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Low temperature heat capacities and standard molar enthalpy of formation of sodium benzoate C_6H_5COONa (s)

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ABSTRACT

Sodium benzoate was synthesized by the method of liquid phase synthesis, in which benzoic acid and anhydrous sodium carbonate were chosen as the reactants. The structure and composition of the compound were characterized by FTIR, chemical analysis, elemental analysis and X-ray powder diffraction techniques. Low temperature heat capacities of the compound were measured by a precision automated adiabatic calorimeter over the temperature range from 78 to 400 K. A polynomial equation of the heat capacities as a function of the temperature was fitted by least square method. The smoothed heat capacities and the thermodynamic functions of the compound relative to 298.15 K have been calculated based on the equation. In accordance with Hess law, the standard molar enthalpy of formation of the title compound C_6H_5COONa (s) was determined to be $\Delta_f H^\circ{}_m[C_6H_5COONa, s] = -(642.56 \pm 0.64)\,kJ\,mol^{-1}$ by using an isoperibol solution-reaction calorimeter.

1. Introduction

Sodium is an essential element which exists in the form of positive ion in human body. It has the important physiological functions and nutritional values, and participates in the metabolism of water in the biological body. It can maintain the acid–base equilibrium in the human body and is also one of the important components in human body's muscle and nerve cells. The shortage of sodium may result in many kinds of diseases, such as nausea, cataplexy, low blood pressure, severe convulsion and so on. Benzoic acid has prominent physiological and chemical activity as a fine chemical, medical intermediate and food additive in the fields of medicine, cosmetic and nutrient, which can be used to synthesize a series of important products. The compounds of benzoic acid with many biological metals are the food preservatives and anti-microbial agents widely used in many foods from soup to cereals because they can inhibit microbial growth [1,2]. In addition, it can greatly increase the solubility of medicament in body fluids, and obviously enhance the absorption ratio of useful drug in the human body [3].

The synthesis and characterization of sodium benzoate have been reported in literature [4]. However, until now, thermodynamic properties of the compound have not been found, which restricted the progress of relevant theoretical study and application development. The purpose of the present study is to measure low temperature heat capacities of the compound by adiabatic calorimetry and determine the dissolution enthalpies of the reactants and the products of the liquid phase reaction of sodium acetate with benzoic acid by an isoperibol solution-reaction calorimetry. Finally, some thermodynamic parameters such as the enthalpy change of the reaction and the standard molar enthalpy of formation of the product C_6H_5COONa (s) were derived from these experimental results.

2. Experimental

2.1. Synthesis and characterization of the sodium benzoate C_6H_5COONa (s)

The compound was synthesized according to the method reported in the literature [4]. Benzoic acid and anhydrous sodium carbonate were chosen as the reactants, accurately weighed at the molar ratio of $n(C_6H_5COOH){:}n(Na_2CO_3) = 2{:}1$, put anhydrous sodium carbonate (about 5.30 g, 0.05 mol) into a beaker with a volume of 250 mL, and add 20 mL double deionized water. When the solution was heated up nearly to boil, then benzoic acid (about 12.2 g or 0.1 mol) dissolved in the water beforehand was slowly dripped into the above solution with a burette under sufficient stirring, and the pH was adjusted to 6.8–7.2. The transparent solu-

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Table 1
Characteristic vibration absorptions of main groups obtained from FTIR spectra of the title compound and benzoic acid (cm^{-1}).

Compound	$\nu_{C=O}$	$\nu_{—OH}$	$\nu_{C=C}$	$\nu_{C—H}$	$\delta_{C—H}$	$\delta_{C—O}$
C_6H_5COOH	1690	3600	1575	3100 2925	710	1200
C_6H_5COONa	1632	–	1596 1550	2926 2852	719	1119

tion was heated for about 30 min with electric cooker until crystal membrane emerged. The final solution was cooled to room temperature slowly and filtered. The filter cake was washed three times using anhydrous ethanol (A.R.), white product was gained. Then, the product was recrystallized for three times with the mixed solution of anhydrous ethanol and double deionized water, and white crystal was obtained. Finally, the sample was placed in a vacuum desiccator at the temperature of 50 °C to vacuum dry for 6 h. The final product took a whiteness with a weight of 5.1 g. Theoretical contents of Na, C, H and O in the compound have been calculated to be 15.95, 58.34, 3.50 and 22.21%, respectively. Chemical and element analyses (model: PE-2400, Perkin Elmer, USA) have shown that practical contents of Na, C, and H in the compound have been measured to be 15.98, 58.32 and 3.47%, respectively. This showed that the purity of the sample prepared was higher than 0.9910 in mass fractions.

