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Thermodynamics of alkali alkanoates X. Heat capacities and thermodynamic properties of lithium methanoate and lithium ethanoate at temperatures from ≈5 K to 580 K[a]

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Heat capacities of lithium methanoate and ethanoate (CA Registry numbers [556-63-8] and [546-89-4]) have been measured by adiabatic intermittent-heating equilibrium calorimetry from temperatures T near 5 K to 350 K and by differential scanning calorimetry (d.s.c.) from 330 K through melting (solid to isotropic liquid) to 580 K. Smoothed values of $C_{p,m}$, $\Delta_0^T S_m^\circ$, $\Delta_0^T H_m^\circ$, and Φ_m° were calculated at selected temperatures. At $T = 298.15$ K the values are: $8.768 \cdot R$, $9.873 \cdot R$, $1528.6 \cdot R \cdot$K, and $4.746 \cdot R$ for HCOOLi, and $11.607 \cdot R$, $14.412 \cdot R$, $2065.4 \cdot R \cdot$K, and $7.484 \cdot R$ for CH_3COOLi ($R = 8.31451$ J·K^{-1}·mol^{-1}). No transition was observed in the heat-capacity curves of either salt at $T < 490$ K. The existence in HCOOLi of a solid-to-solid phase transition at $T = (495 \pm 1)$ K, with $\Delta_{trs} H_m^\circ = (222 \pm 5) \cdot R \cdot$K and $\Delta_{trs} S_m^\circ = (0.44_9 \pm 0.07) \cdot R$ was confirmed. The present results are briefly discussed in comparison with those previously obtained on other alkali-metal methanoates and ethanoates.

1. Introduction

The thermophysical properties of some alkali-metal alkanoates have been the subject of the previous papers of this series. In particular, heat capacities of sodium methanoate and ethanoate,[1] and of potassium ethanoate,[2] were determined, as well as those of lithium linear alkanoates with number of carbon atoms in the aliphatic chain ranging from 3 to 7.[3–5] In this study, the thermophysics of lithium methanoate (HCOOLi) and ethanoate (CH_3COOLi) is examined and their behavior is compared with that of the alkali-metal methanoates and ethanoates previously investigated.

[a] The first paper in the series is reference number 1.

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Besides the numerous applications they usually find as reagents or catalysts in organic chemistry, HCOOLi and CH_3COOLi display interesting physicochemical properties inasmuch as they are the simplest members of the lithium-soap series, and among the alkali-metal alkanoates they are the only ones easily forming glassy phases. Lithium methanoate and ethanoate were also considered as components of many phase diagrams of binary, ternary, and reciprocal-ternary-salt systems in early work of Russian researchers. These systems have been collected and evaluated in a recent review.[6] Moreover, the hydrates of the two salts behave as lithium ionophores in a variety of biological systems,[7] and $HCOOLi \cdot H_2O$ displays significant non-linear optical properties.[8]

Information obtained by means of differential scanning calorimetry (d.s.c.) on the thermal behavior of both salts was provided in a previous paper,[9] whereas X-ray diffraction,[10-12] thermal,[11,12] and Raman spectroscopic[12] results have been recently reported for lithium methanoate. In particular, a crystal-II-to-crystal-I phase transition from hexagonal to monoclinic was brought out in HCOOLi at $T \approx 500$ K,

TABLE 1. Phase changes of lithium methanoate and ethanoate as reported in previous literature $\{M(HCOOLi) = 51.958\ g \cdot mol^{-1};\ M(CH_3COOLi) = 65.985\ g \cdot mol^{-1};\ R = 8.31451\ J \cdot K^{-1} \cdot mol^{-1}\}$

Phase change	T_{trs}/K	$\Delta_{trs}H^{\circ}_m/(R \cdot K)$	Method	Year	Reference
		HCOOLi			
glass	354 ± 2		d.s.c.	1975	9
nstr[a]	496 ± 2	216.38	d.s.c.	1975	9
II-to-I	501		d.t.a.[b]	1992	12
nstr	503	288.65 ± 15.64	d.s.c.	1990	11
fusion	545		d.t.a.	1992	12
fusion	546		vis-pol[c]	1958	13
fusion	546			1968	14
fusion	546	1947.45	d.s.c.	1975	9
		CH_3COOLi			
glass	394 ± 2		d.t.a.	1970	15
glass	401		d.s.c.	1974	16
nstr	405		vis-pol	1974	17
glass	401 ± 2		d.s.c.	1975	9
glass	413 ± 2		d.s.c.	1982	18
nstr	530 to 536		vis-pol	1956	19
fusion	564		vis-pol	1956	19
fusion	557		vis-pol	1961	20
fusion	564			1968	14
fusion	553		d.t.a.	1970	21
fusion	562		d.t.a.	1970	15
fusion	553			1971	22
fusion	557		d.t.a.	1974	23
fusion	561		vis-pol	1974	23
fusion	561	1546.89	d.s.c.	1974	16
fusion	557 ± 2	1429.14	d.s.c.	1975	9
fusion	553 ± 2	1228.58 ± 66.41	d.s.c.	1982	18

[a] nstr, non-specified transition.
[b] d.t.a., differential thermal analysis.
[c] vis-pol, visual-polythermal analysis.

and should be considered as a reversible one, in spite of noticeable hysteresis.[9, 11, 12] In crystalline CH_3COOLi no anomalies were detected by means of d.s.c. between $T = 110$ K and the melting temperature,[9] but the fact that in sodium ethanoate a phase transition was found[1] at $T = 21$ K was intriguing and the possible existence of a similar transition in lithium ethanoate could not *a priori* be excluded. In table 1, thermal quantities reported in the more recent literature are summarized.

