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CALORIMETRIC STUDY OF PHASE TRANSITIONS IN THE THIOUREA 1,1,2,2-TETRACHLOROETHANE CLATHRATE COMPOUND*

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Heat capacities of the thiourea clathrate compound of 1,1,2,2-tetrachloroethane, $\{(NH_2)_2CS\}_3(CHCl_2)_2$, were measured at temperatures between 13 and 330 K. Two phase transitions were found. The enthalpy and entropy changes of the transition are 5940 $J\cdot mol^{-1}$ and 28.1 $JK^{-1}\cdot mol^{-1}$ for the one occurring at 224 K and 2756 $J\cdot mol^{-1}$ and 11.3 $JK^{-1}\cdot mol^{-1}$ for the other at 248 K. It is concluded from the transition entropy values that the guest molecules are orientionally disordered nearly to the same extent as in the neat liquid.

Keywords: calorimetric study, clathrate compound, heat capacity

Introduction

There are three distinct molecular interactions in a clathrate compound: host-host, host-guest and guest-guest interactions. In many cases the interaction between the host molecules is directional and anisotropic, giving rise to an open structure in which the guest molecules are trapped. Hydrogen bonding is a typical interaction of this type between the host molecules in clathrate hydrates [1], hydroquinone clathrates [2] and urea and thiourea adducts [3, 4]. The second molecular interaction, the host-guest interaction, stabilizes the clathrate compound against decomposition into its components. This interaction is usually isotropic and arises from the van der Waals forces. Induction and electrostatic interactions may also be involved in the host-guest interaction. Because of this isotropic and non-specific character of the host-guest interaction, a host lattice

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can accommodate molecules of different shape and size within certain limits in the same basic crystal structure.

Guest-guest interactions were previously regarded as negligible, because the experiments against which theories of clathrate compounds were tested involved determination of their stability. Quantities directly related to the stability, such as enthalpy of clathrate formation, depend primarily on the host-guest interaction and are not particularly sensitive to guest-guest interaction. The guest-guest interaction, even if it may not have been negligible, could easily be absorbed in the parameters describing the host-guest interaction in the analysis of the experimental data.

It was pointed out that the angle-dependent part of guest-guest interaction might reveal itself at low temperatures where even the weak molecular interaction would be strong enough to overcome the randomizing thermal motion and the guest molecules, disordered at higher temperatures, would become aligned under the influence of the neighbouring guest molecules. This was shown to occur in hydroquinone [5–12], urea [13, 14] and thiourea [15–17] clathrate compounds, as they undergo phase transitions at low temperatures. A more complicated situation occurs in clathrate hydrates in which the orientations of the host and guest molecules are both disordered in the high temperature phase [18–23]. Importance of guest-guest interaction is now being recognized in the theory of clathrate stability [24–26].

In the present paper we describe a calorimetric experiment on the thiourea clathrate compound containing 1,1,2,2-tetrachloroethane $\{(NH_2)_2CS\}_3(CHCl_2)_2$.

Experimental

The sample was prepared by crystallizing thiourea from 1:1 (by mass) mixture of 1,1,2,2-tetrachloroethane and acetic acid in the following way [27]. The solution saturated at 90°C was cooled overnight. The clathrate compound crystallizing as needles was separated and dried in a desiccator containing potassium hydroxide pellets. Elemental analysis gave the following results in mass percent:

C;12.25(12.16), H;3.57(3.56), N;21.10(21.21), S;24.09(24.28), Cl;35.51(35.79).

The numbers in the parentheses were calculated for the formula $\{(NH_2)_2CS\}_3(CHCl_2)_2$. The stoichiometry was also determined from the decrease of the mass on thermal decomposition of the compound with hot water. It was found in a separate experiment that thiourea did not sublime to any significant extent during drying. Two determinations gave 2.991 and 3.008, av. 3.000 for the number of thiourea molecules per guest molecule. Thus, the clathrate compound is actually a stoichiometric combination of the two species by 3:1.