FTIR (Nicolet 5700 FT-IR, USA, KBr) was used to determine the bond mode of sodium ion with benzoic acid in the range of the wavelength 400–4000 cm^{-1}. Vibration characteristic absorptions of main groups obtained from FTIR spectra of the compound and benzoic acid were listed in Table 1. It can be seen from Table 1 that, as for absorption peak of O—H stretching vibration ($\gamma_{O–H}$) of benzoic acid, a strong peaked absorption peak appeared at 3600 cm^{-1}. However, the organic component of the compound possesses distinctly different characteristic absorption peaks relative to those of benzoic acid, especially, the absorption peak of the O—H stretching vibration $\gamma_{O–H}$ has disappeared in the title compound. It is shown that the oxygen atom of the organic component in the compound is directly linked with the sodium ion, and the hydrogen atom of —COOH in benzoic acid has been replaced by the sodium ion, so the carboxyl (—COOH) behaves as a carboxylate ($—COO^-$). The absorption peak of the C═O stretching vibration ($\gamma_{C=O}$) in the sodium benzoate was shifted to a low wave number due to the formation of a big delocalization π bond including benzene ring and carboxylate ($—COO^-$), which decreased the electron cloud density of carboxylate ($—COO^-$). Moreover, the shift of some other absorption peaks was possibly attributed to the formation of Na—O bond in the title compound.

Whether the new synthesized compound is novel or cannot also be determined by X-ray powder diffraction (XRD) technique. XRD spectra of benzoic acid, anhydrous sodium carbonate and sodium benzoate have been plotted in Fig. 1. The step length of powder diffraction angle was 0.01°, wave length was 0.154056 nm (Cu Kα1 radiation), electric voltage was 36 kV and electric current was 20 mA. The scanning rate was 4° min^{-1} and the graphite monochromator was used for the filtration. It was found out from Fig. 1 that two obvious absorption peaks were seen in the angle range of $2\theta = 16–18°$ in the diffraction chart of the benzoic acid. There was two absorption peaks appearing near $2\theta = 30°$ and 38° in the chart of anhydrous sodium carbonate, two distinct characteristic absorption peaks were seen in the angle range of $2\theta = 28°$ and 32° in the chart of sodium benzoate. Therefore, novel characteristic peaks different from those of benzoic acid and anhydrous sodium carbonate appeared in the diffraction spectrum of sodium benzoate. It was shown that a new substance was produced by the liquid phase reaction of benzoic acid with anhydrous sodium carbonate.

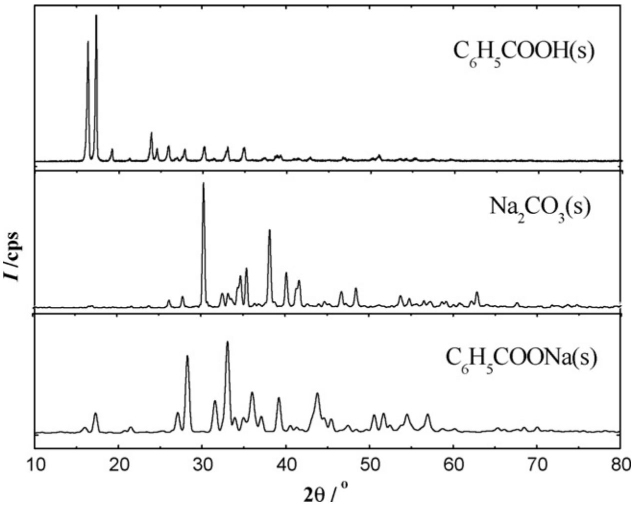

Fig. 1. XRD spectra of benzoic acid, anhydrous sodium carbonate and sodium benzoate.

