Enthalpy of Solution of 5-R-$Na_2bdc \cdot nH_2O$ (H_2bdc = Isophthalic Acid, R = H, NH_2, OH, CH_3, NO_2) at 298.15 K

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A series of sodium isophthalic acid derivatives 5-R-$Na_2bdc \cdot nH_2O$ (H_2bdc = isophthalic acid, R = H, NH_2, OH, CH_3, NO_2, n = 0.5, 1, 1, 1, 1) were synthesized in water. Molar enthalpies of dissolution ($\Delta_{sol}H_m$) of the compounds in double-distilled water under various molalities were determined at 298.15 K by an RD496-2000 type microcalorimeter. Following Pitzer's theory, the molar enthalpy of dissolution of the title compounds at infinite dilution ($\Delta_{sol}H_m^{\infty}$) and Pitzer's parameters ($\beta_{MX}^{(0)L}$ and $\beta_{MX}^{(1)L}$) were obtained. The values of the title compounds of relative apparent molar enthalpies ($\Delta_{sol}H_\phi$), relative partial molar enthalpies ($\Delta_{sol}H_{L,2}$), and relative partial molar enthalpies ($\Delta_{sol}H_{L,1}$) of the solvent at different concentrations c/(mol·L^{-1}) were derived from the experimental values of the enthalpies of dissolution of the compounds, respectively.

Introduction

Isophthalic acid and derivatives of isophthalic acid are important raw materials used to produce paint, polyester resin, unsaturated polyester resin, special fiber, and hot melt adhesives.[1−5] On the basis of the rigid structure of aromatic carboxylic acid and a variety of coordination modes, aromatic polycarboxylic acids, especially isophthalic acid derivatives, were extensively applied to construct porous coordination polymers and organic−inorganic hybrid materials.[6−14] Actually, because isophthalic acid and derivatives can not dissolve in water, sodium isophthalic acid derivatives are often employed as reactants in the process of synthesizing functional metal−organic coordination compounds.

In spite of the recent rise in the research on sodium isophthalic acid derivatives,[15,16] little is still known about their solution properties of mixtures.[17] A detailed understanding of the solution behavior of sodium isophthalic acid derivatives in water is certainly important from both theoretical and practical perspectives. As we knew, accurate data of the enthalpy of dilution are required for the optimization design of industrial processes.[18] To our knowledge, no measurements of the enthalpies of dilution for sodium isophthalic acid derivatives are presently available.

In the present work, we synthesized a series of sodium isophthalic acid derivatives 5-R-$Na_2bdc \cdot nH_2O$ (H_2bdc = isophthalic acid, R = H, NH_2, OH, CH_3, NO_2, n = 0.5, 1, 1, 1, 1) and measured the molar enthalpies of dilution, $\Delta_{sol}H_m$, of these compounds at various molalities at (298.15 ± 0.01) K. Then we calculated the molar enthalpy of dissolution of all the compounds at infinite dilution, $\Delta_{sol}H_m^{\infty}$, and Pitzer's parameters. The values of relative apparent molar enthalpies, $\Delta_{sol}H_\phi$, relative partial molar enthalpies of the compounds, $\Delta_{sol}H_{L,2}$, and relative partial molar enthalpies of the solvent, $\Delta_{sol}H_{L,1}$, at different concentrations c/(mol·L^{-1}) were, respectively, derived from the experimental values of the title compounds through Pitzer's model.[19]

Table 1. Results of Elemental Analyses and Purities of the Title Samples

sample		1	2	3	4	5
calculated	C	0.3952	0.3936	0.4464	0.3518	0.4385
	H	0.0290	0.0248	0.0333	0.0185	0.0276
	O	0.3290	0.3933	0.3304	0.4101	0.3286
	N	0.0576	0	0	0.0513	0
found	C	0.3958	0.3939	0.4426	0.3512	0.4329
	H	0.0297	0.0259	0.0361	0.0179	0.0272
	O	0.3281	0.3942	0.3328	0.4112	0.3263
	N	0.0572	0	0	0.0508	0
purity[a]		0.9972	0.9970	0.9969	0.9967	0.9976

[a] The purity was defined by high-performance liquid chromatography.