The heat capacities were measured at temperatures between 13 and 330 K with an adiabatic calorimeter described elsewhere [28]. The mass of the calorimetric sample was 2.7975 g in vacuo corresponding to 7.0606 mmol of the clathrate compound.

Infrared spectra was recorded at temperatures between 96 and 300 K to determine the conformation of the guest molecule in the clathrate channel.

Results and discussion

The heat capacity data are plotted in Fig. 1 and the numerical values given in Table 1. Two peaks were found at 224 and 248 K. There is a small hump in the heat capacity at 207 K. The dotted curve in Fig. 1 represents the vibrational heat capacity calculated in the following way. One formula unit of $\{(NH_2)_2CS\}_3(CHCl_2)_2$ has 96 vibrational degrees of freedom, which can be divided into 54 intramolecular and 18 external vibrations of three thiourea molecules and 18 intamolecular and 6 external vibrations of a tetrachloroethane molecule. Frequencies of all of the intramolecular vibrations are known from infrared and Raman spectroscopies [29–31]. Frequencies of the external vibrations are not known. Therefore, they were determined by fitting Debye and Einstein heat capacity functions to the experimental heat capacities. The fitting parameters were the characteristic temperatures of the Debye and Einstein functions. The calculated heat capacity of all the intramolecular vibrations was added to the fitting function. The fitting procedure has been described in detail elsewhere [32–35]. As one sees in Fig. 1, the calculated vibrational heat capacity interpolates the experimental points smoothly into the temperature region of the phase transitions. The transitional heat capacity was determined by subtracting the calculated base

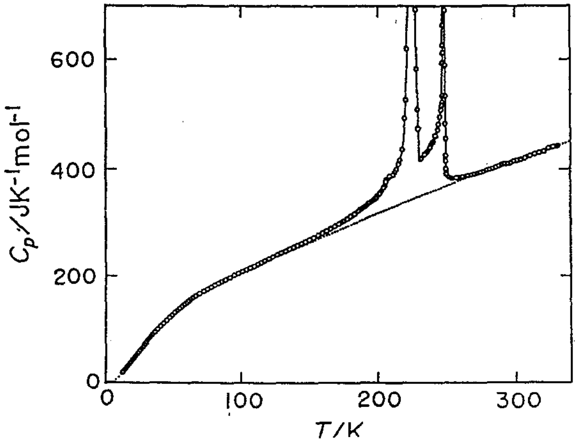

Fig. 1 Heat capacity of thiourea 1,1,2,2-tetrachloroethane clathrate compound

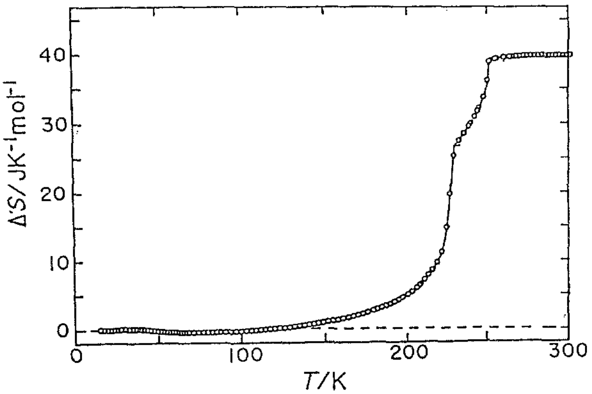

Fig. 2 Transitional entropy of thiourea 1,1,2,2-tetrachloroethane clathrate compound

line from the experimental values. The excess heat capacity thus separated was divided by T and integrated numerically, giving the transitional entropy as a function of temperature. The accumulated transition entropy is plotted in Fig. 2, in which one recognizes gradual increase of the entropy at the beginning of each of the transitions and sharp rise at the first order transitions. Numerical values of the temperatures, entropies and enthalpies of the transitions are listed in Table 2. As one sees in Fig. 1, the heat capacity does not decrease back to the base line between the peaks. The two phase transitions were separated at the temperature of the minimum heat capacity and the numerical values are given as such in Table 2.

