Calorimetric study of a new inclusion complex, $ZnS_{23.4}\cdot$ β-cyclodextrin·$6H_2O$

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Abstract: Heat capacity properties of a new inclusion complex $ZnS_{23.4}\cdot$ β - cyclodextrin·$6H_2O$ and a mechanical mixture of ZnS and β -cyclodextrin were investigated in the range of 80~350 K by means of a miniaturized adiabatic calorimeter with a precision of ± 0.2%. Glass transition phenomena were observed in relation to the freezing of configurational change of the protons engaged in the four-membered hydrogen-bonded ring. The difference in heat capacities of the two samples was thermodynamically accounted for in terms of quantum size effect and interfacial effect.

INTRODUCTION

In literature, the properties of crystalline solids are ordinarily catalogued without reference to their size. With respect to many strong variations in size-dependent properties of their nanoscale particles reported in literature over decades, a great change in such catalogues would appear in near future. The variations of physical and chemical properties with size-tuning, principally arising from systematic transformations in the density of electronic energy levels as a decrease of particle size to nanoscale region, known as quantum size effect [1], have already drawn much attention of scientists from diverse disciplines.

On the other hand, host-guest chemistry should be considered one of the most prospective methods to fabricate nanoparticles. Low-dimensional nanoparticles, as a guest, can be readily embedded inside another material with larger cavities, as a host which confers solubility and prevent agglomeration. β -Cyclodextrin (denoted as BCD) is a ring-shaped and tube-shaped host molecule, comprised of seven glucopyranose units, the inner diameter of which is about 10 Å [2]. As a good host, it can easily accommodate guest molecules of a suitable size and then form a stable inclusion complex[3]. Driving force to form a BCD inclusion complex is believed to be hydrophobic, Van der Waals, dipolar interactions, conformational strain and hydrogen bonding energy[4]. In the formation of an inclusion complex, all these driving forces aforementioned exist, but how much the contribution of each force will mainly be dependent on the properties of the guest. In general, Van der Waals is predominant, and hydrophobic second.

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Inclusion complex of zinc sulfide and BCD (ZnS/BCD) is a new compound [5]. ZnS particles in it have already been characterized by several methods like STM, XRD, SAXS (small-angle X-ray scattering), IR, optical absorption and emission spectroscopes and so on. These experiments showed that the included ZnS particles were sphalerite-type crystalline and the grain size was in the range of 9.7 to 12.2 Å . These ultrafine particles are known as ones of quantum confinement, showing quantum size effect. The inclusion complex was also used as a photocatalyst and a highly effective photocatalytic activity was observed in simultaneous production of hydrogen and ethylene glycol from aqueous methanol solution [6, 7].

Calorimetric studies on BCD undecahydrate had been made by H.Suga *et al*[8]. They studied the ordering process of the highly disordered β -cyclodextrin undecahydrate with calorimetry, in which a glass transition phenomenon was found. The glass transition phenomenon was ascribed to a configurational change of the protons engaged in the four-meandered hydrogen-bonded ring. However, to the best of our knowledge, few calorimetric investigations had been done on those inclusion complexes associated with inorganic nanometer semiconductors.

To take into account the difference of the proton configurations of BCD with and without ZnS nanoparticles and the difference of states of the ZnS particles inside and outside BCD, the glass transition temperature and/or heat capacity of them would be changed. To this point, this work investigated the heat capacity properties of the ZnS/BCD inclusion complex and a mechanic mixture of ZnS and BCD (denoted as ZnS//BCD) in the temperature range between 80 and 350 K.

EXPERIMENTAL

Sample

The method of preparation was previously described in detail [5, 6,]. Briefly, it was prepared from BCD, $ZnSO_4$ and Na_2S in aqueous solution. In preparation, the key is how to form ultrafine ZnS particles with a rapid precipitation technique, so that the extremely small particles could be moved into the cavities of BCD and accommodated. The sample was kept at normal pressure and 75 ℃ for 71 hours to dehydrate physically-adsorbed water. The average molecule numbers of the included ZnS particles and water in the inclusion complex were determined to be 23.4 and 6, respectively, by SAXS and gravimetric method. Thus, an almost stoichiometric specimen $ZnS_{23.4}$ β -CD·$6H_2O$ was obtained for the calorimetric study. The molar mass was taken as 3522.94 g mol^{-1}.