2.2. Adiabatic calorimetry

A precision automatic adiabatic calorimeter was used to measure heat capacities of the compound over the temperature range $78 \le (T\,(K)) \le 400$. The calorimeter was established in the Thermochemistry Laboratory in the College of Chemistry and Chemical Engineering, Liaocheng University, China. The principle and structure of the adiabatic calorimeter were described in detail elsewhere [5,6]. Briefly, the calorimeter mainly comprised a sample cell, a platinum resistance thermometer, an electric heater, inner, middle and outer adiabatic shields, three sets of six-junction chromel–constantan thermopiles installed between the calorimetric cell and the inner shield, between the inner and middle shields, and between the middle and outer shields, respectively, and a high vacuum can. The miniature platinum resistance thermometer (IPRT No.2, produced by Shanghai Institute of Industrial Automatic Meters, 16 mm in length, 1.6 mm in diameter and a nominal resistance of 100 Ω) was applied to measure the temperature of the sample. The thermometer was calibrated on the basis of ITS-90 by the Station of Low-Temperature Metrology and Measurements, Academia Sinica. The electrical energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded by use of a Data Acquisition/Switch Unit (Model 34970A, Agilent, USA), and processed on line by a computer.

To verify the accuracy of the calorimeter, the heat capacities of the reference standard material (α-Al_2O_3) were measured over the temperature range $78 \le (T\,(K)) \le 400$. The sample mass used was 1.7143 g, which was equivalent to 0.0168 mol based on its molar mass, $M\,(Al_2O_3) = 101.9613\ g\,mol^{-1}$. Deviations of the experimental results from those of the smoothed curve lie within ±0.2%, while the uncertainty is ±0.3%, as compared with the values given by the former National Bureau of Standards [7] over the whole temperature range.

Heat capacity measurements were continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were generally controlled at (0.1–0.4) K min^{-1} and (1–3) K. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within (10^{-3} to 10^{-4}) K min^{-1} during the acquisition of all heat-capacity data. The data of heat capacities and corresponding equilibrium temperature have been corrected for heat exchange of the sample cell with its surroundings [5]. The sample mass used for calorimetric measurements was 2.4360 g, which was equivalent to 0.0169 mol in terms of its molar mass, $M = 144.10\ \mathrm{g\ mol^{-1}}$.

2.3. Isoperibol solution-reaction calorimetry

The isoperibol solution-reaction calorimeter consisted primarily of a precision temperature controlling system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precision temperature measuring system and a data acquisition system. The principle and structure of the calorimeter were described in detail elsewhere [5,8].

The reliability of the calorimeter was verified previously by measuring dissolution enthalpy of KCl (calorimetrically primary standard) in double distilled water at $T = 298.15$ K. The mean dissolution enthalpy was $(17{,}547 \pm 13)\ \mathrm{J\ mol^{-1}}$ for KCl, which compared with corresponding published data $(17{,}536 \pm 3.4)\ \mathrm{J\ mol^{-1}}$ [9].

In all dissolution experiments of the sample, 100 mL of $1.0\ \mathrm{mol\ L^{-1}}$ NaOH was chosen as the calorimetric solvent for measuring the dissolution enthalpies of the reactants and products at $T = 298.15$ K.

Finally, UV/vis spectroscopy and the data of the refractive indexes were used to confirm whether solution A was in the same thermodynamic state as that of solution B. These results have indicated that the chemical components and physicochemical properties of solution A were consistent with those of solution B.

3. Results and discussion

3.1. Low-temperature heat capacities

Table 2
Experimental molar heat capacities of sodium benzoate C_6H_5COONa (s) [$M = 144.10\ \mathrm{g\ mol^{-1}}$].