A part of the infrared spectra is reproduced in Fig. 3. The spectra show a multiplet at ~750 cm^{-1} due to an intramolecular vibration of thiourea and a weaker peak at ~790 cm^{-1}. The latter peak increased in intensity at 96 K. A corresponding absorption of the trans conformer occurs at 740 cm^{-1} in liquid 1,1,2,2-tetrachloroethane but not in the solid [30, 31]. There exist absorption lines at the same frequency in the spectrum of the clathrate compound. However, they arise from the host molecule [29], even though overlapping of the host and guest absorption cannot be excluded.

The gauche conformer of 1,1,2,2-tetrachloroethane has the C_2 symmetry. For this polar molecular form, there are 12 equivalent orientations for the guest molecule to take at random in the clathrate cavity of the D_3 symmetry. The entropy associated with this randomness is R ln12 = 20.66 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ to be compared with the sum 39.44 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ of the transition entropies. The large difference 18.78 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ shows that the guest molecules are much more disordered than the highest possible degree permitted within the site symmetry. The decrease of the absorption intensity of the 790 cm^{-1} peak above 220 K may indicate that the guest molecules exist also in the trans form in the intermediate and high temperature phases. The conformational disorder may also be involved in the transition entropy.

Table 1 The molar heat capacities of $\{(NH_2)_2CS\}_3(CHCl_2)_2$

T_{av} / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}	T_{av} / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}	T_{av} / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}
		170.95	297.5	224.84	878.5
series – 1		173.93	302.3	226.60	692.4
289.53	407.0	176.88	306.4	228.60	472.3
291.71	409.8	179.98	311.6	230.81	418.1
293.88	409.8	183.22	317.2	233.05	423.7
296.04	411.1	186.43	322.8	235.29	430.8
		189.62	328.9	237.50	438.8
series – 2		192.80	335.5	239.70	448.7
85.12	189.6	195.95	341.3	241.88	461.7
88.40	193.7	199.07	348.8	244.02	481.5
91.57	197.7	202.17	358.0	246.11	531.7
94.65	201.4	205.23	376.0	247.90	997.9
97.67	205.1	208.25	385.3	249.78	420.8
100.63	208.7	211.40	389.9	252.02	384.4
103.54	212.3	214.66	409.2	254.30	382.4
106.39	215.6	217.84	445.7	256.57	382.5
109.21	218.7	220.79	619.7	258.84	383.1
111.98	222.2	223.42	782.7	261.11	384.0
114.72	225.7	225.84	863.5	263.37	385.5
117.43	229.1	228.51	508.5	265.62	387.2
120.30	232.7	231.61	419.8	267.86	388.4
123.34	236.3	234.79	428.7	270.11	390.1
126.35	239.9			272.34	391.9
129.32	243.5	series – 3		274.57	393.4
132.26	247.0	195.75	338.9	276.79	395.2
135.17	250.8	198.23	344.5	279.00	397.1
138.05	254.2	200.69	351.2	281.21	398.7
140.91	257.7	203.12	356.8	283.41	400.5
143.75	261.4	205.54	367.1	285.60	402.9
146.57	264.9	207.92	379.1	287.79	405.2
149.54	268.8	210.29	382.6	289.97	408.5
152.67	272.5	212.63	394.4	292.14	410.5
155.77	276.4	214.94	410.7	294.31	410.5
158.85	280.4	217.21	435.5	296.48	411.1
161.91	284.8	219.41	490.4	298.64	414.4
164.95	289.1	221.40	710.5	300.79	415.6
167.96	293.3	223.17	843.5		

