O-295

J. Chem. Thermodynamics **1988**, 20, 1321–1326

The thermodynamics of ammonium indates

II. The molar heat capacity of the ammonium pentabromoindate monohydrate salt $(NH_4)_2InBr_5 \cdot H_2O$ from 7.8 to 348 K [a]

SANDRA M. ACOSTA, EDGAR F. WESTRUM, JR.,

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055, U.S.A.

R. JULIAN C. BROWN,

Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada

JANE E. CALLANAN,

Center for Chemical Engineering, National Bureau of Standards, Boulder, Colorado 80303, U.S.A.

and RON D. WEIR [b]

Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, Ontario K7K 5LO, Canada

(Received 11 April 1988; in final form 16 May 1988)

The molar heat capacity of ammonium pentabromoindate monohydrate $(NH_4)_2InBr_5 \cdot H_2O$ was measured from 7.8 to 348 K using adiabatic calorimetry. The curve of heat capacity as a function of temperature is continuous. There is no sign of the phase transition predicted by Yamada and Weiss (*Ber. Bunsenges. Phys Chem.* **1983**, 87, 932). Values of the standard molar thermodynamic quantities for $(NH_4)_2InBr_5 \cdot H_2O$ are presented to 345 K.

1. Introduction

The isomorphic complex salts $A_2InX_5 \cdot H_2O$, where A = K, NH_4^+, Rb, Cs; X = Cl, Br, permit the study of the influence of the cations on the In–X bond by nuclear quadrupole resonance (n.q.r.). The ammonium compounds $(NH_4)_2InCl_5 \cdot H_2O$ and

[a] Partial contribution of the U.S. National Bureau of Standards. Not subject to copyright.
[b] To whom correspondence should be sent.

$(NH_4)_2InBr_5 \cdot H_2O$ allow in addition the investigation of dynamic effects of the NH_4^+ on the In–Br or In–Cl bonds, which can be altered by deuteration.

Recent heat-capacity measurements on ammonium pentachloroindate monohydrate $(NH_4)_2InCl_5 \cdot H_2O$ revealed a small anomaly between 110 and 130 K.[1] This is also the region where discontinuities appear in the slope of two of the ^{35}Cl n.q.r. frequencies against temperature and where the slope of the quadrupole-coupling parameters against temperature for ^{115}In becomes unusually large.[2] The n.q.r. frequencies of the ammonium pentabromoindate $(NH_4)_2InBr_5 \cdot H_2O$ are also anomalous.[3] Two of the ^{81}Br n.q.r. lines split at (82 ± 1) K, which has been interpreted as evidence of a phase transition.[3]

The structure of $(NH_4)_2InBr_5 \cdot H_2O$ is orthorhombic at room temperature and is isostructural with the chlorine compound.[3,4] Its space group is [Pnma or No. 62 D_{2h}^{16}] with four molecules per unit cell. The cell parameters[4] are $a = 1.4525$ nm, $b = 1.0574$ nm, and $c = 0.7527$ nm.

Heat-capacity measurents on $(NH_4)_2InBr \cdot H_2O$ are not reported in the literature and were therefore undertaken by us as part of our on-going studies of ammonium salts and phase transitions. The results from 7.8 to 348 K together with their interpretation are presented here.

2. Experimental

The $(NH_4)_2InBr_5 \cdot H_2O$ sample was prepared by mixing aqueous solutions containing stoichiometric amounts of $InBr_3$ and NH_4Br and permitting the mixture to evaporate at room temperature. A report[3] that the pentabromide salt is isostructural with the pentachloride is supported by preliminary crystallographic results,[4] and confirmed by powder-diffraction studies of our sample. The cell parameters of our sample[5] are $a = (1.4561 \pm 0.0002)$ nm, $b = (1.0600 \pm 0.0002)$ nm, and $c = (0.75440 \pm 0.00008)$ nm.

The heat capacities were measured in the Mark X cryostat, which is a version upgraded by addition of a guard shield surrounding the adiabatic shield of the Mark II cryostat described previously.[6] The procurement of heat capacities from about 7 to 348 K was assisted by a computer,[7,8] programmed for a series of determinations. Throughout the drift periods, both the calorimeter temperature and the first and second derivatives of temperature with time were recorded to establish the equilibrium temperature of the calorimeter before and after the energy input. While the calorimeter heater was on, the heater current, electric potential difference, and the duration of the heating interval were obtained. Also recorded were the apparent heat capacity of the system including the calorimeter, heater, thermometer, and sample.