In the molten state, both salts display remarkable undercooling and may form glassy phases which are relatively stable at room temperature.[9] However, upon heating the glass, a glass transition is usually observed at a characteristic glass-transition temperature T_g, above which crystallization occurs and the crystalline phase is easily obtained.[9] An example of a heating and cooling cycle taken by d.s.c. on either salt is illustrated in figure 1, where no crystallization peaks are seen in the cooling traces, and crystallization phenomena appear in the heating curves. Heat capacities measured also by d.s.c. on molten and glassy CH_3COOLi were reported by Tucker,[16] and Gonchukova,[18] but the latter presented values only in graphical form.

The aim of the present paper is to provide heat-capacity measurements on crystalline and molten lithium methanoate and ethanoate in the temperature range between ≈ 5 K and 580 K, *i.e.* a temperature at which either salt displays a relatively stable molten phase. The values of the standard thermodynamic quantities calculated from the heat capacities and tabulated for selected temperatures between 5 K and 350 K are also given.

In the case of the ethanoate, the results obtained on the molten and solid compound can be compared with those reported in previous papers,[16, 18] in both of which, however, attention was mainly focused on the glass-transition temperature of the material. In this work, no calorimetric investigation was undertaken on the glassy

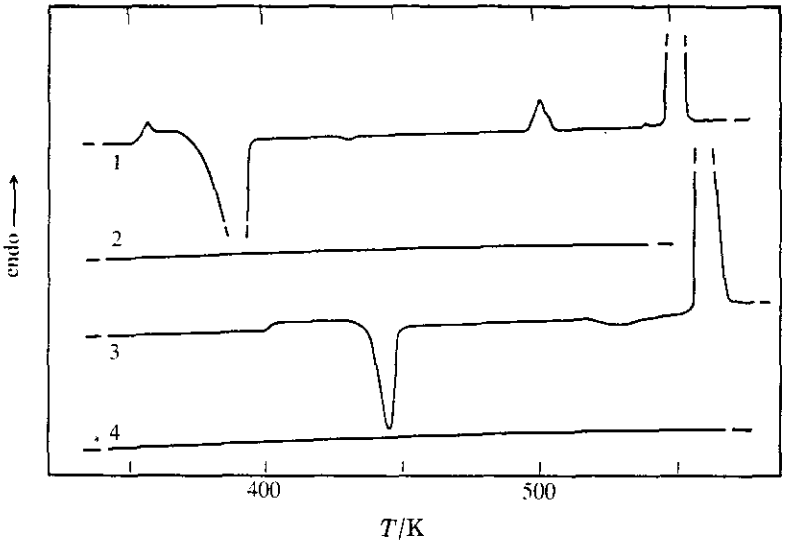

FIGURE 1. D.s.c. traces recorded in a heating and cooling cycle on 1,2: HCOOLi and 3,4: CH_3COOLi.

TABLE 2. Experimental molar heat capacities for HCOOLi and CH_3COOLi ($R = 8.31451\ J \cdot K^{-1} \cdot mol^{-1}$)

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
			Lithium methanoate (HCOOLi)				
By adiabatic calorimetry							
				Crystal II			
	Series I	147.258	5.678	289.344	8.571	16.575	0.168
40.868	1.288	152.335	5.823	295.920	8.672	17.776	0.204
43.292	1.418	157.422	5.963	302.376	8.761	19.055	0.246
45.341	1.535	162.525	6.079	309.209	8.867	20.431	0.295
47.514	1.656	167.621	6.218			21.907	0.350
49.797	1.779	172.722	6.346		Series II	23.480	0.411
52.196	1.908	177.821	6.513	281.049	8.443	25.147	0.484
54.714	2.046	182.99	6.601	286.234	8.542	26.911	0.563
57.362	2.185	188.119	6.694	291.587	8.619	28.780	0.651
60.143	2.337	193.263	6.821	296.904	8.696	30.750	0.748
63.064	2.488	198.388	6.939	302.178	8.753	32.820	0.855
66.140	2.639	203.522	7.043	307.399	8.867	34.996	0.971
69.370	2.799	208.659	7.157	312.584	8.936	37.321	1.095
72.769	2.962	213.799	7.258	317.738	9.000	39.794	1.230
76.349	3.120	224.142	7.468	322.846	9.089		
80.104	3.300	229.617	7.542	327.938	9.117	Series IV	
84.051	3.480	235.862	7.682	332.981	9.205	264.220	8.159
88.202	3.659	242.431	7.807	337.989	9.278	270.485	8.264
92.567	3.843	247.982	7.893	342.958	9.341	279.773	8.432
97.169	4.020	253.711	7.980	347.900	9.367	282.834	8.481
102.017	4.194	259.331	8.079			285.879	8.520
106.997	4.373	265.207	8.204		Series III	288.912	8.590
111.996	4.554	271.179	8.266	9.953	0.035	294.949	8.676
117.011	4.718	249.526	7.899	10.912	0.048	300.905	8.755
121.995	4.905	254.896	7.995	12.014	0.064	306.825	8.868
127.009	5.070	260.209	8.109	13.123	0.084	315.591	9.000
132.062	5.229	265.473	8.200	14.247	0.108	318.504	8.998
137.122	5.383	270.684	8.297	15.404	0.136	321.383	9.081
142.198	5.512	275.858	8.360				
By differential scanning calorimetry							
	Crystal II	410.0	10.22	480.0	10.99		Liquid
340.0	9.23	415.0	10.31	490.0	11.03	545.0	15.70
345.0	9.34	420.0	10.36	495.0	11.13	560.0	16.18
350.0	9.46	425.0	10.42			565.0	16.30
355.0	9.50	430.0	10.48		Crystal I	570.0	16.36
360.0	9.58	435.0	10.53	495.0	11.65	575.0	16.47
365.0	9.64	440.0	10.56	510.0	11.70	580.0	16.49
370.0	9.76	445.0	10.57	515.0	11.76		
375.0	9.79	450.0	10.65	520.0	11.81		
380.0	9.88	455.0	10.68	525.0	11.82		
385.0	9.90	460.0	10.78	530.0	11.86		
390.0	9.98	465.0	10.83	535.0	11.87		
395.0	10.04	470.0	10.90	540.0	12.04		
405.0	10.17	475.0	10.92	545.0	12.15		
			Lithium ethanoate (CH_3COOLi)				
			Crystal I				
By adiabatic calorimetry							
	Series I	41.049	2.575	115.689	6.379	261.133	10.612
5.840	0.043	43.800	2.785	120.743	6.569	267.267	10.781