Table 1 Continued

T_{av} / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}	T_{av} / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}	T_{av} / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}
		40.73	106.5	219.98	525.4
series – 4		42.86	112.1	221.89	848.9
303.51	417.3	45.03	117.5	223.68	694.7
306.89	420.8	47.05	122.6	225.48	813.5
310.27	423.7	48.95	127.2	227.28	692.1
313.62	426.7	50.76	132.4	229.29	474.9
316.97	429.6	52.50	135.5	231.50	420.5
320.30	431.9	54.25	139.4	233.74	426.8
323.62	437.6	56.02	143.4	235.96	433.1
326.93	439.6	57.73	146.8	238.17	442.0
330.23	441.4	59.37	149.9	240.36	452.3
		60.97	153.0	242.52	466.6
series – 5		62.53	155.8	244.65	488.4
12.97	20.54	64.12	158.6	246.69	593.0
14.02	23.82	66.39	162.5	248.49	891.5
15.10	27.28	69.33	167.2	250.45	389.4
16.21	30.88	72.24	171.7	252.74	383.4
17.23	34.23	75.04	175.7	255.03	381.5
18.18	37.56	77.75	179.5	257.32	383.0
19.14	40.79	80.37	183.1	259.59	383.4
20.12	44.17	82.92	186.6	261.86	384.7
21.04	47.21				
21.92	50.05	series – 6		series – 7	
22.81	52.87	186.33	322.3	172.24	299.4
23.96	56.59	188.86	327.0	174.88	302.8
25.28	60.72	191.38	331.6	177.49	307.1
26.50	64.48	193.88	336.9	180.08	311.2
27.72	68.39	196.36	342.1	182.66	315.4
28.92	72.25	198.83	348.3	185.21	320.1
30.00	75.60	201.28	355.1	187.75	324.5
30.98	78.63	203.71	364.9	190.26	328.9
31.91	81.61	206.10	379.8	192.76	334.1
32.82	84.36	208.47	386.5	195.24	339.4
33.70	86.93	210.85	388.2	197.70	344.8
34.91	90.52	213.21	399.5	200.84	352.6
36.60	95.25	215.53	416.6	204.65	367.9
38.62	100.9	217.80	444.5	208.38	385.0

Table 1 Continued

T_{av} / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}	T_{av} / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}	T_{av} / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}
212.06	393.9	243.46	475.5	250.36	389.7
215.69	420.3	243.67	474.2	250.57	386.9
219.17	492.4	243.87	478.8	250.79	385.2
222.22	809.2	244.07	480.1	251.01	384.0
224.97	760.4	244.28	482.3	251.22	385.2
227.92	581.9	244.48	483.0	251.44	383.1
231.24	424.4	244.68	485.8	251.66	383.2
234.75	429.8	244.88	489.2	251.88	381.9
238.23	443.2	245.09	491.6	252.09	383.9
241.66	460.0	245.29	492.1	252.31	382.0
245.01	494.7	245.49	499.0	252.53	382.9
248.02	794.3	245.69	503.7	252.74	381.4
251.16	387.5	245.88	507.0	252.96	382.7
254.74	382.0	246.08	510.4	253.18	383.0
258.31	382.8	246.28	517.3	253.40	380.3
		246.48	525.6	253.61	381.3
series – 8		246.67	556.6	253.83	382.9
239.33	447.4	246.86	611.6	254.05	381.9
239.54	449.5	247.04	625.5	254.26	381.5
239.75	448.8	247.22	662.9	254.48	381.6
239.96	448.4	247.40	740.3	254.69	383.0
240.16	449.9	247.56	822.1	254.91	384.9
240.37	449.6	247.72	874.8		
240.58	452.6	247.88	956.0	series – 9	
240.79	454.8	248.02	1073	244.81	489.4
241.00	453.0	248.16	1197	245.01	492.0
241.20	460.3	248.29	1378	245.30	495.6
241.41	460.3	248.40	1500	245.58	499.4
241.62	454.1	248.53	1104	245.78	504.2
241.82	460.4	248.68	690.8	245.98	508.1
242.03	459.3	248.87	532.0	246.18	514.6
242.23	460.2	249.07	454.3	246.38	520.6
242.44	462.7	249.28	414.7	246.57	533.2
242.64	468.4	249.49	400.7	246.76	590.2
242.85	468.2	249.71	397.1	246.95	620.8
243.05	470.8	249.92	391.9	247.13	639.9
243.26	472.3	250.14	390.5	247.31	706.0