T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\ mol^{-1}\ K^{-1}}$)	T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\ mol^{-1}\ K^{-1}}$)	T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\ mol^{-1}\ K^{-1}}$)
78.858	74.655	166.41	120.71	304.35	186.94
80.427	75.059	169.54	122.29	307.33	188.32
82.622	76.575	172.67	124.15	310.32	189.49
84.789	77.939	175.80	125.53	313.30	190.87
87.064	79.001	178.78	127.20	316.29	191.75
89.076	80.343	182.05	128.48	319.28	192.93
91.156	81.603	186.18	130.74	322.12	194.21
93.237	82.942	190.73	133.09	325.11	195.49
95.317	83.729	194.71	134.96	327.81	196.77
97.259	84.832	198.69	136.73	329.51	197.36
99.201	86.092	202.67	138.89	332.93	198.63
101.14	87.273	206.65	140.95	335.35	199.91
103.01	88.198	210.78	143.02	338.05	200.79
104.89	89.107	214.62	144.69	340.89	202.17
106.30	89.815	218.60	147.24	343.88	202.96
107.72	90.522	222.72	148.91	346.72	204.33
109.44	91.634	226.56	150.78	349.42	205.02
111.32	92.544	230.54	152.55	352.27	206.20
113.05	93.554	234.67	154.30	355.25	207.28
114.93	94.666	238.65	156.48	358.10	208.56
116.50	95.373	242.63	158.35	360.85	209.38
118.38	95.980	247.75	160.90	363.79	210.82
120.05	97.426	252.79	162.99	366.63	212.19
122.61	98.899	256.71	164.60	369.62	213.57
126.31	100.57	260.69	166.70	372.46	214.53
129.87	102.54	264.71	168.34	375.30	215.93
133.42	104.11	268.80	170.63	378.15	217.20
137.05	105.58	272.92	172.89	380.99	218.09
140.25	107.64	276.90	174.76	383.98	219.66
143.52	109.31	280.74	176.43	386.68	220.45
146.93	111.38	284.72	178.39	389.52	221.82
150.20	112.85	288.70	179.87	392.37	223.20
153.61	114.42	292.69	181.54	395.21	224.18
156.74	115.80	295.10	182.91	397.91	225.75
159.94	117.10	298.37	184.58		
163.08	118.62	301.36	185.56		

The experimental molar heat capacities were listed in Table 2 and plotted in Fig. 2. It was found out from Fig. 2 that the heat capacity curve of the compound was smoothly increased with the temperature, which showed that the structure of the compound was stable over the temperature range between $T = 78$ K and 400 K, no phase change, association nor thermal decomposition occurred. The 106 experimental points in the temperature region between $T = 78$ K and 400 K were fitted by the least square method, and a polynomial equation of molar heat capacities ($C_{p,\mathrm{m}}$) vs. reduced temperature (X), $X = f(T)$, has been obtained:

$$C_{p,\mathrm{m}}(\mathrm{J\ K^{-1}\ mol^{-1}}) = 156.698 + 76.266X - 6.855X^2 - 0.712X^3 + 0.218X^4$$

in which $X = (T - 239)/161$. This equation is valid over the temperature range 78–400 K.

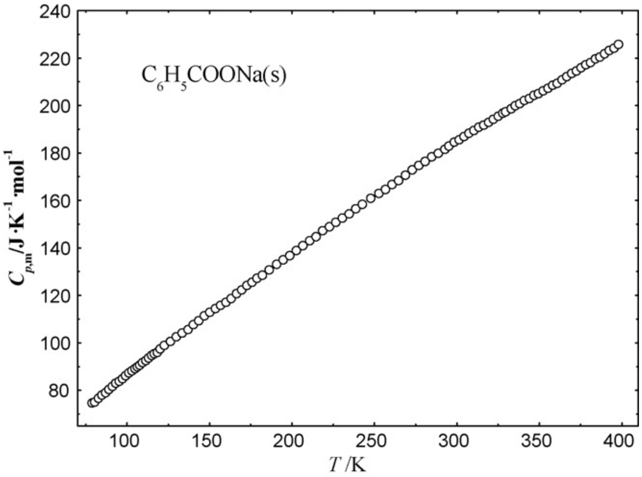

Fig. 2. Curve of the experimental molar heat capacities of the compound C_6H_5COONa (s) vs. the temperature (T).

The standard deviations of experimental molar heat capacities from the smoothed heat capacities calculated by the polynomial equation were within ±0.3% except for several points around the lower and upper temperature limits. The coefficient of determination for the fitting R^2 equals 0.99995. The uncertainties of the coefficients of the fitted equation have been determined to be 0.0005, 0.002, 0.06, 0.31 and 2.06%, respectively.