A gold-plated copper calorimeter (laboratory designation W-139) with four internal vertical vanes and a central re-entrant well for the (heater + thermometer) was loaded with $(NH_4)_2InBr_5 \cdot H_2O$ within a dry box. Following the loading, the calorimeter was evacuated and pumping was continued for several hours at room temperature until successive weighings showed that moisture was no longer freed from the sample. Less than 20 mg of gas was evolved and was removed within the

first hour of pumping. This suggested removal of adsorbed moisture rather than water of hydration. Helium gas was then added to the vessel to a pressure of about 3 kPa at 300 K to facilitate thermal equilibration. The vessel was then sealed by means of an annealed gold gasket pressed tightly against the stainless-steel knife edge of the calorimeter top by a screw closure about 5 mm in diameter.

Buoyancy corrections were calculated on the basis of a crystallographic density $3.242\ g \cdot cm^{-3}$ derived from the results of Heyding.[5] The mass of $(NH_4)_2InBr_5 \cdot H_2O$ amounted to 12.9759 g $\hat{=}$ 0.0228280 mol, based on its molar mass of $568.432\ g \cdot mol^{-1}$ calculated from the 1983 IUPAC recommended molar masses of the elements.

3. Results and discussion

The experimental molar heat capacities for $(NH_4)_2InBr_5 \cdot H_2O$ are presented in table 1. There was no evidence that the $C_{p,m}$ values depended upon the thermal history of the sample, so they are given in order of increasing temperature. The probable errors in our heat capacity decrease from about 1 per cent at 10 K to less than 0.15 per cent at temperatures above 30 K. The heat capacity of our sample represented about 50 to 90 per cent of the total measured heat capacity.

A plot of $C_{p,m}/R$ against T from 7.8 to 348 K is shown in figure 1. No obvious λ-type transition is evident. For the temperature region from 50 to 90 K, the slope of the curve changes smoothly up to 70 K where the $C_{p,m}/R$ appears to level off. At this temperature, a slight change in the curvature causes the slope to increase. To assess this change, a straight line was forced through the experimental $C_{p,m}/R$ points at 50.11 and 91.22 K with the resulting equation: $C_{p,m}(\text{calc.})/R = 1.9674 + 0.26806(T/\text{K})$. The differences between the experimental points $C_{p,m}/R$ and those calculated from the line $C_{p,m}(\text{calc.})/R$ were determined and are shown in figure 2 where error bars of 0.2 per cent accompany each point. A check of the run series showed that the point at 67.64 K occurred at the end of a series of measurements

Table 1. Experimental molar heat capacity of $(NH_4)_2InBr_5 \cdot H_2O$ ($M = 568.432\ g \cdot mol^{-1}$, $R = 8.31441\ J \cdot K^{-1} \cdot mol^{-1}$)

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
7.75	0.427	15.09	2.502	50.11	15.40	113.89	29.31	193.64	32.66	285.83	33.93
8.18	0.475	16.70	3.030	53.98	16.65	119.70	29.83	200.65	32.62	293.08	34.25
8.69	0.546	18.56	3.665	58.24	17.90	125.78	30.38	207.68	32.78	300.28	34.45
9.36	0.757	20.43	4.312	62.79	19.14	131.90	30.68	214.71	32.97	307.56	34.64
9.91	0.994	22.66	5.094	67.64	20.42	138.03	30.97	221.74	33.01	314.79	34.88
10.22	1.102	25.22	6.051	69.71	20.99	144.19	31.17	228.77	33.03	322.03	34.93
11.06	1.302	27.93	7.107	75.13	22.52	150.57	31.58	235.82	33.15	329.11	35.11
11.16	1.320	30.83	8.266	80.44	23.99	157.23	31.89	242.78	33.23	336.17	35.35
11.81	1.515	33.77	9.430	85.80	25.28	163.89	32.07	249.81	33.31	343.21	35.60
12.43	1.723	36.72	10.54	91.22	26.42	170.59	32.19	256.94	33.46	348.32	36.04
12.60	1.769	39.88	11.73	96.85	27.31	177.32	32.39	264.17	33.47		
13.43	2.010	43.25	12.96	102.67	28.03	183.98	32.48	271.39	33.60		
13.75	2.101	46.65	14.20	108.34	28.71	186.75	32.62	278.60	33.71		

