Thermochimica Acta, 123 (1988) 15–22
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMIC PROPERTIES AND PHASE TRANSITIONS OF DODECYLAMMONIUM TETRACHLOROMANGANATE(II) AND TETRACHLOROZINCATE(II) FROM 280 TO 500 K *

ZHANG ZHI YING and YANG MENG LIN

Thermochemistry Laboratory, Northwestern University, Xi'an (People's Republic of China)

(Received 6 January 1987)

ABSTRACT

The heat capacities of $(n\text{-}C_{12}H_{25}NH_3)_2MCl_4$ (M = Mn, Zn) were measured from 280 to 500 K by means of an automated adiabatic calorimeter. Two phase transitions for each compound were found, the temperatures of the maxima occurring at 330.6 K (solid III → II) and 334.5 K (solid II → I) for the manganese compound and at 364.3 K (solid II → I) and 435.1 K (solid I → liquid) for the zinc compound. The enthalpies and entropies of the transitions were found to be 47.78 and 144.5 kJ mol^{-1} (solid III → II) and 5.96 and 17.82 J K^{-1} mol^{-1} (solid III → I) for the manganese compound and 66.79 and 183.3 J K^{-1} mol^{-1} (solid II → I) and 9.12 and 20.96 J K^{-1} mol^{-1} (solid I → liquid) for the zinc compound. The selected thermodynamic functions were tabulated at intervals of 10 K from 280 to 500 K.

INTRODUCTION

The thermal investigation of solid–solid phase transitions can lead to insight into the changes in ordering within the solid states and also provide the necessary transition parameters for compounds having the potential storage energy of solid–solid phase transitions. Owing to the considerable enthalpy of a solid–solid phase transition in the temperature range 300–380 K, compounds of the type $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ have attracted attention from both chemists and engineers. Although the DSC measurements were made on $(n\text{-}C_{12}H_{25}NH_3)_2MCl_4$ (M = Mn, Zn) [1–3], they are probably unable to provide information which is as accurate as that obtainable by adiabatic calorimetry on the heat capacity and the transition temperatures, enthalpies and entropies. Thus, as will be shown below, the present adiabatic calorimetry measurements were carried out on the two compounds, and revealed a new aspect of the phase transition in the manganese compound.

---

* Paper presented at the Sino-Japanese Joint Symposium on Calorimetry and Thermal Analysis, Hangzhou, People's Republic of China, 5–7 November 1986.

0040-6031/88/$03.50

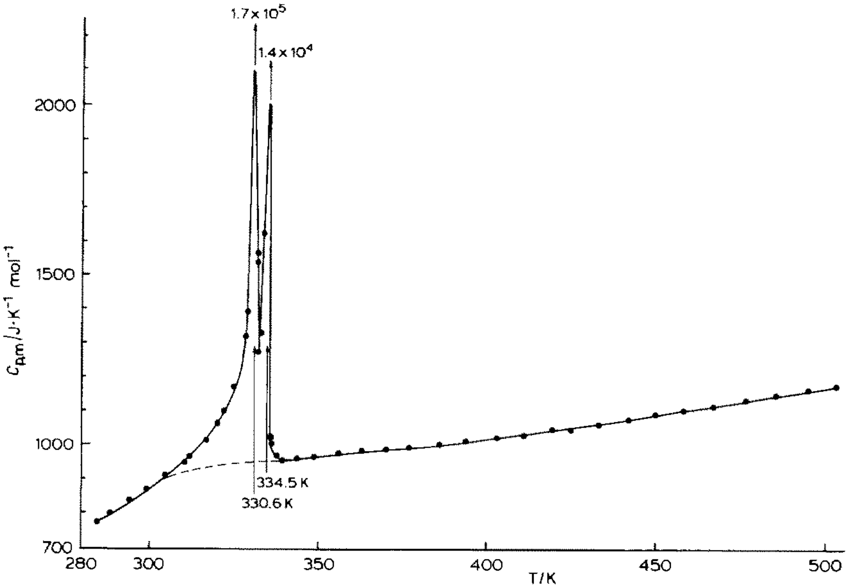

Fig. 1. Experimental molar heat capacity of $(n\text{-}C_{12}H_{25}NH_3)_2MnCl_4$.