Table 1 Continued

T_{av} / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}	T_{av} / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}	T_{av} / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}
247.48	785.3	248.96	482.2	251.11	386.8
247.64	842.7	249.17	424.5	251.33	385.7
247.80	909.6	249.38	404.5	251.54	384.1
247.94	1015	249.59	399.0	251.76	381.4
248.08	1134	249.81	391.3	251.98	376.1
248.22	1297	250.03	389.4	252.20	381.5
248.34	1495	250.24	389.1	252.41	382.3
248.45	1361	250.46	388.3	252.63	382.9
248.59	831.7	250.67	387.7	252.85	383.9
248.77	588.8	250.89	385.1	253.07	383.0

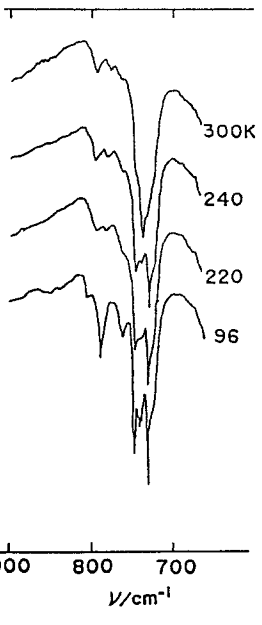

Fig. 3 Infrared spectra of thiourea 1,1,2,2-tetrachloroethane clathrate compound

The size of the guest molecule calculated by adding the van der Waals radii of the atoms is shown in Fig. 4. The molecule is approximately spherical in shape and thus fits nicely in the clathrate channel with its C–C axis either perpendicular or parallel to the axis of the channel. This, along with the small polarity of the molecule, will allow the molecule to occupy the cavity in highly disordered orien-

Table 2 The temperatures, enthalpies and entropies of the transitions of $\{(NH_2)_2CS\}_3(CHCl_2)_2$

T_{trs} / K	$\Delta_{trs}H$/J·mol^{-1}	$\Delta_{trs}S$/J K^{-1}mol^{-1}
224	5940	28.1
248	2756	11.3
	total 8696	total 39.4

tations. For the sake of comparison, the sum of the entropies of transition and fusion of 1,1,2,2-tetrachloroethane crystal is 44.2 J·K^{-1}·mol^{-1} [36]. Thus, the guest molecules are nearly as much disordered in the cavity of the clathrate lattice as in the liquid state.

The molecular origin of the guest-guest interaction responsible for the transitions is not known at present. The transition enthalpy is a measure of the magnitude of the molecular interaction. It is 8696 J/mol for the present compound. The corresponding value of the analogous clathrate compound containing CCl_4 is 149 + 241 = 390 J·mol^{-1} [17]. Thus the ordering energy between 1,1,2,2-tetrachloroethane molecules in the clathrate lattice is 22 times as large as that of carbon tetrachloride in the same environment. Considering the similarity of the two molecules in other respects (e.g., in their solvent property), explanation for the large difference in the transition enthalpies should be sought in mechanisms involving molecular interactions other than the direct guest-guest interaction. A possible mechanism may be found in the anisotropy of the crystal field experienced by the guest molecule in the host channel. As discussed above, the guest molecules appear to be more disordered than is expected from the symmetry of the high temperature phase. This means that some of the guest molecules take the orientations crystallographically nonequivalent with those the others. The difference in the energy of the different orientations (i.e., anisotropy of the crystal field) should be included in the transition enthalpy in addition to the energy of the direct guest-guest interaction, giving rise to a large increase of the energy at the transition. This will explain the large transition enthalpy of the present compound. If this mechanism is actually correct, the transition enthalpy involves the energy of not only the guest-guest interaction but also a part of the host-guest in-

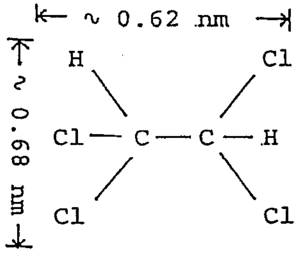

Fig. 4 Approximate molecular size of 1,1,2,2-tetrachloroethane

teraction. For the carbon tetrachloride compound, the guest molecule is more spherical in shape and thus the anisotropic interaction will be less important. An experimental test of the transition mechanism will be found in the crystal structure of the different phases of the present compound and the one containing carbon tetrachloride. A sufficiently detailed structural determination may reveal the tetrachloroethane molecules lying in the nonequivalent orientations in the channel.