Experimental Section

Chemicals. 5-NH_2-H_2bdc; 5-OH-H_2bdc; 5-CH_3-H_2bdc; 5-NO_2-H_2bdc, and H_2bdc were purchased from the Tokyo Kasti Kogyo Co., Ltd. and were of GC grade with a purity of 99 %. Potassium chloride (mass fraction 0.9999) was purchased from the Shanghai No. 1 Reagent Factory, Shanghai, China, and dried in a vacuum oven at 500 K for 8 h prior to use.

Synthesis and Analysis. 5-R-H_2bdc was mixed with sodium hydroxide in water at the molar ratio of n(5-R-H_2bdc):n(NaOH) = 1:2 at a temperature of T = 313.15 K (R = H, OH, NH_2, NO_2, CH_3). It is followed by evaporation and filtration, leading to crystal samples. Elemental analyses for the title samples 5-NH_2-$Na_2bdc \cdot H_2O$ (**1**), 5-OH-$Na_2bdc \cdot H_2O$ (**2**), 5-CH_3-$Na_2bdc \cdot H_2O$ (**3**), 5-NO_2-$Na_2bdc \cdot H_2O$ (**4**), and $Na_2bdc \cdot 0.5H_2O$ (**5**) were performed on an Elemental Vario EL III CHNOS analyzer, and the values of the relative data are listed in Table 1. TG-DTG were performed on a NETZSCH STA 449C instrument under a dynamic atmosphere of high-purity O_2 with a heating rate of 5 K·min^{-1}. As shown in Figures S1 to S5 of the Supporting Information, the curves of the title compounds

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Table 2. Pitzer's Parameters of Title Samples

sample	α_0	$\beta^{(0)L}_{MX}$	$\beta^{(1)L}_{MX}$	$\Delta_{sol}H^{\infty}_m$ (kJ·mol^{-1})	standard deviation of fitting	correlation coefficient
1	−0.03064	−0.04565	0.03059	−45.290	$8.34419\cdot10^{-5}$	0.98136
2	−0.02489	−0.02923	0.01522	−36.790	$6.01942\cdot10^{-5}$	0.98373
3	−0.00835	−0.04102	0.04938	−12.342	$3.33825\cdot10^{-5}$	0.97310
4	0.01489	−0.00167	0.05454	22.009	$4.11746\cdot10^{-5}$	0.99647
5	−0.02016	−0.03901	0.03936	−29.799	$5.13632\cdot10^{-5}$	0.97479

TG-DTG show a hydration number. The relative atomic masses used were those recommended by the IUPAC Commission in 1999.[20]

The purity of the sample was identified by high-performance reversed-phase liquid chromatography under isobaric condition. The column was packed with C_{18} sorbents (150 × 4.6 mm) with a particle diameter of 5 μm; the mobile phase contained 20 mmol of KH_2PO_4 in methanol; and the pH value was adjusted to 2. The flow rate was 1 mL·min^{-1}, and the components were detected at 254 nm. Values of normalized areas of peaks are listed in Table 1. Results demonstrated that the samples have high purity, and the requirements of thermochemical measurements are attained.

Measurement of Enthalpy of Solution for the Samples. The enthalpies of solution of the samples were measured by an RD496-2000 type microcalorimeter. The main experimental procedures were described previously.[21] The design, assemblage, and test of the microcalorimeter were published in ref 22. The calorimetric constant at (298.15 ± 0.01) K was determined by the Joule effect before the experiment, which were (63.901 ± 0.030) μV·mW^{-1}. The enthalpy of solution of KCl in deionized water was measured to be (17.581 ± 0.039) kJ·mol^{-1}, which is in good agreement with the value of (17.584 ± 0.007) kJ·mol^{-1} in ref 23. The relative deviation of the experimental result from the value in the reference is 0.02 %, which indicates that the calorimetric system is accurate and reliable.

Results and Discussion

Molar Enthalpies of Dissolution at Infinite Dilution and Pitzer's Parameters. The title compounds are readily soluble in double-distilled water. The experimental values of enthalpies of dissolution of the title compounds, $\Delta_{sol}H_m$, in deionized water are given in Table 2. The curvilinear relationships of $\Delta_{sol}H_m$ with c for the samples are shown in Figures 1 to 5.