continued

TABLE 2—*continued*

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
6.376	0.056	46.570	2.993	125.809	6.744	273.436	10.926
6.974	0.069	49.544	3.212	130.883	6.922	279.626	11.097
7.452	0.084	52.725	3.418	135.966	7.092	285.803	11.256
7.975	0.099	55.922	3.627	141.052	7.266	291.978	11.425
8.418	0.116	59.318	3.856	146.147	7.428	298.182	11.551
8.854	0.147	62.926	4.067	151.239	7.586	304.340	11.696
9.360	0.171	66.008	4.246	156.351	7.743		
9.798	0.187	69.142	4.406	161.467	7.898	Series III	
10.485	0.212			166.563	8.069	254.271	10.441
11.466	0.272	Series II		171.679	8.218	260.152	10.620
12.568	0.343	53.132	3.452	176.807	8.365	266.334	10.725
13.678	0.410	56.418	3.666	181.935	8.511	272.482	10.896
14.811	0.484	59.181	3.841	187.065	8.643	278.652	11.038
16.081	0.571	62.104	4.016	192.597	8.809	284.801	11.194
17.493	0.675	65.163	4.201	196.870	8.926	290.955	11.400
18.917	0.782	68.386	4.364	201.649	9.059	297.137	11.508
20.357	0.893	71.785	4.540	207.740	9.220	303.322	11.639
21.943	1.008	75.359	4.723	211.125	9.319	309.502	11.787
23.666	1.146	79.112	4.910	215.901	9.425	315.686	11.897
25.403	1.285	83.058	5.097	221.331	9.586	321.855	12.029
27.285	1.434	87.205	5.289	226.995	9.734	328.021	12.162
29.311	1.612	91.572	5.466	232.633	9.936	334.202	12.288
31.353	1.778	96.166	5.648	238.259	10.029	340.394	12.369
33.584	1.973	101.000	5.833	243.927	10.156	346.581	12.445
35.987	2.202	105.794	6.018	249.572	10.332		
38.437	2.367	110.637	6.195	255.227	10.446		
By differential scanning calorimetry							
Crystal I		400.0	13.54	465.0	14.73	530.0	15.71
340.0	12.18	405.0	13.61	470.0	14.85	535.0	15.77
345.0	12.34	410.0	13.81	475.0	14.93	540.0	15.87
350.0	12.48	415.0	13.86	480.0	15.01	545.0	15.95
355.0	12.56	420.0	13.93	485.0	15.10	550.0	16.03
360.0	12.68	425.0	14.03	490.0	15.21	555.0	16.21
365.0	12.78	430.0	14.13	495.0	15.29		
370.0	12.91	435.0	14.17	500.0	15.32	Liquid	
375.0	12.96	440.0	14.28	505.0	15.46	570.0	22.41
380.0	13.09	445.0	14.34	510.0	15.39	575.0	22.57
385.0	13.22	450.0	14.46	515.0	15.40	580.0	22.55
390.0	13.35	455.0	14.52	520.0	15.54		
395.0	13.38	460.0	14.64	525.0	15.59		

phases of the two salts since in glasses, which are not in thermodynamic equilibrium, structural relaxation is controlled by kinetic quantities, in particular by the cooling rate from the melt, requiring further study. The collected results are briefly discussed with reference to heat capacities presently available on the above-mentioned alkali alkanoates.

