

Thermodynamics of alkali alkanooates

IX.^a Heat capacity and thermodynamic functions of lithium 2-methylpropanoate at temperatures from 7 K to 535 K

Stanley P. Ngeyi,

*Department of Chemistry, Madonna University,
Livonia, MI 48150, U.S.A.*

Ramin Abhari,^b and Edgar F. Westrum, Jr.

*Department of Chemistry, University of Michigan,
Ann Arbor, MI 48109, U.S.A.*

(Received 31 March 1993)

The heat capacity of lithium 2-methylpropanoate was measured by equilibrium adiabatic calorimetry at temperatures T from 7 K up to 350 K and by d.s.c. from 330 K through melting to 535 K. A small diffuse hump was observed in the range $T = 125$ K to 250 K. A solid-to-solid (intercrystalline) transition was observed at $T = 445$ K, and melting to the isotropic liquid occurred at 510 K. The enthalpies $\Delta_{\text{trs}}H_m^\circ$ and entropies $\Delta_{\text{trs}}S_m^\circ$ of transition were calculated to be $903R \cdot K$ and $2.03R$ for the solid-to-solid transformation (assumed to be first order) and $1045R \cdot K$ and $2.05R$ for melting.

1. Introduction

The thermophysical properties of potassium butanoate (K4C)⁽¹⁾ and lithium butanoate (Li4C)⁽²⁾ have been measured and reported earlier. In K4C two close but distinct intercrystalline transformations were observed at temperatures T between 100 K and 200 K. In Li4C, however, only a broad thermodynamic transformation spanning a temperature interval of over 100 K was observed at about 160 K. Such transformations—as in Li4C—were also observed in lithium hexanoate (Li6C)⁽²⁾ but they occurred over two temperature intervals—about (120 to 250) K and about (260 to 330) K.

In this study we examine the thermophysics of lithium 2-methylpropanoate, hereafter designated Li4iC (*i.e.* “isobutanoate”) which is a branched-chain member of the homologous series of lithium alkanooates. This is one of the first branched-chain alkanooates to have been studied by adiabatic calorimetry. The study of this compound is pertinent (a), to establish the role of branched chains on the phase

^a The preceding paper in this series was mistakenly numbered VII rather than VIII.

^b Work done while a student at the College of Wooster, Wooster, Ohio, U.S.A.

transformation of long-chain compounds; (b), to establish the role played by branched chains on the heat capacity of long-chain compounds; (c), to establish that branched-chain compounds of organic soaps are stable enough to be studied (such compounds have had little or no attention because they were assumed to be unstable under the thermal conditions of study;⁽³⁾ (d), to understand further why these compounds do not form mesomorphic (liquid-crystalline) phases (it has been suggested that this is so because branched-chain carboxylates do not provide the rigid anions necessary for the formation of the liquid-crystalline phase;⁽³⁾ and (e), to verify that the scheme for the heat-capacity increment ΔC_p of a CH_2 group⁽²⁾ developed using the $C_{p,s}$ of Li4C and Li6C , which are straight-chain compounds, can be extended to branched-chain compounds.

Li4iC does not exhibit a mesomorphic phase.⁽³⁾ The existence of the broad hump observed between $T \approx 125$ K and $T \approx 250$ K is similar to and almost coincident with the same phenomenon observed in Li4C and Li6C .⁽²⁾

Good agreement between d.s.c. and equilibrium adiabatic calorimetry was obtained over the common temperature range of determination.

2. Experimental

The lithium 2-methylpropanoate used was prepared by the method described elsewhere^(1,2) except that an excess of lithium carbonate was used instead of an excess of 2-methylpropionic acid.^(3,4) The use of excess lithium carbonate was necessitated by earlier observation of a molecular complex formed when excess acid was used.⁽⁵⁾ The purity was determined by using d.s.c.-4 purity software with the Dupont Thermal Analysis Data Station (TADS) program as described earlier,⁽⁶⁾ and was considered adequate for thermodynamic studies. The use of this instrument for heat-capacity acquisition using the heat-capacity software from Dupont and treatment of the sample for purity determination are also discussed in the same reference.⁽⁶⁾