The relationship between $\Delta_{sol}H_m$ and $\Delta_{sol}H_\phi$ can be expressed as eq 1[24]

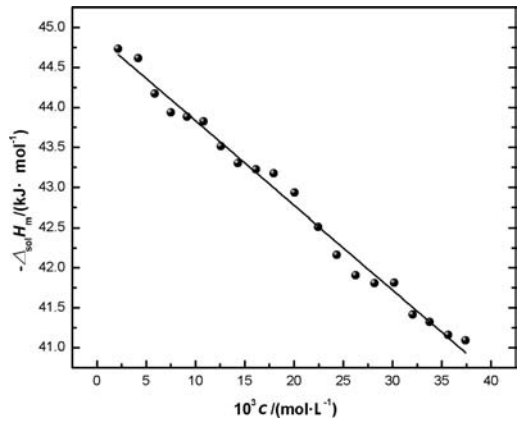

Figure 1. Curvilinear relationship of $\Delta_{sol}H_m$/(kJ·mol^{-1}) with c/(mol·L^{-1}) for sample **1**.

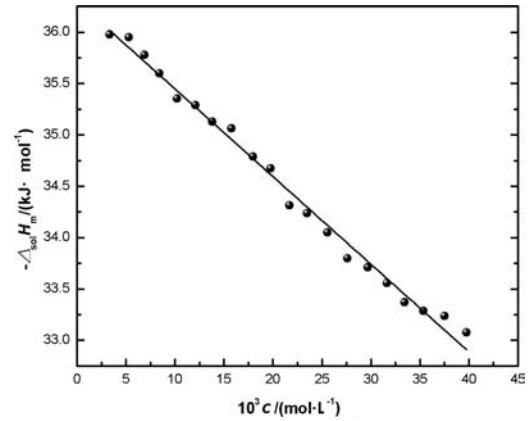

Figure 2. Curvilinear relationship of $\Delta_{sol}H_m$/(kJ·mol^{-1}) with c/(mol·L^{-1}) for sample **2**.

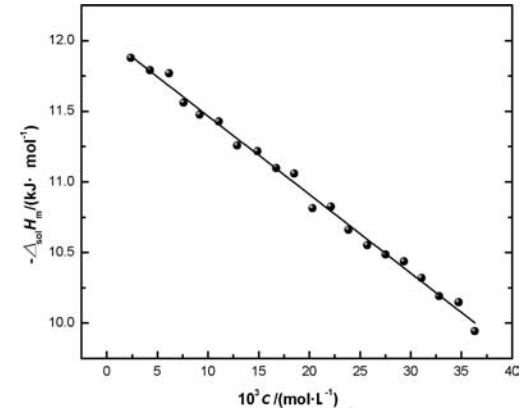

Figure 3. Curvilinear relationship of $\Delta_{sol}H_m$/(kJ·mol^{-1}) with c/(mol·L^{-1}) for sample **3**.

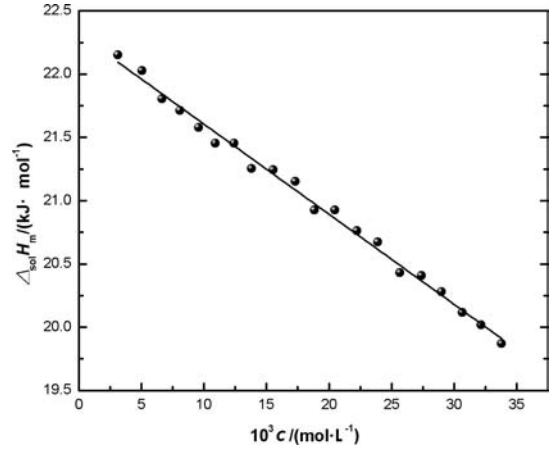

Figure 4. Curvilinear relationship of $\Delta_{sol}H_m$/(kJ·mol^{-1}) with c/(mol·L^{-1}) for sample **4**.