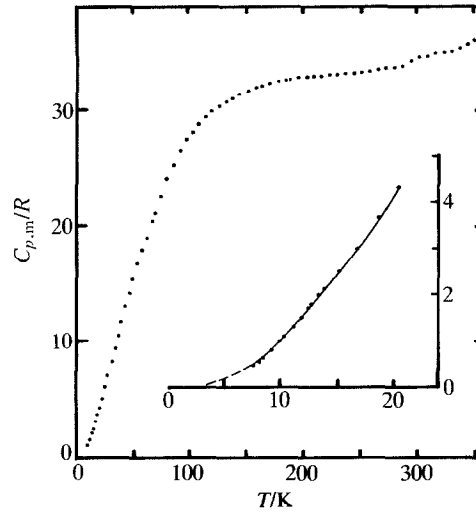

FIGURE 1. Molar heat capacities $C_{p,m}/R$ of $(NH_4)_2InBr_5 \cdot H_2O$ between 8 and 348 K. The region below 20 K is enlarged in the lower right-hand corner.

TABLE 2. Standard molar thermodynamic quantities for pure $(NH_4)_2InBr_5 \cdot H_2O$; $M = 568.432\ g \cdot mol^{-1}$, $p^\circ = 101.325$ kPa, $R = 8.31441\ J \cdot K^{-1} \cdot mol^{-1}$, $\Phi_m^\circ \stackrel{def}{=} \Delta_0^T S_m^\circ - \Delta_0^T H_m^\circ / T$

$\frac{T}{K}$	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{R \cdot K}$	$\frac{\Phi_m^\circ}{R}$	$\frac{T}{K}$	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{R \cdot K}$	$\frac{\Phi_m^\circ}{R}$
5	(0.1624)	(0.0541)	(0.208)	(0.013)	130	30.57	32.83	2315.6	15.02
10	1.046	0.392	2.91	0.102	140	31.09	35.11	2623.9	16.37
15	2.478	1.075	11.58	0.303	150	31.56	37.27	2937.1	17.69
20	4.168	2.014	28.11	0.609	160	31.96	39.32	3254.9	18.98
25	5.996	3.134	53.52	0.994	170	32.20	41.27	3575.7	20.24
30	7.944	4.396	88.37	1.451	180	32.44	43.12	3898.9	21.46
35	9.941	5.768	133.1	1.966	190	32.64	44.88	4224.3	22.64
40	11.77	7.214	187.4	2.530	200	32.61	46.55	4550.6	23.80
45	13.68	8.709	251.0	3.132	210	32.87	48.15	4878.0	24.92
50	15.37	10.24	323.6	3.766	220	33.02	49.68	5207.6	26.01
55	16.98	11.78	404.5	4.424	230	33.04	51.15	5537.8	27.07
60	18.43	13.32	493.0	5.101	240	33.21	52.57	5869.0	28.11
65	19.75	14.85	588.5	5.792	250	33.34	53.92	6201.9	29.11
70	21.06	16.36	690.5	6.493	260	33.47	55.23	6635.9	30.09
75	22.50	17.86	799.4	7.201	270	33.57	56.49	6871.1	31.05
80	23.87	19.36	915.3	7.914	280	33.75	57.72	7207.7	31.98
85	25.11	20.84	1037.8	8.631	290	34.12	58.91	7546.9	32.88
90	26.19	22.31	1166.0	9.350	300	34.44	60.07	7889.7	33.77
95	27.05	23.75	1299.1	10.07	310	34.70	61.20	8235.5	34.64
100	27.73	25.15	1436.1	10.79	320	34.90	62.31	8583.5	35.49
105	28.32	26.52	1576.2	11.51	330	35.14	63.39	8933.6	36.31
110	28.90	27.85	1719.2	12.22	340	35.45	64.44	9286.5	37.13
115	29.41	29.15	1865.0	12.93	345	35.70	64.96	9464.3	37.53
120	29.86	30.41	2013.2	13.63	298.15	34.37 ± 0.04	59.86 ± 0.08	7826.1 ± 11.7	33.61 ± 0.05
125	30.26	31.64	2163.5	14.33					