The remaining sample of mass 7.1125 g was loaded into a gold-plated oxygen-free high-conductivity copper calorimeter (laboratory designation W-139). The sample was loaded and after thorough evacuation checked by a leak detector; dry helium gas, at a pressure of 4.3 kPa, was added to facilitate thermal equilibration during acquisition of results. The calorimeter was placed in the Mark X cryostat⁽⁷⁾ provided with a facility for computer-assisted acquisition and logging of results. The Leeds and Northrup platinum resistance thermometer used was calibrated by the U.S. National Bureau of Standards (NBS). Moreover, other crucial calibration values were also referred to standards at NBS. Buoyancy corrections were evaluated for the sample mass using a density of $1.09 \text{ g} \cdot \text{cm}^{-3}$ estimated from that of other members of the homologous series.

3. Results and discussion

The experimental heat-capacity values are provided in table 1 for both techniques used in these determinations; the thermodynamics of the two transitions are

TABLE 1. Experimental heat capacities of lithium 2-methylpropanoate ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

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	$C_{p,m}/R$
By adiabatic calorimetry											
7.84	0.060	30.51	1.625	65.20	4.730	101.18	7.402	158.07	11.239	252.89	15.661
8.76	0.062	32.56	1.859	66.67	4.894	102.90	7.570	163.16	11.741	259.14	15.891
9.42	0.092	34.79	1.888	69.94	5.096	103.47	7.610	168.25	12.053	265.02	16.131
10.29	0.119	37.00	2.250	70.42	5.217	104.74	7.702	173.38	12.571	271.08	16.329
11.33	0.153	39.31	2.496	73.36	5.435	107.84	7.928	178.83	12.926	277.15	16.669
12.58	0.187	41.65	2.683	74.26	5.450	110.10	8.077	184.48	13.169	283.20	16.934
13.93	0.243	44.00	2.929	76.99	5.681	112.81	8.444	190.06	13.328	289.33	17.234
14.88	0.285	46.27	3.050	79.46	5.885	115.28	8.450	195.69	13.439	295.62	17.547
15.91	0.345	48.43	3.314	80.79	5.960	117.77	8.650	201.17	13.739	301.74	17.863
17.34	0.426	50.85	3.537	84.44	6.319	121.24	8.899	206.84	13.962	307.71	18.195
18.69	0.542	53.55	3.775	84.77	6.334	122.63	9.064	211.88	14.154	313.66	18.514
20.14	0.658	55.72	3.890	88.96	6.632	127.68	9.253	217.29	14.340	319.83	18.895
21.51	0.781	56.24	3.927	89.50	6.700	132.72	9.665	222.79	14.559	325.63	19.250
23.07	0.851	59.01	4.226	93.39	6.856	137.78	9.967	228.47	14.762	331.46	19.640
24.80	1.016	60.64	4.352	94.57	6.969	142.88	10.285	234.43	14.995	337.25	20.029
26.53	1.270	62.01	4.432	98.01	7.275	147.91	10.567	240.65	15.196	342.96	20.603
28.43	1.458	63.57	4.636	99.23	7.303	152.97	11.153	246.88	15.433	347.36	20.607
By differential scanning calorimetry											
330	19.9	365	22.30	400	25.04	435	33.5	480	30.19	515	50
335	20.22	370	22.60	405	25.40	440	55.5	485	30.65	520	29.0
340	20.44	375	22.84	410	25.95	445	125	490	31.29	525	28.9
345	20.74	380	23.33	415	26.35	450	39.6	495	31.84	530	28.7
350	21.09	385	23.79	420	26.74	460	28.31	500	32.36	535	28.7
355	21.49	390	24.21	425	27.38	470	29.19	505	33.46		
360	21.87	395	24.56	430	28.59	475	29.70	510	280		

summarized in table 2. These values are used to plot the heat-capacity curve depicted in figure 1. The heat capacities were fitted to a series of orthogonal polynomials in regions of no anomalies and smoothed values are presented at selected temperatures in table 3. Integration of the appropriate polynomials yielded the thermodynamic functions listed in table 3.