$$\Delta_{sol}H_m = \Delta_{sol}H^{\infty}_m + \Delta_{sol}H_\phi \quad (1)$$

$\Delta_{sol}H^{\infty}_m$ is the molar enthalpy of dissolution at infinite dilution, and relative apparent molar enthalpy, $\Delta_{sol}H_\phi$, in accordance with Pitzer's theory[24] can be expressed as eq 2

$$\Delta_{sol}H_\phi = 2.5A_H \ln\left[1 + 1.2\left(\frac{1}{2}\sum_i c_i z_i^2\right)^{1/2}\right] - 4RT^2[c(\beta^{(0)L}_{MX} + y'\beta^{(1)L}_{MX}) + 1.4c^2C^{\phi L}_{MX}] \quad (2)$$

where $(1/2)\sum_i c_i z_i^2 = (1/2)\sum_i m_i z_i^2 = I$ is ionic strength at very low dilution; $\beta^{(0)L}_{MX}$, $\beta^{(1)L}_{MX}$, and $C^{\phi L}_{MX}$, are the Pitzer parameters for

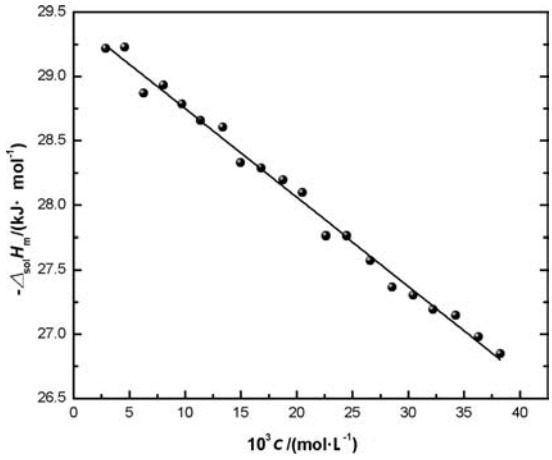

Figure 5. Curvilinear relationship of $\Delta_{sol}H_m/(kJ\cdot mol^{-1})$ with $c/(mol\cdot L^{-1})$ for sample **5**.

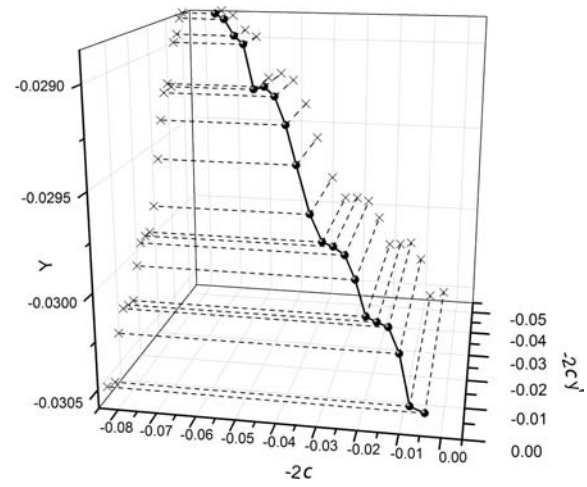

Figure 6. Curvilinear relationship of Y with $-2c$ and $-2cy'$ for sample **1**.

enthalpies; $\beta_{MX}^{(0)L} = (\partial\beta_{MX}^{(0)L}/\partial T)_P$; $\beta_{MX}^{(1)L} = (\partial\beta_{MX}^{(1)L}/\partial T)_P$; $C_{MX}^{\phi L} = (\partial C_{MX}^{\phi L}/\partial T)_P$; the coefficients $\beta_{MX}^{(0)L}$ and $\beta_{MX}^{(1)L}$ account for various types of short-range interactions between M and X and for indirect forces arising from the solvent; and the third coefficient $C_{MX}^{\phi L}$ represents triple ion interactions and is important only at high concentrations. $C_{MX}^{\phi I}$ may be overlooked because the concentration of the sample in dissolution experiments is relatively low. c is the molar concentration of the sample, and R is the molar gas constant, 8.3145 J·mol^{-1}·K^{-1}. The A_H is the Debye−Huckel parameter for enthalpy,[24] and $A_H = 1986$ J·mol^{-1} at $T = 298.15$ K.