Calorimetry

The miniaturized adiabatic calorimeter, including sample cell, thermometer, differential thermocouples, cryostat and a system of temperature control and energy measurement, in our thermochemistry laboratory for heat capacity measurements, was described in detail previously [9]. The inaccuracy of heat capacity measurements with the calorimeter was $\pm$ 0.5%, which was determined by comparing our results with the values recommended for the heat capacity of α -Al_2O_3 reported by Ditmars *et al*[10]. A sample of 3.5071g (0.9955 mmol), was sealed in a gold-plated copper cell of 6 cm^3, together with helium gas at

atmosphere pressure and room temperature. The temperature of the sample cell was measured with a miniaturized platinum resistance thermometer (Model IPRT, No.2 SIAM Co.) based on the IPTS-90 with an uncertainty of 1 mK. The heat capacity measurements were made with discontinuous heating mode which consists of two periods: *i.e.*, heating and equilibration periods. The heating period was usually ten minutes and equilibration period five minutes. The temperature increase for each measurement point was generally 2-3 K in the whole temperature range.

RESULTS AND DISCUSSION

Phase transition and Glass transition

The molar heat capacities of the inclusion complex under the condition of precool rate 5.5 K/min in the temperature range of 80-350 K are listed in Table 1 and reproduced graphically in Fig. 1 (solid circles). Two anomalous regions are observed. One is that in which the heat capacity decreased obviously between 80 K and 120 K. Although the low temperature side of the peak can not be plotted completely owing to the limit of the working temperature range of calorimeter, it is certainly a process of a phase transition. The another is a more subtle one with a slight increase of heat capacity around 175 K. The heat capacity data in this region is reproduced in Fig. 2 on an enlarged scale. A simple extrapolation of the high temperature data of this figure to the low temperature side gives an estimated equilibrium heat capacity.
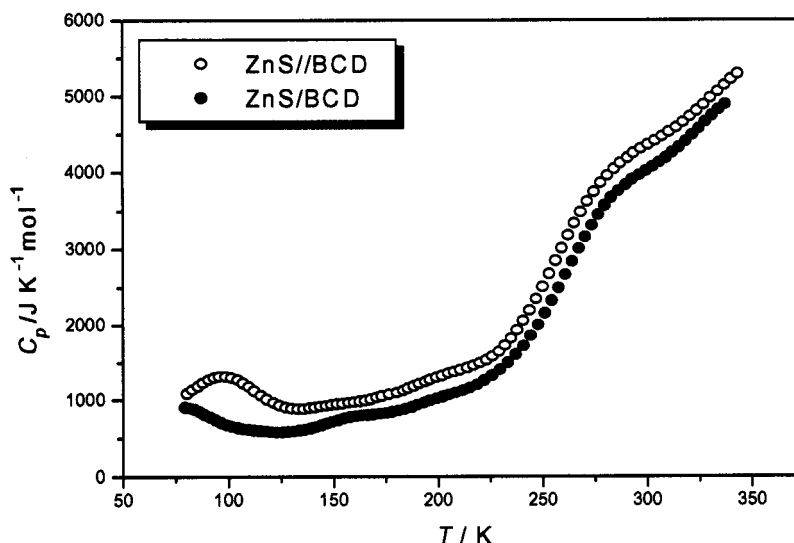

Fig. 1 Molar heat capacities of ZnS/BCD and ZnS//BCD.

H.Suga *et al* found that there was an anomalous gentle increase of heat capacity around 150 K in the calorimetric study of β -cyclodextrin undecahydrate. They believed it be a glass transition resulted from a freezing of proton configuration in respective hydrogen bonded network, with respect to other studies of substances such as SnCl$_2$·2H$_2$O[11], pinacol hexohydrate[12]. The glass transition phenomena are

common in many hydrogen bonding compounds and generally takes place in the temperature range between 110 and 300 K. We , therefore, regard the anomaly of the inclusion complex around 175 K as a glass transition which is responsible for the configurational changes of the protons engaged in the four-membered hydrogen bonds. Nevertheless, the anomaly of the heat capacity of the inclusion complex occurred between 80 K and 120 K, which has not been observed in the heat capacity studies of β - cyclodextrin undecahydrate. We tentatively suggest that such an anomaly be ascribed to another kind of phase transition being different from that corresponding to 175 K .
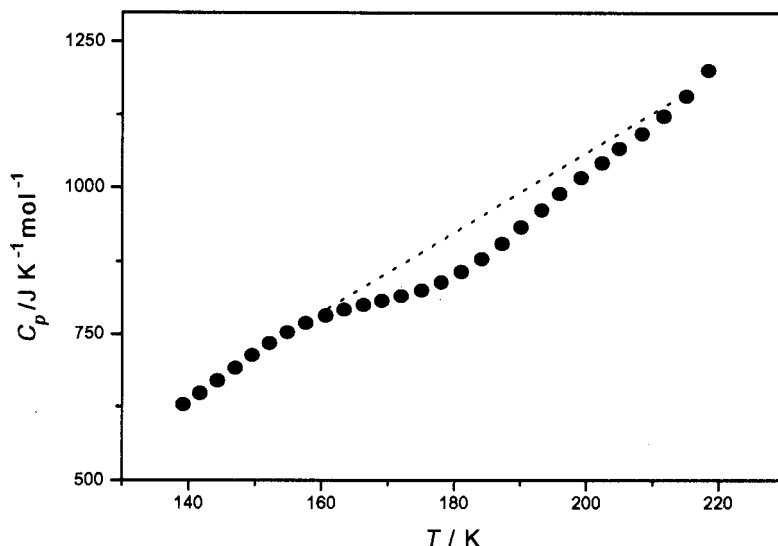

Fig. 2 Molar heat capacities of ZnS/BCD around the glass transition temperature.