2. Experimental

Lithium methanoate was prepared by adding to a hot suspension in deionized water of Fluka puriss. p.a. > 99.5 mass per cent lithium carbonate a slight excess (<0.5

mass per cent) of C. Erba R.P.A. 85 mass per cent of formic acid. After filtration, the solvent was evaporated under reduced pressure in a Rotavapor device at $T \approx 350$ K. The product was dissolved in a hot mixture of water and Fluka puriss. p.a. > 99.5 moles per cent methanol (volume ratio: 1) and lithium methanoate monohydrate was allowed to crystallize overnight at $T \approx 277$ K. This salt was dried under vacuum overnight at $T \approx 350$ K, then ground and finally dried under vacuum for 10 h at $T = 370$ K and for 10 h at $T = 380$ K.

Lithium ethanoate was prepared by adding to a hot suspension in deionized water of Fluka puriss. p.a. > 99.5 mass per cent lithium carbonate a slight excess (< 0.5 mass per cent) of Merck Suprapur 96 mass per cent of acetic acid. After refluxing for 1 h and standing overnight, the solvent was evaporated under reduced pressure in a Rotavapor device at $T \approx 350$ K. This product was dried for 10 h in a vacuum oven at $T \approx 350$ K and for 2 h at $T = 380$ K. The salt was then dissolved in hot anhydrous methanol, the solution was filtered and CH_3COOLi was precipitated with a mixture of $\{4CH_3CH(OH)CH_3 + c\text{-}CH_2CH_2OCH_2CH_2O\}$; all the solvents were Fluka puriss. p.a. grade. After partial evaporation of the solvent, the salt was filtered and dried in a vacuum oven at $T \approx 340$ K overnight, then ground and finally dried under vacuum for 10 h at $T = 380$ K.

The purity of either salt was determined by means of d.s.c., after calibration of the method with the series of phenacetin samples of the "Thermal Analysis purity set" (Standard Reference Material n. 1514) purchased from the National Bureau of Standards (NBS, presently designated as National Institute for Science and Technology, NIST), U.S.A.[24] The mole-fraction purities were found to be 0.9988 and 0.9991 for the HCOOLi and the CH_3COOLi, respectively, and are considered satisfactory for thermodynamic studies.

Density measurements were carried out with the specific-gravity-bottle method, employing C. Erba R.P.E. > 99.5 mass per cent toluene as the liquid of known density. The collected values are the average over at least seven results taken with each of two different bottles at $T = 298.15$ K. The experimental densities were

$$\text{lithium methanoate:} \quad \rho = (1.41 \pm 0.02)\ \text{g·cm}^{-3},$$

$$\text{lithium ethanoate:} \quad \rho = (1.26 \pm 0.02)\ \text{g·cm}^{-3}.$$

Calorimetric techniques. Adiabatic calorimetry: molar heat capacities between $T \approx 5$ K and 350 K were determined by adiabatic equilibrium calorimetry in the Mark XIII calorimetric cryostat. The design is an enhancement of the Mark X type cryostat previously described[25] to include only copper radiation shields, a more convenient mounting of demountable thermocouples on the guard shield, and the fitting of the thermocouple junctions into minute machined oxygen-free high-conductivity (OFHC) copper sheaths.

The same gold-plated OFHC copper calorimeter (laboratory designation W-62) was used for both samples. The calorimeter had a mass of 39.592 g and an internal volume of 79.17 cm^3. The calorimeter temperature was measured with a Leeds & Northrup, platinum-encapsulated platinum resistance thermometer in an entrant well. The thermometer was calibrated by the U.S. NBS against IPTS-48 and is

TABLE 3. Thermodynamic quantities for the phase transitions in HCOOLi and CH_3COOLi $\{M(HCOOLi) = 51.958\ g\cdot mol^{-1};\ M(CH_3COOLi) = 65.985\ g\cdot mol^{-1};\ R = 8.31451\ J\cdot K^{-1}\cdot mol^{-1}\}$

Phase change	T_{trs}/K	$\Delta_{trs}H^{\circ}_m/(R\cdot K)$	$\Delta_{trs}S^{\circ}_m/R$
		HCOOLi	
II-to-I	495 ± 1	222 ± 5	$0.44_9 \pm 0.07$
fusion	545 ± 1	1937 ± 26	$3.55_5 \pm 0.05$
		CH_3COOLi	
fusion	558 ± 1	1431 ± 26	$2.56_5 \pm 0.05$

considered to reproduce thermodynamic temperatures to within 0.03 K from $T = 5$ K to 300 K. The heat capacity of the empty calorimeter was determined in a separate series of measurements.

The HCOOLi and CH_3COOLi samples (44.526 g and 49.607 g) corresponded to 0.85697 mol and 0.75180 mol on the basis of IUPAC 1988 atomic masses (51.958 $g\cdot mol^{-1}$ and 65.985 $g\cdot mol^{-1}$, respectively). To facilitate more rapid thermal equilibration, a pressure ≈ 5.0 kPa of helium gas at $T = 300$ K was introduced into the calorimeter following its evacuation and the calorimeter was sealed. The heat capacity of the sample represented 95 per cent of the total heat capacity at $T = 10$ K and about (80 to 85) per cent at higher temperatures. Buoyancy corrections were calculated using the above-mentioned density values.