To calculate the excess enthalpies and entropies associated with each transformation, appropriate lattice heat-capacity curves were drawn over the regions

TABLE 2. Transitional thermodynamic properties of lithium 2-methylpropanoate ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

Transition phases	T_1/K	T_2/K	$T_{\text{trs}}/\text{K}^a$	$\Delta_{\text{trs}}H_m^\circ/(R \cdot \text{K})^b$ (This work)	$\Delta_{\text{trs}}H_m^\circ/(R \cdot \text{K})$ (Ref. 9)	$\Delta_{\text{trs}}S_m^\circ/R$ (This work)
II \rightarrow I ^c	325	460	445	903 ± 20	885 ± 35	2.03
I \rightarrow Isotropic-liquid (i.e. melting at triple point) ^c	500	520	510	1045 ± 20	1036 ± 25	2.05

^aThese are peak temperatures.

^bThe uncertainties are estimated standard deviations. Transition values calculated by extrapolating lattice heat capacities from T_1 and T_2 to the transition temperatures.

^cThis work.

TABLE 3. Smoothed heat capacities and derived thermodynamic values of lithium 2-methylpropanoate at selected temperatures ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)^a

T/K	$C_{p,m}/R$	$\Delta_0^T S_m^0/R$	$\Delta_0^T H_m^0/(R \cdot \text{K})$	Φ_m^0/R
Phase II				
0	(0)	(0)	(0)	(0)
10	0.100	0.037	0.274	0.010
15	0.291	0.113	1.236	0.030
20	0.641	0.241	3.507	0.065
25	1.047	0.423	7.624	0.118
30	1.594	0.669	14.405	0.188
35	1.923	0.931	22.937	0.276
40	2.543	1.235	34.361	0.376
45	2.932	1.561	48.215	0.490
50	3.451	2.104	73.83	0.628
60	4.309	2.813	112.86	0.933
70	5.141	3.539	160.02	1.253
80	5.961	4.280	215.63	1.585
100	7.349	5.760	348.76	2.272
120	8.834	7.232	510.8	2.976
140	10.064	8.689	700.0	3.689
160	11.486	10.121	914.9	4.403
180	12.896	11.560	1159.5	5.118
200	13.713	12.965	1426.4	5.833
220	14.425	14.304	1707.5	6.543
240	15.21	15.59	2004.0	7.244
260	15.90	16.84	2315.0	7.934
280	16.79	18.05	2641.6	8.614
298.15	17.67	19.13	2954.3	9.221
300	17.76	19.24	2987.1	9.282
320	18.92	20.42	3353.5	9.942
325 ^b	19.22	20.72	3448.8	10.11
	[19.22]	[20.72]	[3448.8]	[10.11]
350	21.1	22.22	3952.8	10.93
	[20.8]	[22.21]	[3949.1]	[10.93]
375	22.9	23.73	4502.8	11.72
	[22.4]	[23.69]	[4489.1]	[11.72]
400	25.0	25.27	5101.6	12.52
	[24.0]	[25.17]	[5069.1]	[12.50]
425	27.6	26.85	5759.1	13.30
	[25.6]	[26.63]	[5689.1]	[13.24]
445 ^c	(~125)	27.80	6210.0	13.84
	[26.8]	[27.80]	[6210]	[13.84]
Phase I				
445 ^c	(~125)	(29.83)	(7116)	(13.84)
	[26.8]	[27.80]	[6210]	[13.84]
460 ^b	28.3	30.75	7530	14.38
	[28.3]	[28.72]	[6624]	[14.32]
475	29.7	31.67	7965	14.90
500 ^b	32.4	33.38	8741	15.90
	[32.4]	[31.36]	[7835]	[15.69]
510 ^c	(~280)	[34.04]	(9070)	(16.26)
	[33.4]	[32.02]	[8164]	[16.01]

TABLE 3—continued

T/K	$C_{p,m}/R$	$\Delta_0^{\circ}S_m^{\circ}/R$	$\Delta_0^{\circ}H_m^{\circ}/(R \cdot K)$	Φ_m°/R
Liquid				
510 ^b	(~280)	(36.09)	(10113)	(16.26)
	[29.0]	[32.02]	[8164]	[16.01]
520 ^b	28.9	36.63	10403	16.62
	[28.9]	[32.56]	[8454]	[16.30]
535	28.7	37.44	10836	17.19
	[28.7]	[33.37]	[8886]	[16.76]

^aThe adiabatic calorimetric results extend up to $T = 350$ K and the d.s.c. results from 330 K through the triple-point temperature to 535 K.