From the above equations, a working equation[25] to determine the Pitzer parameters is shown as

$$Y = \{\Delta_{sol}H_m - 2.5A_H \ln[1 + 0.6(\sum_i c_i z_i^2)^{1/2}]\}/(2RT^2) = \alpha_0 - 2c\beta_{MX}^{(0)L} - 2cy'\beta_{MX}^{(1)L} \quad (3)$$

where Y is the extrapolation function; $\alpha_0 = \Delta_{sol}H_m^{\infty}/(2RT^2)$; and $y' = 1 - [1 + (\sum_i c_i z_i^2)^{1/2}]\exp[-(\sum_i c_i z_i^2)^{1/2}]/(\sum_i c_i z_i^2)$. Regression of Y against $-2c$ and $-2cy'$ was made by least-squares to obtain α_0, $\beta_{MX}^{(0)L}$, $\beta_{MX}^{(1)L}$, and $\Delta_{sol}H_m^{\infty}$ for the title compounds, and results are listed in Table 2, respectively. The typical curvilinear relationship of Y with $-2c$ and $-2cy'$ for **1** is shown in Figure 6, and those for **2** to **5** are shown in Figures S6 to S9 (Supporting Information).

It is seen from Table 2 that Pitzer's parameters ($\beta_{MX}^{(0)L}$ and $\beta_{MX}^{(1)L}$) of the title compounds in deionized water are small, indicating weak interaction between the ions in the solutions obtained from dissolution of the samples. The values of molar enthalpy of dissolution, $\Delta_{sol}H_m^{\infty}$, at infinite dilution are ranked in the sequence of samples **1** to **5**. If only the characteristic substituted groups in fifth place of the benzene rings are considered, the sequence is expressed as: $-NH_2$, $-OH$, $-H$, $-CH_3$, and $-NO_2$. The $-NH_2$ and $-OH$ have a strong hydration action with water molecules in the aqueous solution owing to formation of the hydrogen bonds and strong polarity for themselves so that the ionization of the groups $-NH_2$ and $-OH$ takes place in water. This gives off a big exothermic quantity existing in the dissolution of samples **1** and **2** in water. The $-CH_3$ is a hydrophobic group and can weaken the interaction between the water molecule and aromatic ring so that less heat is produced. A strong π bond is formed between $-NO_2$ and the benzene ring, which greatly enhances the hydrophobic action of the benzene ring and makes the dissolution of the sample **4** absorb certain heat.

Relative Partial Molar Enthalpies of the Title Compounds. The formula to determine relative partial molar enthalpy ($\Delta_{sol}H_{L,2}$) of the compound is

$$\Delta_{sol}H_{L,2} = \Delta_{sol}H_{\phi} + c(\partial\Delta_{sol}H_{\phi}/\partial c)_{T,P} \quad (4)$$

The partial derivative of eq 2 ($C_{MX}^{\phi L}$ is neglected) against c under constant temperature and pressure is expressed as

$$(\partial\Phi_L/\partial c)_{T,P} = 2.60A_H/(c^{1/2} + 2.08c) - 4RT^2[\beta_{MX}^{(0)L} + \beta_{MX}^{(1)L}\exp(-3.64c^{1/2})] \quad (5)$$

and the relative partial molar enthalpy ($\Delta_{sol}H_{L,1}$) of the solvent of double-distilled water is expressed as

$$\Delta_{sol}H_{L,1} = -M_{H_2O}c^2(\partial\Delta_{sol}H_{\phi}/\partial c)_{T,P} \quad (6)$$

According to the relationship shown in eqs 1, 4, and 6, the relative apparent molar enthalpy ($\Delta_{sol}H_{\phi}$), relative partial molar enthalpy ($\Delta_{sol}H_{L,2}$) of the compound, and relative partial molar enthalpy ($\Delta_{sol}H_{L,1}$) of double-distilled water as the solvent are obtained. The calculated results above are listed in Table 3.