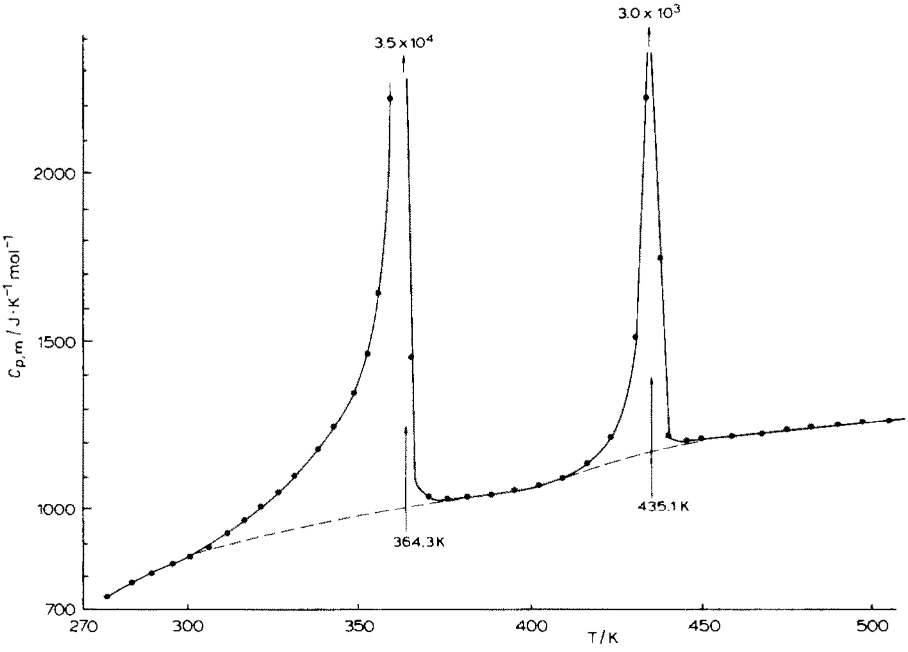

Fig. 2. Experimental molar heat capacity of $(n\text{-}C_{12}H_{25}NH_3)_2ZnCl_4$.

EXPERIMENTAL

Samples for this work were prepared according to the following general method [4]. n-$C_{12}H_{25}NH_2$ (C.R., made by Chemical Plant of Peking) was dissolved in absolute ethanol and allowed to react with stoichiometric amounts of concentrated HCl and $MnCl_2 \cdot 4H_2O$ (A.R., made by Chemical Plant of Peking) or $ZnCl_2$ (A.R., made by Reagent Manufactory of Xi'an) dissolved in the same solvent, and the resulting solutions were boiled for 15 min. After cooling to room temperature, the crystalline precipitates were filtered off and recrystallized twice from absolute ethanol. Chemical analysis gave the following results (theoretical mass percentage in brackets): C, 49.98

TABLE 1

Experimental molar heat capacities of $(n\text{-}C_{12}H_{25}NH_3)_2MnCl_4$

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})
Series 1		*Series 3*		348.58	973.3
284.90	764.1	ΔH_t(solid III → II) Detn. 1		355.60	985.5
288.65	801.9	332.54	1275.2	362.56	988.8
293.95	844.2	334.74	7377.0	369.46	993.2
299.31	876.4	335.68	2138.5	376.31	997.8
304.77	911.9	337.30	965.4		
310.01	950.5			*Series 9*	
		Series 4		386.45	1009.1
Series 2		ΔH_t (solid III → II) Detn. 2		393.11	1019.2
311.70	960.3	332.89	1331.7	401.65	1025.4
316.95	1018.5	334.53	13924	410.07	1034.0
320.86	1070.0	336.45	1013.1	418.46	1051.8
324.57	1175.7				
328.03	1326.1	*Series 5*		*Series 10*	
329.06	1405.2	331.12	4635.9	423.93	1056.3
330.19	9366.0	ΔH_t (solid II → I) Detn. 1		432.62	1070.2
330.47	54384			441.20	1083.9
330.53	134165	*Series 6*		449.68	1099.2
330.54	141529	331.09	4738.9	458.10	1112.6
330.57	172934	ΔH_t (solid II → I) Detn. 2		466.47	1128.9
330.63	42000			476.19	1146.0
331.72	1546.7	*Series 7*		484.99	1162.2
333.48	1630.8	ΔH_t (solid III → II) Detn. 3		494.25	1172.9
334.32	7811.0	332.37	1577.9	503.42	1182.2
334.61	13127	ΔH_t (solid II → I) Detn. 3			
335.78	1028.9				
		Series 8			
		335.59	2871.4		
		338.76	957.4		
		342.96	965.6		

(50.61); H, 9.62 (9.91) for the manganese compound and C, 49.26 (49.71); H, 9.39 (9.73) for the zinc compound.