3.2. Thermodynamic functions of the compound

The smoothed molar heat capacities and thermodynamic functions of the sample were calculated based on the fitted polynomial of the heat capacity as a function of the reduced temperature (X) according to the following thermodynamic equations:

$$H_{(T)} - H_{(298.15\,\mathrm{K})} = \int_{298.15\,\mathrm{K}}^{T} C_{p,\mathrm{m}}\,\mathrm{d}T$$

$$S_{(T)} - S_{(298.15\,\mathrm{K})} = \int_{298.15\,\mathrm{K}}^{T} C_{p,\mathrm{m}}\,T^{-1}\,\mathrm{d}T$$

$$G_{(T)} - G_{(298.15\,\mathrm{K})} = \int_{298.15\,\mathrm{K}}^{T} C_{p,\mathrm{m}}\,\mathrm{d}T - T\int_{298.15\,\mathrm{K}}^{T} C_{p,\mathrm{m}}\,T^{-1}\,\mathrm{d}T$$

Table 3
Smoothed molar heat capacities and thermodynamic functions of the sample C_6H_5COONa (s) (M = 144.10 g mol^{-1}).

T (K)	$C_{p,m}$ (J mol^{-1} K^{-1})	$H_T - H_{298.15\,K}$ (kJ mol^{-1})	$S_T - S_{298.15\,K}$ (J K^{-1} mol^{-1})	$G_T - G_{298.15\,K}$ (kJ mol^{-1})
80	75.587	−28.69	−157.7	−16.07
85	78.281	−28.30	−153.1	−15.29
90	80.969	−27.90	−148.5	−14.54
95	83.650	−27.49	−144.1	−13.80
100	86.323	−27.07	−139.7	−13.10
105	88.988	−26.63	−135.4	−12.41
110	91.645	−26.18	−131.2	−11.75
115	94.294	−25.71	−127.0	−11.10
120	96.935	−25.23	−123.0	−10.48
125	99.566	−24.74	−118.9	−9.875
130	102.19	−24.24	−115.0	−9.292
135	104.80	−23.72	−111.1	−8.728
140	107.41	−23.19	−107.2	−8.182
145	110.00	−22.65	−103.4	−7.656
150	112.58	−22.09	−99.61	−7.148
155	115.16	−21.52	−95.88	−6.659
160	117.72	−20.94	−92.19	−6.187
165	120.27	−20.34	−88.54	−5.734
170	122.82	−19.74	−84.92	−5.299
175	125.35	−19.11	−81.34	−4.881
180	127.87	−18.48	−77.78	−4.481
185	130.38	−17.84	−74.25	−4.099
190	132.87	−17.18	−70.75	−3.735
195	135.36	−16.51	−67.28	−3.388
200	137.83	−15.82	−63.83	−3.058
205	140.29	−15.13	−60.40	−2.746
210	142.74	−14.42	−57.00	−2.452
215	145.18	−13.70	−53.62	−2.174
220	147.60	−12.97	−50.25	−1.914
225	150.01	−12.23	−46.91	−1.671
230	152.41	−11.47	−43.59	−1.444
235	154.80	−10.70	−40.28	−1.235
240	157.17	−9.922	−37.00	−1.043
245	159.53	−9.130	−33.73	−0.8670
250	161.88	−8.326	−30.47	−0.7079
255	164.21	−7.511	−27.24	−0.5653
260	166.53	−6.684	−24.02	−0.4391
265	168.83	−5.846	−20.82	−0.3291
270	171.12	−4.996	−17.63	−0.2352
275	173.40	−4.135	−14.46	−0.1573
280	175.66	−3.262	−11.31	−0.09514
285	177.91	−2.378	−8.174	−0.04867
290	180.15	−1.483	−5.053	−0.01768
295	182.37	−0.5767	−1.948	−0.002043
298.15	183.76	0	0	0
300	184.58	0.3407	1.141	−0.001597
305	186.77	1.269	4.214	−0.01620
310	188.94	2.208	7.271	−0.04570
315	191.11	3.159	10.31	−0.08998
320	193.26	4.119	13.34	−0.1489
325	195.39	5.091	16.35	−0.2224
330	197.51	6.073	19.34	−0.3104
335	199.61	7.066	22.33	−0.4128
340	201.70	8.069	25.29	−0.5295
345	203.78	9.083	28.24	−0.6606
350	205.84	10.11	31.18	−0.8061
355	207.88	11.14	34.11	−0.9660
360	209.91	12.19	37.02	−1.140
365	211.93	13.24	39.92	−1.330
370	213.93	14.31	42.81	−1.534
375	215.91	15.38	45.69	−1.753
380	217.88	16.46	48.56	−1.987
385	219.84	17.56	51.42	−2.238
390	221.78	18.66	54.28	−2.505
395	223.70	19.78	57.13	−2.788