Differential scanning calorimetry was performed by means of a Perkin-Elmer DSC-2 instrument calibrated as previously described,[26] and operated with the scanning procedure. The powder samples were pressed in form of pellets, ≈ 1 mm high and 4 mm in diameter. After preparation, these pellets were kept for 24 h at $T = 373$ K under vacuum, then stored in a vacuum desiccator with P_2O_5 for 15 d, and finally tightly sealed in Al volatile-sample pans kept at $T \approx 370$ K. The sample masses were in the range (12 to 25) mg. The reported results have been collected on four samples of either salt, according to the procedure used for heat-capacity measurements in previous works.[9, 26] In the temperature range considered, the uncertainty of the temperature measurements at the adopted scan speed of 0.167 $K\cdot s^{-1}$ was within ±0.2 K.

3. Results and discussion

The experimental molar heat-capacity values for HCOOLi and CH_3COOLi from adiabatic calorimetry and differential scanning calorimetry determinations are presented in table 2. The smoothed values are compared in figure 2.

The low-temperature values will be seen to be sigmate with no obvious excess contributions over that entire temperature range of measurement. In the d.s.c. region, the methanoate undergoes the crystal-II-to-crystal-I transition, with the latter phase extending into a region of metastability (not shown in the figure) below the transition

TABLE 4. Smoothed molar thermodynamic functions at selected temperatures for lithium methanoate and lithium ethanoate ($R = 8.31451\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)

T/K	$C_{p,m}/R$	$\Delta_0^T S_m^\circ/R$	$\Delta_0^T H_m^\circ/(R \cdot K)$	Φ_m°/R
		Lithium methanoate (HCOOLi) Crystal II		
0	0	0	0	0
5	(0.004)	(0.001)	(0.005)	(0.000)
10	0.036	0.012	0.088	0.003
15	0.126	0.041	0.465	0.010
20	0.279	0.097	1.452	0.024
25	0.477	0.180	3.328	0.047
30	0.710	0.287	6.282	0.077
35	0.971	0.416	10.478	0.116
40	1.240	0.563	16.007	0.163
45	1.515	0.725	22.890	0.216
50	1.789	0.899	31.161	0.275
60	2.332	1.274	51.80	0.410
70	2.832	1.671	77.66	0.562
80	3.293	2.080	108.31	0.726
90	3.721	2.493	143.41	0.899
100	4.118	2.906	182.63	1.079
110	4.489	3.316	225.69	1.264
120	4.836	3.721	272.33	1.452
130	5.160	4.121	322.33	1.642
140	5.466	4.515	375.47	1.833
150	5.753	4.902	431.58	2.025
160	6.025	5.282	490.48	2.217
170	6.281	5.655	552.0	2.408
180	6.524	6.021	616.1	2.598
190	6.754	6.380	682.5	2.788
200	6.974	6.732	751.1	2.976
210	7.182	7.077	821.9	3.164
220	7.382	7.416	894.7	3.349
230	7.573	7.748	969.5	3.533
240	7.756	8.075	1046.2	3.716
250	7.932	8.395	1124.6	3.896
260	8.102	8.709	1204.8	4.076
270	8.267	9.018	1286.6	4.253
280	8.427	9.322	1370.1	4.429
290	8.583	9.620	1455.1	4.602
298.15	8.707	9.860	1525.6	4.743
300	8.735	9.914	1541.7	4.775
325	9.101	10.627	1764.7	5.198
350	9.452	11.315	1996.7	5.610
375	9.786	11.978	2237.2	6.013
400	10.103	12.620	2485.8	6.406
425	10.399	13.242	2742.2	6.790
450	10.670	13.844	3005.6	7.165
475	10.920	14.428	3275.5	7.532
495	(11.114)	(14.882)	(3495.8)	(7.820)

continued

TABLE 4—*continued*

T/K	$C_{p,m}/R$	$\Delta_0^T S^\circ_m/R$	$\Delta_0^T H^\circ_m/(R\cdot K)$	Φ°_m/R
		Crystal I		
495	(11.648)	(15.33)	(3717.8)	(7.820)
500	11.688	15.45	3776.2	7.895
525	11.807	16.02	4069.8	8.269
545	(12.150)	(16.47)	(4308.6)	(8.561)
		Liquid		
545	(15.70)	(20.02)	(6246)	(8.561)
550	15.88	20.17	6325	8.666
575	16.45	20.89	6730	9.182
580	16.49	21.03	6812	9.283
		Lithium ethanoate (CH_3COOLi)		
		Crystal I		
0	0	0	0	0
5	(0.028)	(0.010)	(0.036)	(0.002)
10	0.192	0.070	0.519	0.018
15	0.499	0.203	2.203	0.056
20	0.863	0.396	5.600	0.116
25	1.256	0.629	10.868	0.194
30	1.683	0.896	18.233	0.289
35	2.096	1.187	27.687	0.396
40	2.494	1.493	39.168	0.514
45	2.873	1.809	52.59	0.640
50	3.231	2.130	67.86	0.773
60	3.884	2.778	103.50	1.053
70	4.456	3.421	145.27	1.346
80	4.960	4.050	192.40	1.645
90	5.408	4.660	244.28	1.946
100	5.814	5.251	300.42	2.247
110	6.191	5.823	360.46	2.546
120	6.545	6.377	424.16	2.843
130	6.885	6.915	491.32	3.135
140	7.213	7.437	561.8	3.424
150	7.532	7.946	635.5	3.709
160	7.843	8.442	712.4	3.989
170	8.147	8.926	792.4	4.265
180	8.444	9.400	875.3	4.537
190	8.735	9.865	961.2	4.806
200	9.020	10.320	1050.0	5.070
210	9.298	10.767	1141.6	5.331
220	9.570	11.206	1236.0	5.588
230	9.837	11.637	1333.0	5.841
240	10.098	12.061	1432.7	6.092
250	10.354	12.479	1534.9	6.339
260	10.604	12.890	1639.7	6.583
270	10.848	13.294	1747.0	6.824
280	11.085	13.693	1856.7	7.062
290	11.315	14.086	1968.7	7.298
298.15	11.497	14.402	2061.6	7.488
300	11.537	14.474	2083.0	7.530
325	12.059	15.42	2378.0	8.101