The heat capacities and enthalpies of phase transitions were measured with an automated adiabatic calorimeter for use up to 600 K [5]. A calorimeter cell of silver equipped with a brass flange and a gold O-ring contained $(n\text{-}C_{12}H_{25}NH_3)_2MnCl_4$ (42.930 g) or $(n\text{-}C_{12}H_{25}NH_3)_2ZnCl_4$ (66.801 g) and a small amount of helium gas to aid the heat transfer. A cryostat includes an adiabatic shield and a guard shield, together with heaters, three unheated radiation shields and a vacuum can. To obtain good adiabatic conditions between the calorimeter cell and its environment, four similar adiabatic control circuits are used to control the temperatures of the

TABLE 2

Experimental molar heat capacities of $(n\text{-}C_{12}H_{25}NH_3)_2ZnCl_4$

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})
Series 1		*Series 6*		433.48	2224.8
277.84	762.6	ΔH_t (solid II → I) Detn. 3		435.11	3037.6
283.84	789.6			436.95	1746.8
289.72	812.8	*Series 7*		439.67	1215.5
295.47	842.3	361.27	2358.6	444.67	1202.2
		362.66	5835.0		
Series 2		363.33	11 248	*Series 9*	
300.97	863.3	363.70	15 970	ΔH_m (solid I → liquid) Detn. 1	
306.14	891.6	363.94	22 498		
311.47	937.2	364.08	29 217	*Series 10*	
316.63	974.7	364.18	33 378	ΔH_m (solid 1 → liquid) Detn. 2	
321.61	1024.8	364.26	34 917		
326.43	1063.7	364.32	28 027	*Series 11*	
331.06	1110.3	364.39	24 293	ΔH_m (solid I → liquid) Detn. 3	
		364.45	19 832	449.30	1222.0
Series 3		364.67	8032.3	458.87	1227.9
332.73	1126.5	365.95	1448.4		
338.06	1197.8	370.18	1029.8	*Series 12*	
343.02	1254.8	375.76	1039.0	467.25	1235.2
347.71	1347.2	381.79	1045.2	474.36	1246.5
352.12	1453.0	388.40	1055.4	481.82	1249.7
356.17	1640.6	394.91	1059.8	489.25	1260.8
359.65	2222.8			496.67	1269.4
362.09	4044.0	*Series 8*		504.06	1278.8
		401.83	1082.3		
Series 4		409.23	1101.5		
ΔH_t (solid II → I) Detn. 1		416.45	1139.8		
		423.40	1221.6		
Series 5		429.67	1511.2		
ΔH_t (solid II → I) Detn. 2					

guard shield and of the three parts (the top, bottom and cylindrical middle parts) of the adiabatic shield. Each control circuit consists of a modified DWT-702 precise temperature regulator (made by No. 6 Automatic Meter Plant of Shanghai) and a thermocouple pile. When these control circuits are operating, the temperature difference between the calorimeter cell and its environment is kept to about 0.5 mK over the entire operational sequence. A 25 Ω platinum resistance thermometer (No. 207183, made by H. Tinsley and Co. Ltd., England) used in the calorimeter has been calibrated on the basis of the IPTS-68 temperature scale. In order to assess the accuracy of this calorimeter, the molar heat capacity of α-Al_2O_3 was measured from 80 to 600 K. Our smoothed results agree with those of the National Bureau of Standards [6] within ±0.3% over the entire working temperature range.

The experimental heat capacities for $(n\text{-}C_{12}H_{25}NH_3)_2MCl_4$ (M = Mn, Zn) are shown in Figs. 1 and 2 respectively. From these figures two transitions can be found for each compound with the temperatures of the maxima occurring at 330.6 and 334.5 K for the manganese compound and at

TABLE 3

Transition parameters of $(n\text{-}C_{12}H_{25}NH_3)_2MCl_4$ (M = Mn, Zn)

T_{trs} (K)	T_1 (K)	T_2 (K)	$\Delta_{trs}H_m$ (kJ mol^{-1})	$\Delta_{trs}S_m$ (J K^{-1} mol^{-1})
$(n\text{-}C_{12}H_{25}NH_3)_2MnCl_4$				
Solid III → II				
	305.65	332.53	47.90	
	309.92	332.95	48.09	
	307.01	332.52	47.34	
330.6	Mean value:		47.78 ± 0.29	144.5 ± 0.9
Solid II → I				
	332.91	346.97	5.97	
	332.90	347.63	6.01	
	330.05	346.89	5.88	
	331.79	340.82	6.00 [a]	
334.5	Mean value:		5.96 ± 0.05	17.8 ± 0.15
$(n\text{-}C_{12}H_{25}NH_3)_2ZnCl_4$				
Solid II → I				
	310.99	379.27	66.50	
	311.75	382.76	66.56	
	312.14	376.90	67.32	
364.3	Mean value:		66.79 ± 0.35	183.3 ± 1.0
Solid I → liquid				
	410.78	446.55	9.33	
	412.50	450.35	8.97	
	412.90	448.13	9.06	
435.1	Mean value:		9.12 ± 0.14	20.96 ± 0.32

[a] Integrated from the heat capacity measurements nos. 16–18.

364.3 and 435.1 K for the zinc compound. Depending on macroscopic observations, the two transitions are solid–solid phase transitions for the manganese compound, while they are a solid–solid and a solid–liquid phase transition for the zinc compound.