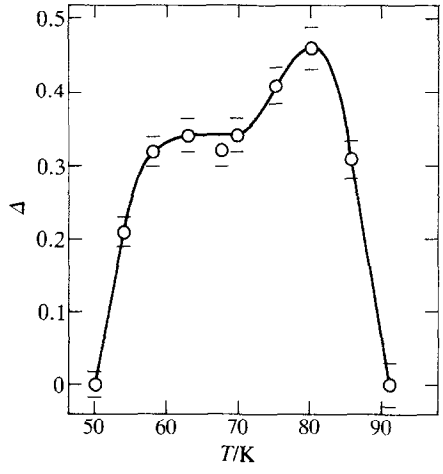

FIGURE 2. Difference plot of $\Delta = \{C_{p,m} - C_{p,m}(\text{calc.})\}/R$ from 50.11 to 91.22 K where $C_{p,m}(\text{calc.})/R = 1.9674 + 0.26806(T/\text{K})$ (see text). The error bars correspond to 0.2 per cent.

and the point at 69.71 K was the start of another series two days later. This lack of overlap must temper the interpretation of these results. Yamada and Weiss[3] predicted a phase transition at (82 ± 1) K based upon their interpretation of n.q.r. results. Our heat capacities do not support their prediction of a phase transition, but our difference plot in figure 2 suggests a small anomaly in the region of about 60 to 85 K. Throughout this region, the times required for our sample to equilibrate after heating were normal and identical with those at other temperatures. It would be helpful to know what is happening to the lattice parameters and n.m.r. in this region. Unfortunately, none of these measurements has been reported in the literature. There is no sign of a shoulder on our heat-capacity curve for $(NH_4)_2InBr_5 \cdot H_2O$, as was found for $(NH_4)_2InCl_5 \cdot H_2O$.[1] For the bromoindate salt from 280 to 326 K, there is an increase in $C_{p,m}$ that amounts to $\Delta H_m = 118.5\ \text{J} \cdot \text{mol}^{-1}$ above the smooth background curve. It is unlikely that this is due to water trapped within the crystal, since melting is expected to occur at approximately 270 K. The n.q.r. frequencies and quadrupole coupling parameters are normal in the region from 280 to 326 K.[3]

Values of the smoothed heat capacities and standard molar thermodynamic functions obtained by integration of the smoothed results for $(NH_4)_2InBr_5 \cdot H_2O$ are presented at selected temperatures in table 2. The heat capacities below 8 K were obtained by fitting experimental values below 20 K to the limiting form of the Debye equation using a plot of $C_{p,m}/T$ as a function of T^2 and extrapolating $T \rightarrow 0$. Because the temperatures in this work were not low enough to reach the linear region below the maximum in a plot of $C_{p,m}/T^3$ against T^2, this relation could not be used for the extrapolation.

REFERENCES

1. Brown, R. J. C.; Callanan, J. E.; Weir, R. D.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1988,** 20, 847.
2. Carr, S. L.; Garrett, B. B.; Moulton, W. G. *J. Chem. Phys.* **1967,** 47, 1170.
3. Yamada, K.; Weiss, A. *Ber. Bunsenges. Phys. Chem.* **1983,** 87, 932.
4. Yamada, K.; Weiden, N.; Weiss, A. *J. Mol. Struct.* **1983,** 111, 217.
5. Heyding, R. D. (Chemistry Department, Queen's University, Kingston, Ontario K7L 3N6, Canada.) Personal communication. **1987.**
6. Westrum, E. F., Jr.; Furukawa, G. T.; McCullough, J. P. *Experimental Thermodynamics, Vol I.* McCullough, J. P.; Scott, D. W.: editors. Butterworths: London. **1968,** p. 133.
7. Westrum, E. F., Jr. *Proceedings NATO Advanced Study Institute on Thermochemistry, Viana do Castello, Portugal.* Ribeiro da Silva, M. A. V.: editor. Reidel: New York. **1984,** p. 745.
8. Andrews, J. T. S.; Norton, P. A.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1978,** 10, 949.