^bThese are the (minimum) points on the heat-capacity curve for a given transition from which extrapolation of the "lattice" heat capacity was made for the calculation of transitional (excess) values of the thermodynamic functions.

^cFor the purposes of this table, the phase transitions are assumed to be truly isothermal and the values at the transition temperatures in parentheses () are consistent with that convention. The values in brackets [] represent the lattice (vibrational) heat capacities and thermodynamic properties in regions near transitions.

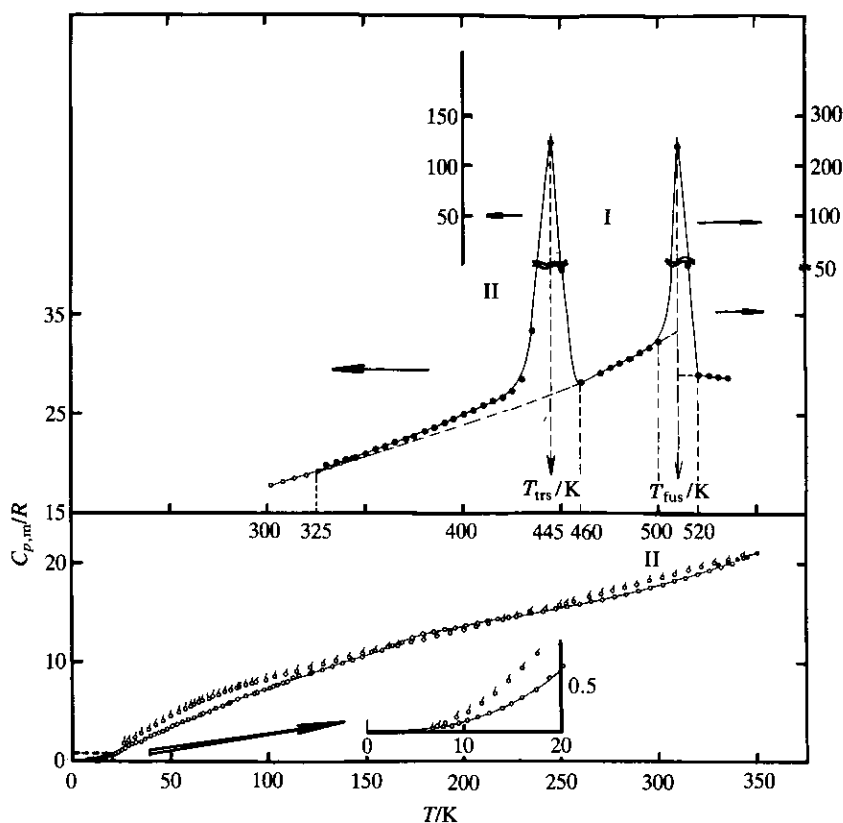


FIGURE 1. The heat capacities of lithium 2-methylpropanoate: ○, this research; of lithium butanoate: ◐, reference 2; and ●, of d.s.c. values of this research.

of interest. Excess enthalpies were obtained by integration of the $C_{p,m}/R$ against T curve while excess entropies were obtained by integration of the $C_{p,m}/RT$ against T plot, considering the temperature of maximum heat capacity as the transition temperature.