continued

TABLE 4—*continued*

T/K	$C_{p,m}/R$	$\Delta_0^T S_m^\circ/R$	$\Delta_0^T H_m^\circ/(R\cdot K)$	Φ_m°/R
350	12.542	16.33	2685.6	8.656
375	13.009	17.21	3005.0	9.198
400	13.487	18.07	3336.1	9.725
425	13.990	18.90	3679.5	10.240
450	14.493	19.71	4035.6	10.744
475	14.943	20.51	4403.8	11.237
500	15.30	21.28	4782.0	11.720
550	16.07	22.77	5564	12.658
558	(16.27)	(23.01)	(5693)	(12.805)
		Liquid		
558	(22.26)	(25.57)	(7124)	(12.805)
560	22.28	25.65	7169	12.850
565	22.36	25.85	7280	12.964
570	22.43	26.05	7392	13.078
575	22.50	26.24	7504	13.192
580	22.57	26.44	7617	13.305

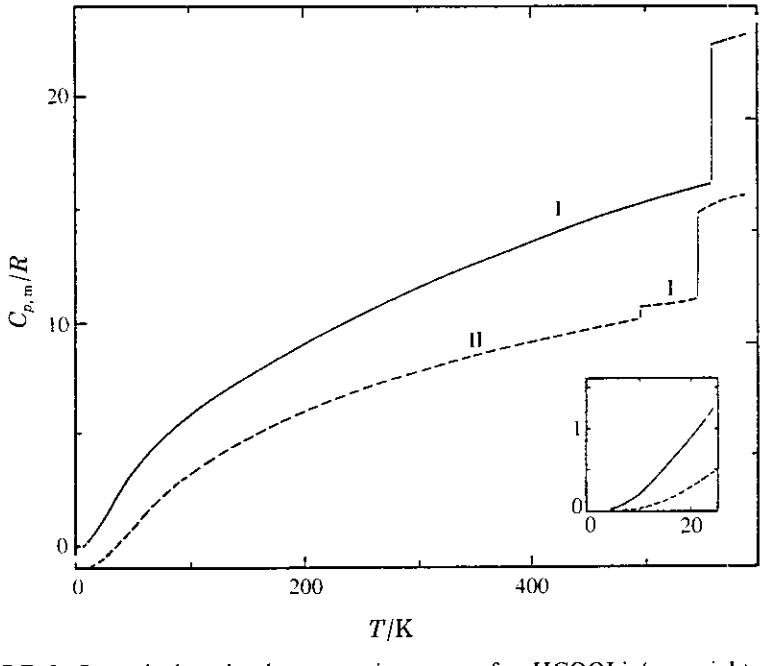

FIGURE 2. Smoothed molar heat-capacity curves for HCOOLi (- - -, right scale) and CH_3COOLi (——, left scale). The two scales are drawn at slightly different heights to prevent confusion in the high-temperature range.

region. This transition has been described[12] as a change from the hexagonal structure, obtained by crystallization from solution and stable at room temperature, to the monoclinic structure which can be crystallized from the melt[10] and is stable at high temperature. From figure 1 it is clear that the hexagonal phase corresponding to crystal II can be also obtained from the crystallization of the metastable glassy material upon heating.

Both compounds show a crystal-I-to-liquid transition to an isotropic-liquid region. In a temperature range of (20 to 30) K above fusion the molten phase is stable enough to allow one to record some reproducible d.s.c. scans without significant decomposition phenomena, since the mass of each sample was checked and found approximately constant (within $\pm 5\,\mu g$) after the measurements.

The thermodynamic functions as determined by d.s.c. for the considered phase transitions are presented in table 3, and can be compared with prior values determined with various techniques reported in table 1. In the present work, glass-transition temperatures of (354 ± 2) K for HCOOLi and (407 ± 2) K for CH_3COOLi were found, in good agreement with those previously observed.[9,15-18] As for the solid-to-solid transition occurring in the methanoate, a reasonable agreement also exists between the present and previous results.[9,11] This phase change should be identified with the transition from crystal-II-to-crystal-I described by Müller *et al.*[12] as a fast transition when it takes place on heating, and a slow one, when it occurs on cooling. Thus, no contradiction seems to exist in the fact that molten HCOOLi on cooling may crystallize in the form of monoclinic crystals of the I type, whereas glassy HCOOLi on heating above T_g crystallizes in hexagonal crystals of the II type, which in turn undergo the mentioned transition at $T = 495$ K.

