindered rotational motion of the end methyl group about a C—C bond: these are gradual rather than discontinuous thermodynamic transformations. Moreover, contributions to the overall heat capacity might also come from the progressive activation of vibrational degrees of freedom. Since vibrational (or hindered rotational) modes involve potential as well as kinetic energy, their classical (equipartition) contribution to $C_{p,m}/Rs$ will obviously be equal to unity, or multiples thereof, when fully activated.

In lithium n-hexanoate (shown in figure 3) two distinct thermodynamic transformations develop in a continuous way between about 120 and 250 K, and between about 260 and 330 K, respectively. In the absence of structural information, it is difficult to infer with certainty the nature of such processes. However, the trend of the curve of $C_{p,m}/R$ against T is consistent with the general statements developed above (and with expectation based on figure 2).

The shape of the lithium n-butanoate curve (figure 3) suggests in turn that a thermodynamic transformation commences near 160 K (*i.e.* at a temperature higher than for n-hexanoate), and approaches completion over a temperature interval larger than in n-hexanoate. This is consistent with the fact that, on the basis of a previous assertion, shorter anionic tails are expected to be held more rigidly by the electrostatic field.

The odd-homolog neighbors of lithium n-hexanoate behave differently from it (and from n-butanoate) although rather similarly to one another. The morphology

of these differences and similarities will be discussed in the next paper of the present series.[(12)]

To obtain "lattice" curves for the lithium salts already studied {*i.e.* propanoate;[(2)] *n*-butanoate and *n*-hexanoate (this paper); and *n*-pentanoate and *n*-heptanoate}[(12)] an attempt was made to use an approach already argued by White[(13)] and utilized on long(er) alkyl chains embedded in a crystalline matrix {(n-$C_{18}H_{37}NH_3$)$_2$CdCl$_4$}. The energetics and dynamics of long hydrocarbon chains have already been studied in a variety of materials and interpreted in terms of the number $m(CH_2) = (n_C - 2)$, of CH_2 increments in the chain.

Odd and even values of $m(CH_2)$ in the alkanes and also in the alkanoates seem to behave differently in some respects, particularly when n_C is small. With the (modest) amount of thermophysical information available to us such differences have to be neglected, along with the fact that the thermophysics of propanoate is rather different from that of the homologs with $4 \leqslant n_C \leqslant 11$ (see Introduction). Moreover, detailed structural information on the compounds we have studied is virtually non-existent.

None the less, the considerable discussion recently made on the magnitude and constancy of the CH_2 increment[(14, 15)] and the method of differences utilized by White[(13)] eliminate all contributions to the heat capacities other than that of the CH_2 unit. Since our present results are constrained to small values of n_C we have developed by a similar approach a heat-capacity curve for our compounds which lies well within the envelope of White's calculated values (as shown in figure 4) based, with modifications, on Pitzer's hydrocarbon model.[(16)] In figure 4 the dotted line represents the calculated contribution of C–C stretch, C–C bend, and C–H vibrations as in reference 16. The dashed line is the sum of the latter contributions and a highly hindered Einstein vibrational contribution for CH_2 oscillations. The solid line represents the increments judged from our results on lithium compounds (with $3 \leqslant n_C \leqslant 7$) and the frequencies of the alkanes reported by Socrates.[(17)]
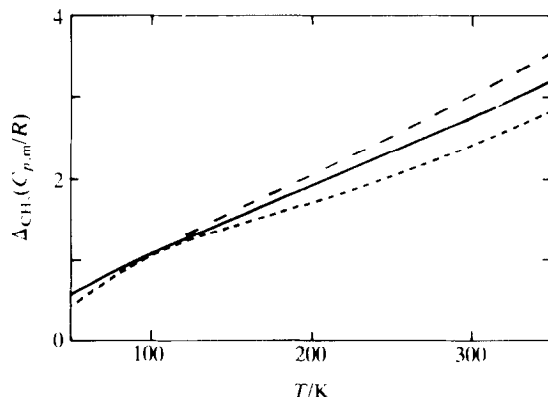

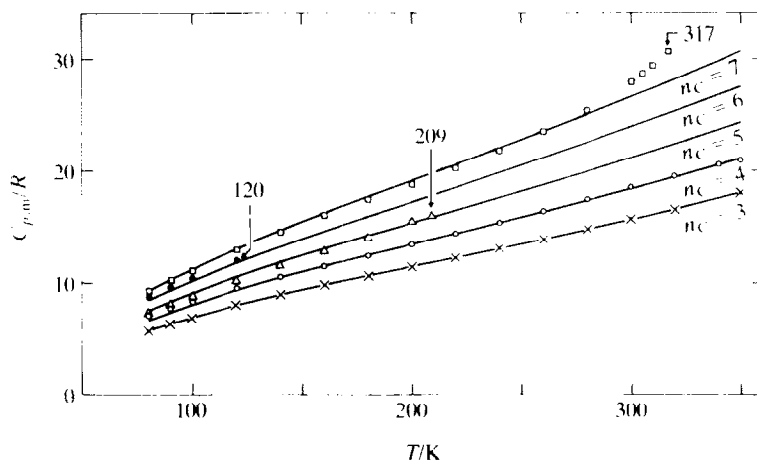FIGURE 4. $C_{p,m}/R$ contributions from a CH_2 group in a homologous alkyl series (for explanation, see text).