The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of the sample relative to the standard reference temperature 298.15 K were tabulated in Table 3 with an interval of 5 K.

3.3. The determination of enthalpy change for the liquid phase reaction of CH_3COONa (s) with benzoic acid

The C_6H_5COONa (s) is supposed to be one of the products in the following liquid phase reaction:

$$C_6H_5COOH(s) + CH_3COONa(s) \rightarrow CH_3COOH(l) + C_6H_5COONa(s) \tag{1}$$

The enthalpy change of the reaction (1) can be determined by respective measuring enthalpies of dissolution of the C_6H_5COOH (s) and CH_3COOH (l) in 1.0 mol L^{-1} NaOH, CH_3COONa (s) in 1.0 mol L^{-1} NaOH solution containing certain amounts of the benzoic acid, and C_6H_5COONa (s) in 1.0 mol L^{-1} NaOH solution containing certain amounts of the acetic acid at 298.15 K.

First, benzoic acid and sodium acetate must be dried in the vacuum desiccator at 50 °C for several hours. About 1×10^{-3} mol or 0.122 g of C_6H_5COOH (s) was dissolved in 100 mL of 1.0 mol L^{-1} NaOH at 298.15 K. If "S" = calorimetric solvent, 1.0 mol L^{-1} NaOH, then:

$$\{C_6H_5COOH(s)\} + \text{“S''} = \text{solutionA}'$$

According to the $n(CH_3COONa)$:$n(C_6H_5COOH)$ = 1:1 in the reaction (1), about 1×10^{-3} mol or 0.082 g of $\{CH_3COONa$ (s)$\}$ were dissolved in the solution A′, i.e.:

$$\{CH_3COONa(s)\} + \text{solutionA}' = \text{solutionA}$$

About 1×10^{-3} mol or 0.060 g of $\{CH_3COOH$ (l)$\}$ were dissolved in 100 mL of 1.0 mol L^{-1} NaOH. Because of the volatilization of acetic acid, when the liquid were weighed, the temperature in room must be controlled at 17–18 °C to reduce the rate of volatilization, the sample cell in which acetic acid was put should be covered with plug made of the polytetrafluoroethylene. The dissolution enthalpy of CH_3COOH (l) in 1.0 mol L^{-1} NaOH was measured under the same condition as the above:

$$\{CH_3COOH(l)\} + \text{“S''} = \text{solutionB}'$$

The dissolution enthalpy of about 1×10^{-3} mol or 0.144 g C_6H_5COONa (s) in 1.0 mol L^{-1} NaOH solution containing certain amounts of the acetic acid was measured under the same condition as the above:

$$\{C_6H_5COONa(s)\} + \text{solutionB}' = \text{solutionB}$$

The measurement results of dissolution enthalpies for the reactants and products of reaction (1) were listed in Table 4.