Conclusions

This paper reports the molar enthalpies of dissolution of 5-NH_2-$Na_2bdc\cdot H_2O$, 5-OH-$Na_2bdc\cdot H_2O$, 5-CH_3-$Na_2bdc\cdot H_2O$, 5-NO_2-$Na_2bdc\cdot H_2O$, and $Na_2bdc\cdot 0.5H_2O$ in water measured by a heat conduction microcalorimeter. The Pitzer's parameters of the title compounds were derived from these experimental results in terms of Pitzer's theory. The molar enthalpies of dissolution of the title compounds at infinite dilution were determined to be (−45.290, −36.790, −12.342, 22.009, and −29.799) kJ·mol^{-1}, respectively, which indicated that four of the compounds are exothermic reactions and enthalpy-driven processes except for the compound 5-NO_2-$Na_2bdc\cdot H_2O$. The dissolution enthalpy of the compound 5-NO_2-$Na_2bdc\cdot H_2O$ at infinite dilution is more than zero, which indicates that its dissolution

Table 3. Values of Molar Dissolution Enthalpies of Title Compounds at Various Molar Concentrations at $T = 298.15$ K

10^3c	$\Delta_{sol}H_m$	$\Delta_{sol}H_\phi$	$10^{-5}(\partial\Delta_{sol}H_\phi/\partial m)_{T,P}$	$\Delta_{sol}H_{L,1}$	$\Delta_{sol}H_{L,2}$
(mol·L^{-1})	(kJ·mol^{-1})	(kJ·mol^{-1})		(J·mol^{-1})	(kJ·mol^{-1})
			1		
2.142	−44.733	0.557	1.5967	−13.187	0.899
4.189	−44.614	0.676	1.3298	−42.003	1.233
5.863	−44.171	1.119	1.2374	−76.563	1.845
7.494	−43.938	1.352	1.1847	−119.763	2.240
9.157	−43.881	1.409	1.1501	−173.591	2.462
10.838	−43.822	1.468	1.1264	−238.167	2.689
12.572	−43.513	1.777	1.1094	−315.631	3.172
14.293	−43.303	1.987	1.0975	−403.559	3.556
16.127	−43.223	2.067	1.0884	−509.531	3.822
17.958	−43.175	2.115	1.0821	−628.118	4.058
20.054	−42.933	2.357	1.0772	−779.756	4.517
22.461	−42.509	2.781	1.0738	−975.084	5.193
24.352	−42.161	3.129	1.0723	−1144.622	5.740
26.276	−41.908	3.382	1.0716	−1331.804	6.198
28.172	−41.809	3.481	1.0716	−1530.888	6.500
30.159	−41.812	3.478	1.0721	−1755.247	6.712
32.04	−41.412	3.878	1.0729	−1982.584	7.315
33.772	−41.321	3.969	1.0740	−2204.866	7.596
35.654	−41.161	4.129	1.0753	−2460.577	7.963
37.432	−41.092	4.199	1.0768	−2715.811	8.229
			2		
3.324	−35.977	0.813	1.2953	−25.760	1.244
5.293	−35.952	0.838	1.1308	−57.022	1.437
6.869	−35.778	1.012	1.0578	−89.835	1.739
8.388	−35.616	1.174	1.0099	−127.905	2.021
10.187	−35.356	1.434	0.9696	−181.121	2.428
12.079	−35.290	1.500	0.9389	−246.578	2.634
13.815	−35.129	1.661	0.9175	−315.204	2.929
15.766	−35.063	1.727	0.8988	−402.138	3.144
17.969	−34.788	2.002	0.8824	−512.825	3.588
19.768	−34.675	2.115	0.8716	−613.110	3.838
21.682	−34.316	2.474	0.8622	−729.619	4.344
23.486	−34.240	2.550	0.8548	−848.734	4.558
25.568	−34.051	2.739	0.8477	−997.477	4.906
27.606	−33.823	2.967	0.8419	−1154.827	5.291
29.68	−33.709	3.081	0.8369	−1326.949	5.565
31.628	−33.559	3.231	0.8329	−1499.679	5.865
33.417	−33.370	3.420	0.8297	−1667.792	6.193
35.367	−33.285	3.505	0.8267	−1861.412	6.429
37.508	−33.238	3.552	0.8240	−2086.515	6.642
39.760	−33.077	3.713	0.8215	−2337.482	6.979