For either salt, the temperatures and molar enthalpies of fusion available in the literature are in reasonable accord with the present determinations. The present value for the molar fusion enthalpy of CH_3COOLi is slightly lower than that by Tucker[16] and somewhat higher than that by Gonchukova.[18] The non-specified transition found by Diogenov[19] at $T = (530$ to $536)$ K on lithium ethanoate might be assigned to a small premelting heat effect which has also been recorded in the present work in first d.s.c. scans on CH_3COOLi, and is poorly reproducible in subsequent scans.

With reference to the curves illustrated in figure 2, the two series measured by adiabatic calorimetry and d.s.c. for the methanoate overlap very satisfactorily at $T = (340$ to $350)$ K, their difference being within (1 to 2) per cent. Slightly higher discrepancies, not larger than (1.5 to 2.5) per cent, are found for the ethanoate and are thus within combined reliabilities of both measurements. For both compounds, however, the curves of the adiabatic calorimetry and d.s.c. experimental values seem to display the same slopes.

The smoothed heat capacities at selected temperatures and the derived thermodynamic functions generated by the FITAB-2 program[27] are listed in table 4. Extrapolations below the lowest temperatures of measurements were achieved by plots of $C_{p,m}/R$ against T^2.

The reliability of these results in terms of standard deviations can be characterized as 4 per cent at $T < 10$ K, decreasing gradually to 0.2 per cent at $T = 20$ K, and < 0.2

up to $T = 300$ K, 0.5 up to $T = 350$ K, and (1.5 to 2.5) per cent in the d.s.c. region for both compounds.

A comprehensive picture of the heat capacities measured on the lithium alkanoates with linear hydrocarbon chains from HCOOLi to $CH_3(CH_2)_5COOLi$ is shown in figure 3. It appears that the carboxylates with shorter chains do not undergo phase transitions at low temperatures. In the methanoate and in the propanoate phase changes occur at $T = 495$ and 533 K, *viz.* at temperatures not far from the melting temperature, whereas the pentanoate and the heptanoate undergo phase transitions in the T range (209 to 330) K and around 317 K, respectively.[5] Continuous and gradual transformations were found for the propanoate at $T > 280$ K,[3] for the butanoate at $T > 160$ K,[4] and twice for the hexanoate at $T > 130$ K and $T > 260$ K.[4] These phenomena may be indicative of the progressive activation of either vibrational degrees of freedom or the rotation of the methyl end group.

In a previous paper on the thermodynamic properties of Li alkanoates,[28] an attempt to evaluate the heat capacities of these substances in terms of the number of CH_2 increments in the chain was reported. As for HCOOLi and CH_3COOLi, both compounds are characterized by such a short carbon chain that the CH_2 increment is not yet regular and cannot display a constant value if compared with the homologs with longer linear chains.

On the basis of the present thermodynamic results, one can also make some comparisons with the properties of salts formed with the same anion and different cations.

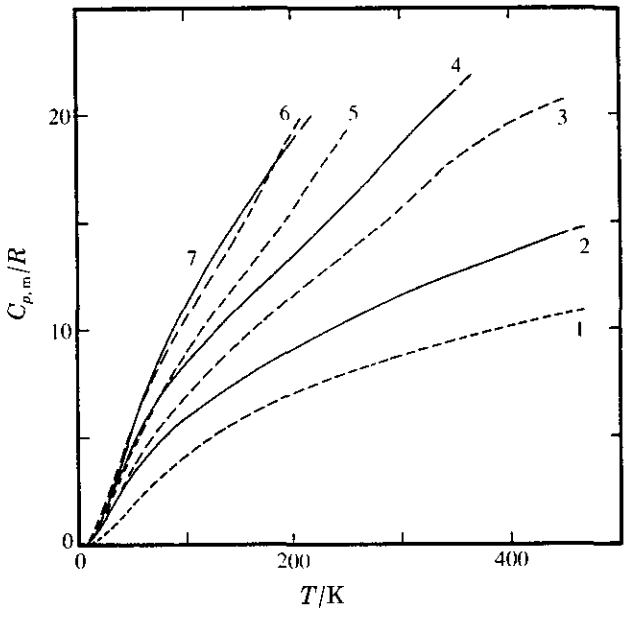

FIGURE 3. Molar heat-capacity curves at low temperatures for the lithium linear alkanoates from 1: HCOOLi to 7: $CH_3(CH_2)_5COOLi$. - - -, Odd and —, even number of carbon atoms in the chain. Curves: 1, 2, this work; 3, from reference 3; 4, 6, from reference 4; 5, 7, from reference 5.

The only other methanoate studied so far is HCOONa.[1,9] In figure 4, the comparison of the heat-capacity curves of the two methanoates is illustrated. Although undergoing one solid-to-solid transition and melting at similar temperatures, they display a different behavior in particular at the phase transition, which occurs with a positive $\Delta C_{p,m}$ in HCOOLi, and with a slightly negative $\Delta C_{p,m}$ in HCOONa. The corresponding molar entropy change is higher for HCOOLi ($\Delta_{trs}S^\circ_m = 0.44_9 \cdot R$) than for HCOONa: ($\Delta_{trs}S^\circ_m = 0.297 \cdot R$),[1] or ($\Delta_{trs}S^\circ_m = 0.282 \cdot R$),[29] whereas the change of the molar fusion entropy is somewhat higher for HCOONa: ($\Delta_{fus}S^\circ_m = 4.015 \cdot R$),[1] or ($\Delta_{fus}S^\circ_m = 3.888 \cdot R$),[29] than for HCOOLi: ($\Delta_{fus}S^\circ_m = 3.555 \cdot R$).