The enthalpy change of the reaction (1) can be calculated in accordance with a thermochemical cycle and the experimental results of the dissolution enthalpy as follows:

$$\begin{aligned}
\Delta_r H^\circ{}_m &= \sum \Delta_s H^\circ{}_{m\ (\text{Reactants})} - \sum \Delta_s H^\circ{}_{m\ (\text{Products})} \\
&= \Delta_s H^\circ{}_{C_6H_5COOH} + \Delta_s H^\circ{}_{CH_3COONa} \\
&\quad - (\Delta_s H^\circ{}_{CH_3COOH} + \Delta_s H^\circ{}_{C_6H_5COONa}) \\
&= \Delta H_1 + \Delta H_2 - (\Delta H_3 + \Delta H_4) \\
&= (-26.195) + (-10.931) - [(-5.124) + (-1.623)] \\
&= -(30.38 \pm 0.15)\,\text{kJ mol}^{-1}
\end{aligned}$$

3.4. The standard molar enthalpy of formation of the compound C_6H_5COONa (s)

A reaction scheme used to determine the standard molar enthalpy of formation of C_6H_5COONa (s) was given in Table 5. The experimental values of the dissolution enthalpies of the reactants

Table 4
Dissolution enthalpies of reactants and products of reaction (1) in the selected solvents at $T = 298.15$ K[a].

System	Solvent	Avg. $\Delta_s H^\circ{}_m$ (kJ mol^{-1})	No.	m (g)	$\Delta E_s/\Delta E_e$	t_e (s)	Q_s (J)	$\Delta_s H^\circ{}_m$ (kJ mol^{-1})
Benzoic acid	1.0 mol·L^{-1} NaOH	–(26.20 ± 0.08)	1	0.12150	0.7106	74.844	–25.807	–25.939
			2	0.12253	0.8329	65.047	–26.289	–26.201
			3	0.12254	0.8624	63.031	–26.376	–26.285
			4	0.12471	0.8728	62.984	–26.675	–26.121
			5	0.12231	0.8898	61.312	–26.473	–26.431
Sodium acetate	Solution A′	–(10.93 ± 0.11)	1	0.08241	1.9750	8.532	–11.185	–11.087
			2	0.08275	2.6182	11.672	–10.840	–10.790
			3	0.08284	1.4461	15.547	–10.909	–10.803
			4	0.08272	1.1123	19.953	–10.769	–10.680
			5	0.08261	1.2310	19.040	–11.373	–11.293
Acetic acid	1.0 mol·L^{-1} NaOH	–(5.12 ± 0.06)	1	0.06005	0.4268	24.781	–5.140	–5.140
			2	0.06015	0.4826	21.407	–5.020	–5.012
			3	0.06020	0.4903	21.500	–5.123	–5.110
			4	0.06006	0.4973	22.093	–5.339	–5.338
			5	0.06008	0.0472	21.906	–5.025	–5.022
Sodium benzoate	Solution B′	–(1.62 ± 0.01)	1	0.14445	0.1598	20.937	–1.624	–1.620
			2	0.14474	0.2398	13.734	–1.598	–1.591
			3	0.14430	0.2856	11.688	–1.620	–1.618
			4	0.14452	0.2523	13.500	–1.653	–1.648
			5	0.14491	0.2540	13.374	–1.649	–1.639

[a] m (g), mass of sample; t_e (s), heating period of electrical calibration; $Q_s = -(\Delta E_s/\Delta E_e)I^2Rt_e$, heat effect during the sample dissolution; ΔE_s (mV), the voltage change during the sample dissolution; ΔE_e (mV), the voltage change during the electrical calibration; $\Delta_s H^\circ{}_m = Q_s/n = -(\Delta E_s/\Delta E_e) \times I^2 R\, t_e(M/m)$, where R is the electro-resistance ($R = 1213.09\ \Omega$ at $T = 298.15$ K), I is the current ($I = 20.015$ mA), and M is the molar mass of the sample.

and products in the liquid phase reaction (1) were combined with other auxiliary thermodynamic data of:

$\Delta_f H^\circ{}_m$ (C_6H_5COOH, s) = –(384.80 ± 0.50) kJ mol^{-1} [10], $\Delta_f H^\circ{}_m$ (CH_3COONa, s) = –710.90 kJ mol^{-1} [11], and $\Delta_f H^\circ{}_m$ (CH_3COOH, l) = –(483.52 ± 0.36) kJ mol^{-1} [12], to derive the standard molar enthalpy of formation of C_6H_5COONa (s):