FIGURE 5. The measured (smoothed) heat capacities for $\times$, lithium propanoate;[2] $\bigcirc$, n-butanoate, $\triangle$, n-pentanoate;[12] $\bullet$, n-hexanoate; and $\square$, n-heptanoate[12] in the temperature ranges specified in the text, and the (normal) "lattice" heat capacities (curves $n_C = 3, \ldots, 7$, respectively) based on CH_2 increments of figure 4.

With appropriate caveats for lack of structural knowledge, odd/even effects, small values of n_C, etc., the estimated "lattice" heat capacities for lithium normal alkanoates with $3 \leqslant n_C \leqslant 7$ are seen in figure 5 (between 80 and 350 K), and appear reasonable in all respects when compared with the corresponding experimental values: between 80 and either 350 K (for n-propanoate and n-butanoate) or the lowest T_{trs} value (i.e. 209 K for n-pentanoate,[12] about 120 K for n-hexanoate, and 317 K for n-heptanoate).[12]

The different behavior of odd and even values of $m(CH_2)$ was necessarily neglected, as said above, in previous calculations (compare figure 4). It is, however, to be stressed that the role played by this different behavior becomes no longer negligible when $T \to 0$. For example, below 80 K the calculated curves of $C_{p,m}/R$ against T for lithium n-pentanoate and n-heptanoate lie increasingly higher than do the measured curves for the same substances, whereas the calculated curves for the homologs with even values of $m(CH_2)$ (or n_C), i.e. n-butanoate and n-hexanoate, lie increasingly lower than the measured curves. Moreover, the sequence (from the least to the greatest $C_{p,m}/R$ at each temperature) of measured values for $C_{p,m}/R$ of lithium n-alkanoates with $3 \leqslant n_C \leqslant 7$ is $n_C = (3, 4, 5, 6, 7)$ only at $T/K > 80$, but becomes $n_C = (3, 5, 4, 7, 6)$ at $T/K = 50$, and $n_C = (3, 5, 7, 4, 6)$ at $T/K < 20$. The situation at $T/K < 20$ is shown in figure 6 (top).

Heat capacities are available also for three sodium n-alkanoates: methanoate,[18] ethanoate,[7] and propanoate.[1] Here again the sequence of $C_{p,m}/R$ magnitudes (shown in figure 6, bottom), i.e. $n_C = (1, 3, 2)$ supports the above assertion that "evens" behave in a markedly different way with respect to "odds" at low temperatures. (The occurrence in the ethanoate of a transition at 21 K might affect the relative magnitudes of the heat capacities in this region. However, the ratios persist down to 7 K.)
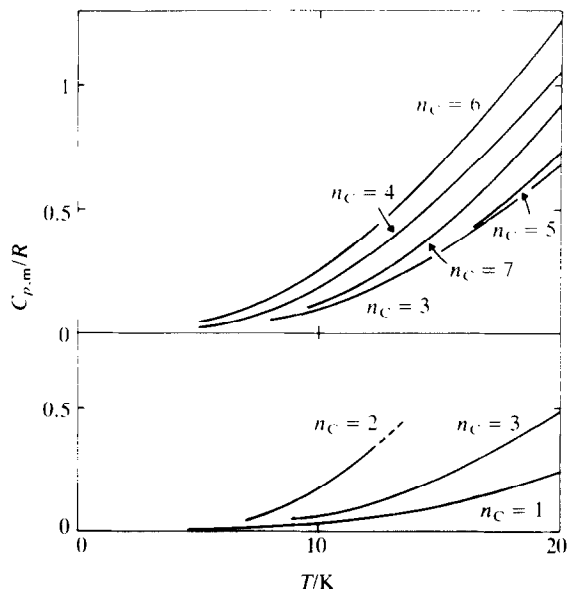
FIGURE 6. Upper part: the measured (smoothed) heat capacities for lithium propanoate,[2] n-butanoate, n-pentanoate,[12] n-hexanoate, and n-heptanoate (curves $n_C = 3, \ldots, 7$, respectively) below 20 K. Lower part: the measured (smoothed) heat capacities for sodium methanoate,[18] ethanoate,[7] and propanoate[1] (curves $n_C = 1, \ldots, 3$, respectively) below 20 K.

More sophisticated calculations will be possible as soon as the research program in progress will make available $C_{p,m}/R$ values for a larger number of alkali alkanoates.

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