The experimental heat capacities of $(n\text{-}C_{12}H_{25}NH_3)_2MCl_4$ (M = Mn, Zn) are also given in Tables 1 and 2 in chronological sequence so that the temperature increments can be deduced approximately from the adjacent mean temperature.

The experimental heat capacities in "non-transition" regions were curvature corrected and fitted to polynomials in reduced temperature by the method of least squares. The deviation between the experimental points and the values calculated from the polynomials is within ±0.2%.

The "normal heat capacities" in the transition regions, as shown by the broken lines in Figs. 1 and 2, were obtained by the method used in the literature [7]. Direct enthalpy measurements were made on the two com-

TABLE 4

Thermodynamic functions of $(n\text{-}C_{12}H_{25}NH_3)_2MnCl_4$

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	$S_m(T)-S_m$ (298.15) (J K^{-1} mol^{-1})	$H_m(T)-H_m$ (298.15) (J mol^{-1})
280	709.3		
290	814.0		
298.15	869.8		
300	880.3	5.41	1618.9
310	950.4	35.38	10754
320	1057.3	66.98	20735
330.6	C_p maximum		
334.5	C_p maximum		
340	961.1	299.2	97873
350	974.7	327.3	107565
360	985.7	354.9	117378
370	995.3	382.1	127293
380	1004.5	408.8	137303
390	1014.1	435.0	147405
400	1024.7	460.9	157609
410	1036.6	486.3	167924
420	1050.1	511.5	178366
430	1065.2	536.4	188952
440	1081.8	561.1	199696
450	1099.5	585.6	210611
460	1117.7	610.0	211707
470	1135.8	634.3	232985
480	1152.9	658.4	244440
490	1167.8	682.4	256056
500	1179.3	706.1	267805

TABLE 5

Thermodynamic functions of $(n\text{-}C_{12}H_{25}NH_3)_2ZnCl_4$

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	$S_m(T) - S_m$ (298.15) (J K^{-1} mol^{-1})	$H_m(T) - H_m$ (298.15) (J mol^{-1})
280	771.7		
290	816.2		
298.15	851.7		
300	860.0	5.29	1583.4
310	916.6	34.32	10444
320	1009.5	64.86	20092
330	1100.0	97.29	30603
340	1239.5	131.7	42156
350	1394.0	169.2	55143
360	2252.0	216.6	71472
364.3	C_p maximum		
370	1029.1	359.7	123597
380	1044.0	387.4	133977
390	1054.7	416.6	144466
400	1075.5	441.6	155107
410	1104.0	468.5	166003
420	1170.0	495.9	177328
430	1530.0	527.0	190313
435.1	C_p maximum		
440	1222.8	574.9	209968
450	1222.2	602.3	222185
460	1229.0	629.3	234436
470	1239.1	655.8	246775
480	1250.1	682.0	259221
490	1261.2	707.9	271777
500	1273.2	733.5	284447

pounds and the parameters of the phase transitions thus obtained are given in Table 3, in which T_1 and T_2 are the starting and finishing temperatures of the experiments in the direct enthalpy measurements.

The thermodynamic functions at selected temperature intervals were obtained by calculation from the polynomials for the heat capacities in the "non-transition" regions and by numerical integration of heat capacity points against large-scale plots in the transition regions. Values for the thermodynamic functions thus obtained are presented in Tables 4 and 5 for both compounds.

DISCUSSION

While there are some DSC reports of the detection and characterization of phase transitions in $(n\text{-}C_{12}H_{25}NH_3)_2MnCl_4$, it appears that the previous investigations found only one solid–solid phase transition between room temperature and the melting point and provided divergent transition temperatures (318 K [1], 324 K [2] and 332 K [3]) for the same transition. However, using the adiabatic calorimeter we found two solid–solid phase transitions, the temperatures of which are very close for the same compound. The difference is probably attributable to the non-equilibrium scanning nature of the DSC experiments, as pointed out by White [8].

REFERENCES

1 E. Landi and M. Vacatello, Thermochim. Acta, 13 (1975) 441.
2 V. Salerno, A. Grieco and M. Vacatell, J. Phys. Chem., 80 (1976) 2444.
3 C. Paraggio, V. Salerno, V. Busico and M. Vacatello, Thermochim. Acta, 42 (1980) 185.
4 J.J. Foster and N.S. Gill, J. Chem. Soc. A, (1968) 2625.
5 Zhang Zhi Ying, Zhongguo Kexue (B), (1986) 469.
6 D.A. Ditmars and T.B. Douglas, J. Res. Nat. Bur. Stand. Sect. A, 75 (1971) 401.
7 R.W. Carling and E.F. Westrum, Jr., J. Chem. Thermodyn., 8 (1976) 565.
8 M.A. White, Thermochim. Acta, 74 (1984) 55.