In order to get more information about the inclusion complex, the heat capacities of a mechanical mixture of crystalline ZnS and β -cyclodextrin, *i.e.*, ZnS//BCD sample with an equimolar amount of each to the inclusion complex, were measured under the same measurement conditions as that for the inclusion complex. The molar heat capacities of the mechanical mixture were tabulated in Table 2 and also plotted in Fig. 1 (open circles). Similarly to that for ZnS/BCD, a subtle glass transition appeared around 175 K for ZnS//BCD due to the configurational change of the protons engaged in the four-membered hydrogen-bonded ring comprised of H_2O and OH groups of β -cyclodextrin. However, a strong anomaly between 80 K and 130 K, obviously different from that for ZnS/BCD, was observed for the mixture.

Perheps, a better understanding of these anomalies would be obtained by simply considering the fact that the ZnS particles of the two samples are different in their physical states that do contribute to the heat capacity values. The included ZnS particles are more thermodynamically stable than the non-included ones, so a significant phase transition appeared for the ZnS//BCD sample.

TABLE 1. The Molar Heat Capacities of ZnS/BCD

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
79.441	903.1	154.84	752.9	247.775	1997.4
81.502	893.8	157.626	769.1	251.150	2153.7
83.798	873.4	160.569	782.1	254.433	2318.6
86.179	844.0	163.441	792.3	257.689	2489.5
88.688	808.8	166.272	800.3	260.917	2663.1
91.308	771.3	169.076	807.5	264.139	2835.8
93.908	734.6	172.021	815.3	267.311	3003.8
96.433	701.2	175.075	825.5	270.475	3163.6
98.936	672.9	178.077	839.1	273.617	3312.1
101.579	650.1	181.125	857.1	276.719	3447.1
104.361	632.4	184.200	879.3	279.798	3567.2
107.076	619.0	187.236	905.0	283.043	3672.1
109.705	608.5	190.149	933.0	286.474	3762.7
112.274	600.0	193.229	961.7	289.860	3840.4
114.830	592.7	196.000	989.8	293.149	3907.7
117.327	586.5	199.243	1016.5	296.398	3967.5
120.032	581.6	202.354	1041.8	299.683	4022.9
122.884	578.6	205.000	1066.5	302.902	4077.2
125.632	578.1	208.465	1092.4	306.005	4133.3
128.410	580.8	211.717	1121.7	309.192	4193.6
131.216	587.2	215.113	1156.8	312.295	4259.8
133.910	597.2	218.465	1200.2	315.458	4332.4
136.557	610.9	222.036	1254.1	318.683	4411.0
139.163	627.8	225.751	1319.9	321.839	4494.2
141.730	647.3	229.448	1398.9	325.038	4579.8
144.351	668.6	233.441	1491.5	328.206	4665.0
146.995	690.8	237.091	1598.1	331.297	4747.2
149.590	713.0	240.830	1718.4	334.381	4824.1
152.202	734.0	244.332	1851.8	337.421	4894.1

TABLE 2. The Molar Heat Capacities of ZnS//BCD

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
80.380	1080.2	162.530	979.4	250.002	2506.4
82.933	1132.9	165.207	993.0	253.086	2673.1
85.526	1183.0	167.858	1009.2	256.160	2842.8
87.999	1228.3	170.496	1028.0	259.216	3012.2
90.538	1265.9	173.092	1049.0	262.250	3177.9
93.183	1293.2	176.441	1072.0	265.250	3336.9
95.764	1307.8	180.320	1096.6	268.246	3486.4
98.499	1308.0	183.200	1122.7	271.402	3624.6
101.383	1293.3	185.624	1150.0	274.716	3750.0
104.208	1264.3	188.238	1178.3	277.979	3862.2
106.974	1223.0	190.965	1207.3	281.212	3961.5
109.689	1172.5	193.633	1236.5	284.428	4048.7
112.371	1116.8	196.269	1265.6	287.612	4125.3
115.267	1060.3	199.061	1293.8	290.755	4193.0
118.346	1007.1	201.979	1320.8	293.866	4253.9
121.379	960.9	204.840	1346.4	297.159	4310.2
124.352	924.3	207.657	1370.9	300.626	4363.8
127.279	898.6	210.684	1395.1	304.057	4417.0
130.125	883.9	213.838	1420.5	307.478	4471.7
132.943	878.9	216.944	1449.0	310.852	4529.4
135.718	881.7	220.018	1483.1	314.182	4591.4
138.448	889.8	223.061	1525.4	317.496	4658.7
141.153	900.9	226.065	1578.2	320.759	4731.5
143.817	912.8	229.038	1643.7	324.007	4809.3
146.446	924.1	231.979	1723.6	327.200	4891.0
149.049	934.1	234.899	1818.8	330.465	4975.1
151.626	942.8	237.784	1929.6	333.823	5059.4
154.315	950.8	240.648	2055.3	337.140	5141.8
157.093	959.0	243.672	2194.8	340.405	5220.3
159.825	968.2	246.861	2346.0	343.628	5293.4