For the ethanoates, available thermodynamic information concerns not only CH_3COONa,[1,9] but also CH_3COOK.[2,9] Figure 5 illustrates the heat-capacity curves of the three compounds between $T = 5$ K and 630 K, showing in particular the simpler behavior of the lithium salt, whereas CH_3COONa and CH_3COOK between $T = 300$ K and fusion (in the regions included in the rectangles) undergo solid-to-solid phase transitions. The melting mechanism seems much simpler for CH_3COOLi, which exists in one crystalline phase only, and more complicated for CH_3COOK and CH_3COONa. Moreover, it may be noticed that the heat capacities of the three salts in the molten state are of about the same size, the present values for CH_3COOLi being slightly higher than those for CH_3COONa,[9] and CH_3COOK.[2]

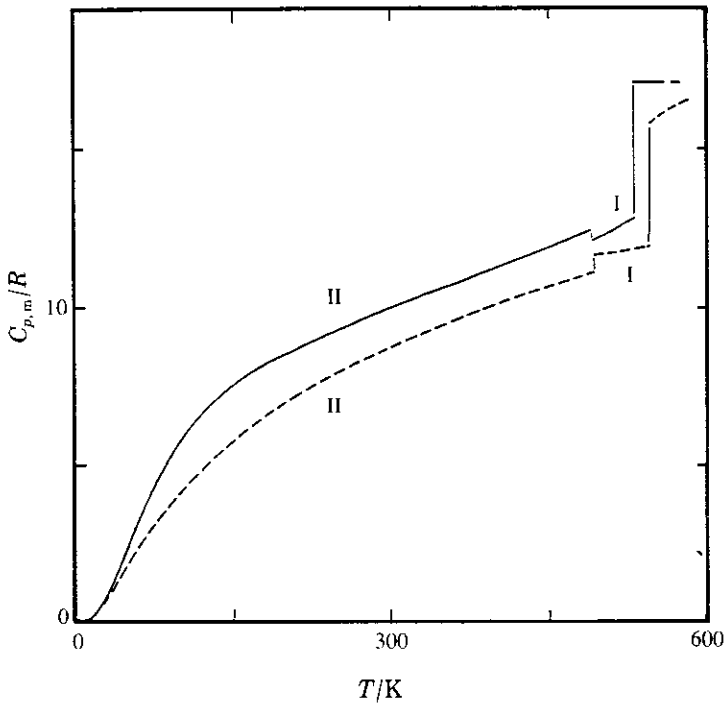

FIGURE 4. Comparison between smoothed molar heat capacities of - - -, HCOOLi (this work) and ——, HCOONa.[1,9]

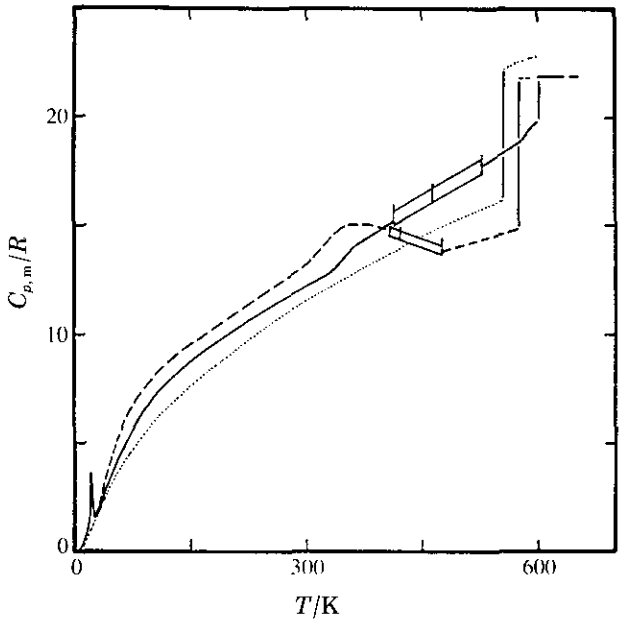

FIGURE 5. Comparison between smoothed molar heat capacities: ····, CH_3COOLi (this work); ——, CH_3COONa;[1,9] - - -, CH_3COOK.[2]

A final comment may be made comparing the heat capacities of CH_3COOLi above room temperature, as determined by d.s.c. in the present work, with those given by Tucker[16] and Gonchukova,[18] also measured by d.s.c. Both their series of heat capacities are lower than the present ones, whereas their molar enthalpies of fusion are approximately the same, as mentioned above. The deviation of Tucker's results is within (6 to 17) per cent for solid CH_3COOLi, and (4 to 5) per cent for the molten phase. Higher discrepancies, of about (26 to 31) per cent, were found between the present results and those of reference 18, possibly due to a lower accuracy of the instrument calibration and of the measurement procedures of that work.

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