			3		
2.382	−11.877	0.465	9.4017	−9.602	0.689
4.254	−11.790	0.552	7.4488	−24.263	0.869
6.14	−11.769	0.573	6.6614	−45.204	0.982
7.583	−11.560	0.782	6.3465	−65.688	1.263
9.175	−11.476	0.866	6.1418	−93.063	1.430
11.053	−11.427	0.915	6.0103	−132.168	1.579
12.886	−11.259	1.083	5.9501	−177.841	1.849
14.861	−11.217	1.125	5.9311	−235.779	2.006
16.742	−11.098	1.244	5.9414	−299.761	2.239
18.523	−11.059	1.283	5.9679	−368.569	2.388
20.310	−10.814	1.528	6.0059	−445.931	2.748
22.117	−10.825	1.517	6.0522	−532.893	2.856
23.882	−10.661	1.681	6.1029	−626.546	3.139
25.722	−10.551	1.791	6.1598	−733.578	3.375
27.527	−10.484	1.858	6.2182	−848.115	3.570
29.343	−10.435	1.907	6.2787	−973.092	3.749
31.072	−10.319	2.023	6.3374	−1101.338	3.992
32.801	−10.191	2.151	6.3966	−1238.776	4.249
34.744	−10.148	2.194	6.4633	−1404.380	4.440
36.343	−9.941	2.401	6.5181	−1549.657	4.770
			4		
3.093	22.153	0.144	−4.4854	7.724	0.005
5.036	22.027	0.018	−5.7789	26.381	−0.273
6.638	21.803	−0.206	−6.2496	49.568	−0.621
8.062	21.713	−0.296	−6.4782	75.790	−0.818
9.565	21.579	−0.430	−6.6137	108.914	−1.063
10.912	21.455	−0.554	−6.6783	143.135	−1.283
12.418	21.455	−0.554	−6.7094	186.235	−1.387
13.815	21.253	−0.756	−6.7120	230.584	−1.683
15.533	21.244	−0.765	−6.6917	290.615	−1.804
17.284	21.152	−0.857	−6.6527	357.733	−2.007
18.817	20.925	−1.084	−6.6083	421.175	−2.327
20.47	20.925	−1.084	−6.5529	494.247	−2.425
22.228	20.761	−1.248	−6.4882	577.028	−2.690
23.886	20.673	−1.336	−6.4234	659.663	−2.870
25.669	20.431	−1.578	−6.3510	753.237	−3.208
27.38	20.407	−1.602	−6.2799	847.411	−3.321
29.008	20.282	−1.727	−6.2115	940.817	−3.529
30.666	20.117	−1.892	−6.1415	1039.587	−3.775
32.163	20.02	−1.989	−6.0783	1131.793	−3.944
33.807	19.87	−2.139	−6.0091	1236.225	−4.171
			5		
2.883	−29.218	0.581	10.5200	−15.739	0.884
4.575	−29.228	0.571	9.0170	−33.972	0.984
6.261	−28.87	0.929	8.2868	−58.472	1.448
8.034	−28.933	0.866	7.8548	−91.258	1.497
9.718	−28.786	1.013	7.6060	−129.295	1.752
11.393	−28.656	1.143	7.4483	−174.023	1.992
13.362	−28.606	1.193	7.3334	−235.680	2.173
14.98	−28.328	1.471	7.2764	−293.909	2.561
16.818	−28.287	1.512	7.2392	−368.564	2.729
18.783	−28.195	1.604	7.2222	−458.643	2.961
20.527	−28.096	1.703	7.2212	−547.687	3.185
22.64	−27.762	2.037	7.2326	−667.293	3.674
24.466	−27.762	2.037	7.2505	−781.210	3.811
26.582	−27.572	2.227	7.2782	−925.702	4.162
28.552	−27.365	2.434	7.3088	−1072.487	4.521
30.453	−27.305	2.494	7.3416	−1225.529	4.730
32.21	−27.191	2.608	7.3740	−1377.076	4.983
34.251	−27.145	2.654	7.4135	−1565.466	5.193
36.287	−26.98	2.819	7.4544	−1766.789	5.524
38.258	−26.848	2.951	7.4948	−1974.591	5.818

is an entropy-driven process instead of an enthalpy-driven process. The expected result is consistent with the computed result.

Supporting Information Available:

Figures S1 to S9. This material is available free of charge via the Internet at http://pubs.acs.org.

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