Difference in heat capacity

Obviously, ZnS/BCD has a smaller heat capacity than ZnS//BCD. The difference (up to 5~20%) between them is unlikely resulted from experimental error. In experiments, the molar amount of each component was confirmed to be equally introduced for the two samples, and the other processes in sample preparation were carefully taken to make sure that the two samples hold parallel heat history. Therefore, the difference in heat capacity was also conceived to be likely resulted from the different states of ZnS particles.

Previously we reported that the ZnS/BCD sample showed very broad and flat XRD peaks associated with the macrocrystalline structure of cubic β -ZnS powders(sphalerite), suggesting the existence of extremely small ZnS particles and the absence of the long-range periodicity like their macrocrystalline particles[5]. Compared to the ZnS//BCD sample, small angle X-ray scattering (SAXS) measurement demonstrated a serious microcrystalline contraction of the included ZnS particles, which led to a higher electronic charge density, for the ZnS/BCD sample (the detailed description of the SAXS results will be reported in subsequent papers). Therefore, the different ZnS states for the two samples should be responsible for the difference in heat capacity. The problem is how to qualitatively account for the difference on the basis of thermodynamics.

According to the viewpoint of statistical thermodynamics, all thermodynamic information can be contained in partition function (Q) which gives an indication of the number of states that are thermally accessible to the system at the temperature of interest. The statistical mechanical heat capacity can thus be expressed in terms of partition function as follows:

$$C_P = \frac{\partial}{\partial T}\left[NkT^2\left(\frac{\partial LnQ}{\partial T}\right)_{P,N}\right]_P \tag{1}$$

The overall heat capacity can also be separated into contributions from various modes of motion

$$Q = \prod_i Q_i \equiv \prod_i \sum_i g_i e^{-\varepsilon_i/kT} \tag{2}$$

where i = t, r, v or e, indicative of transitional, rotational, vibrational or electronic condition respectively.

As for the inclusion complex ZnS/BCD, the included ZnS particles are materials of low degree of freedom, which are subjected to a great spacial and electronic confinement as aforementioned. Therefore, in the case of quantum confinement, the available contributions to heat capacity from various modes or the number of states should be limited or minimized.

Although the intrinsic properties of the interior of nanocrystals would be transformed by quantum size effects due to a decrease in size to a few nanometers, interfacial effect can not be overlooked, which may also play an important role in this context. Surface atoms, more often than not, make a distinct contribution to free energy and thus, the large changes in thermodynamic properties of nanocrystals can ultimately be traced to this. In literature, we noted that some investigations showed higher heat capacities of nanocrystalline materials than that of their extended counterparts and such phenomena were explained in

terms of the interfacial disorder: *i.e.*, the smaller the nanocrystal, the larger the contribution made by surface energy to the overall energy of the system [13,14]. Perhaps, such is not the case for our system. In this work, the 1nm ZnS particles were well-surface-defined in BCD cavities. The interface between the included ZnS particles and inner BCD molecules would be an ideal ohmic contact because of their very closely- matched dielectric constants. Therefore, the included ZnS particles were stable, and the interfacial energy must not be considered higher than that of non-included ZnS particles, surrounded by atmosphere molecules and/or water molecules.

CONCLUSION

The characterization of a new inclusion complex ZnS/BCD by using calorimetric measurements showed that there existed anomalies in heat capacity of this sample and the heat capacity values were obviously smaller than that of its mechanic mixture. Quantum size effect and interfacial effect of the included ZnS particles in BCD cavities would be responsible for these phenomena. To the best of our knowledge, the present work produced the first experiment results demonstrating some unique changes in heat capacity of semiconductor nanoparticles in a host microenvironment.

Since only with the calorimetric method, we could not draw out information sufficiently to elucidate the nature of the difference and the anomaly of the heat capacities, much work still has to be done.

ACKNOWLEDGMENT

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