A diffuse anomaly (compare figure 1) exists between $T = 125$ K and 250 K in the heat-capacity curve. Such diffuse and flattened anomalies do not lend themselves to the reliable evaluation of transitional entropy changes. This is considered to be a gradual but higher-order transformation. A similar effect exists over about the same temperature interval in lithium butanoate—a straight-chain homolog (see figure 1). Two such phenomena are observed in lithium hexanoate. Whether the number of such transformations present increases with increasing chain length (one for Li4C, two for Li6C) can be ascertained only by studying higher homologs. Since lithium pentanoate and heptanoate exhibit first-order transformations below $T = 350$ K,⁽⁸⁾ the phenomenon discussed above may be a property of even homologs which gives way to sharper transformations in the odd homologs.

The heat-capacity curve of lithium butanoate lies consistently higher in figure 1 than that of lithium 2-methylpropanoate (except in the region where the hump exists) which is consistent with the greater molecular freedom of the former.⁽¹⁾ The same observation obtains when the cation is potassium rather than lithium.⁽¹⁾

The transition temperatures in this study agree very well with those reported earlier⁽⁹⁾ if allowance is made for the fact that in reference 9 the transition temperature with increasing temperature is considered as the onset of transformation rather than the temperature of the heat-capacity maximum considered in the present paper. These authors⁽⁹⁾ note "it frequently occurred that the purification procedure did not succeed in giving completely crystalline specimens, and consequently the first heating d.s.c. traces could exhibit endo- or exo-thermic pen deflections (poorly reproducible in different samples from the same batch) due to glass transitions or crystallization phenomena. Hence it was preferred to employ for calculations only traces recorded after a preliminary heating up to the melt region."

Considering (i), the above assertions of the authors of reference 9; (ii), that melting endo-therms and other transformations associated with the first melting of organic soaps might not show properties exactly the same as those observed on previously melted samples,⁽¹⁰⁾ and (iii), that the method by which the lattice heat-capacity curve is drawn can greatly affect the transition properties, we compared some of our $\Delta_{\text{trs}}H_m$ and $\Delta_{\text{trs}}S_m$ values with those of reference 9 and found them to be within the combined experimental uncertainties.

Finally, we found that the solid-to-solid transformation at $T = 445$ K disappeared completely when the sample had recently been scanned through melting and, after cooling to room temperature, was re-scanned at once or even after 2 h. However, after allowing the sample to remain overnight at room temperature, the transition appeared again on heating, at the original temperature, and with the same $\Delta_{\text{trs}}H_m$. Hence, because of the tendency for undercooling of first-order transitions and consequent thermal lag, sufficient time must be allowed for some carboxylate salts to convert completely from one solid phase to another. However, we found that remelting the present sample yields the same value of $\Delta_{\text{fus}}H_m^\circ$ as well as the same

value of $\Delta_{II}^I H_m^\circ$ as that on the unmelted sample when sufficient time for attainment of thermal equilibration was provided. This is less of a problem with the slower cooling rate of the more massive samples in the adiabatic calorimeter than with d.s.c.

REFERENCES

1. Franzosini, P.; Ngeyi, S. P.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1987**, *19*, 113.
2. Ngeyi, S. P.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1986**, *18*, 609.
3. Hazlewood, F. J.; Rhodes, E.; Ubbelohde, A. R. *Trans. Faraday Soc.* **1966**, *62*, 3101.
4. Ngeyi, S. P. Ph.D. Dissertation, University of Michigan, **1985**, *Diss. Abst.* No. DEU 86-00513.
5. López de la Fuente, F. Departamento de Química Física, Universidad Complutense, Madrid, Spain, personal communications (1984).
6. Ngeyi, S. P.; Malik, I.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1990**, *22*, 91.
7. Westrum, E. F., Jr. *Proceedings of NATO Advanced Study, Institute of Thermochemistry at Viana do Castelo, Portugal*. Ribeiro da Silva, M. A. V.: editor. Reidel: New York. **1984**, p. 745.
8. Franzosini, P.; Ngeyi, S. P.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1986**, *18*, 1169.
9. Ferloni, P.; Sanesi, M.; Franzosini, P. *Z. Naturforsch.* **1975**, *30a*, 1447.
10. Franzosini, P.; Sanesi, M. *Thermodynamic and Transport Properties of Organic Salts*. Pergamon Press: London. **1980**, p. 33ff.