Conclusion

The standard thermodynamic functions of $\{(NH_2)_2CS\}_3(CHCl_2)_2$ were calculated from the heat capacity data. For $T < 14$ K where experimental values are not available, the thermodynamic functions were calculated by extrapolation using the model function of the vibrational heat capacity discussed in the main text. The numerical values are given on this appendix in a dimensionless form (R = 8.31451 $J \cdot K^{-1} \cdot mol^{-1}$).

Table A1 Standard thermodynamic functions of $\{(NH_2)_2CS\}_3(CHCl_2)_2$ ($R = 8.31451$ $J \cdot K^{-1} \cdot mol^{-1}$

T /K	$C^*_{p,m}/R$	$[H^*_m(T) - H^*_m(0)]/RT$	$[S^*_m(T) - S^*_m(0)]/R$	$[C^*_m(T) - H^*_m(0)]/RT$
10	1.174	0.3728	0.5160	0.1431
20	5.249	1.194	1.855	0.6603
30	9.115	3.198	4.723	1.525
40	12.60	5.122	7.833	2.711
50	15.60	6.926	10.98	4.051
60	18.13	8.589	14.05	5.462
70	20.24	10.11	17.01	6.902
80	22.02	11.49	19.83	8.343
90	23.59	12.75	22.52	9.769
100	25.04	13.90	25.08	11.17
110	26.45	14.98	27.53	12.55
120	27.87	15.99	29.89	13.90
130	29.33	16.96	32.18	15.21
140	30.84	17.90	34.41	16.51
150	32.40	18.82	36.59	17.77
160	33.99	19.71	38.73	19.02
170	35.65	20.60	40.84	20.24
180	37.45	21.49	42.93	21.44
190	39.53	22.38	45.01	22.63
200	41.95	23.30	47.10	23.80

Table A1 Continued

T /K	$C^*_{p,\mathrm{m}}/R$	$\left[H^*_\mathrm{m}(T)-H^*_\mathrm{m}(0)\right]/RT$	$\left[S^*_\mathrm{m}(T)-S^*_\mathrm{m}(0)\right]/R$	$\left[C^*_\mathrm{m}(T)-H^*_\mathrm{m}(0)\right]/RT$
210	45.72	24.29	49.25	24.96
220			phase transition at 224 K	
230	49.02	28.01	55.32	27.31
240	54.35	29.01	57.53	28.52
250			phase transition at 248 K	
260	46.14	31.15	62.09	30.94
270	46.92	31.72	63.85	32.13
273.15	47.20	31.90	64.40	32.50
280	47.84	32.28	65.57	33.29
290	48.92	32.83	67.27	34.44
298.15	49.80	33.28	68.64	35.35
300	49.94	33.39	68.95	35.56

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Zusammenfassung — Bei Temperaturen zwischen 13 und 330 K wurde die Wärmekapazität der Thioharnstoff-Einschlußverbindung von 1,1,2,2-Tetrachlorethan gemessen. Dabei wurden zwei Phasenumwandlungen festgestellt. Die Enthalpie- und Entropieänderungen der Umwandlungen betragen 5940 $Jmol^{-1}$ und 28.1 $JK^{-1}mol^{-1}$ für die Umwandlung bei 224 K und 2756 $Jmol^{-1}$ bzw. 11.3 $JK^{-1}mol^{-1}$ für die Umwandlung bei 248 K. Aus den Entropiewerten der Umwandlung wird geschlossen, daß die Gastmoleküle in etwa dem gleichen Maße ungeordnet sind, wie in der reinen Flüssigkeit.