$$\begin{aligned}
&\Delta_f H^\circ{}_m(\mathrm{C_6H_5COONa,\ s})\\
&= \Delta H_8 = \Delta_r H^\circ{}_m + \Delta_f H^\circ{}_m(\mathrm{C_6H_5COOH,\ s})\\
&\quad + \Delta_f H^\circ{}_m(\mathrm{CH_3COONa,\ s}) - \Delta_f H^\circ{}_m(\mathrm{CH_3COOH,\ l})\\
&= \Delta H_1 + \Delta H_2 - (\Delta H_3 + \Delta H_4) + \Delta H_5 + \Delta H_6 - \Delta H_7\\
&= (-26.195) + (-10.931) - [(-5.124) + (-1.623)] + (-384.80)\\
&\quad + (-710.90) - (-483.52)\\
&= (-30.379) + (-384.80) + (-710.90) - (-483.52)\\
&= -(642.56 \pm 0.64)\,\mathrm{kJ\,mol^{-1}}
\end{aligned}$$

in which ΔH_1–ΔH_8 were the enthalpy changes of the reactions corresponding to number of reactions in Table 5.

In this paper, all of the reactants and products of the liquid phase reaction can be easily dissolved in the corresponding solvents. The results of UV/vis spectra of solution A obtained from dissolution of the reactants in the liquid phase reaction and solution B from dissolution of the products were shown in Fig. 3. The experimental values of the refractive indexes of solution A and solution B were measured to be 1.3420 ± 0.0003 and 1.3421 ± 0.0002, respectively. These results indicated that solution A were consistent with solution B. Therefore, there is no difference in the structure, chem-

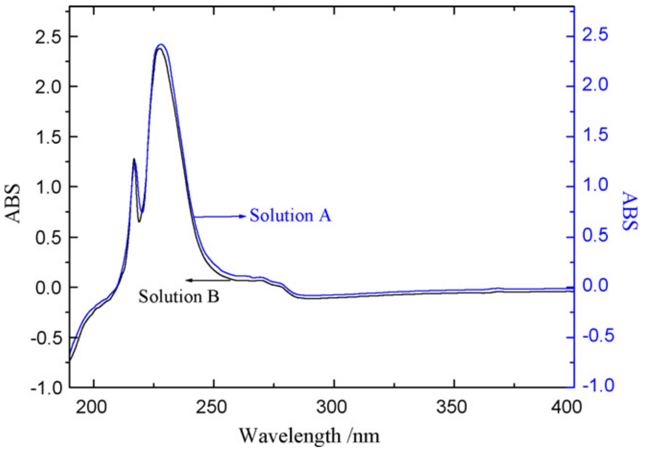

Fig. 3. UV/vis spectra of solution A obtained from dissolution of the reactants in the liquid phase reaction and solution B from dissolution of the products (diluted to 1:20).

Table 5
Reaction scheme used to determine the standard molar enthalpy of formation of sodium benzoate C_6H_5COONa (s).

No.	Reactions	Formed solution	$\Delta_f H^\circ{}_m$ or $(\Delta_s H^\circ{}_m \pm \sigma_a)$[a] (kJ mol^{-1})
1	{C_6H_5COOH (s)} + "S" =	A′	–(26.20 ± 0.08), ΔH_1
2	{CH_3COONa (s)} + solution A′ =	A	–(10.93 ± 0.11), ΔH_2
3	{CH_3COOH (l)} + "S" =	B′	–(5.12 ± 0.06), ΔH_3
4	{C_6H_5COONa (s)} + solution B′ =	B	–(1.62 ± 0.01), ΔH_4
5	7C (s) + $3H_2$ (g) + O_2 (g) = C_6H_5COOH (s)		–(384.80 ± 0.50) [10], ΔH_5
6	2C (s) + $3/2H_2$ (g) + O_2 (g) + Na (s) = CH_3COONa (s)		–710.90 [11], ΔH_6
7	2C (s) + $2H_2$ (g) + O_2 (g) = CH_3COOH (l)		–(483.52 ± 0.36) [12], ΔH_7
8	7C (s) + $5/2H_2$ (g) + O_2 (g) + Na (s) = C_6H_5COONa (s)		–(642.56 ± 0.64), ΔH_8

[a] The calorimetric solvent "S" is 1.0 mol L^{-1} NaOH, $\sigma_a = \sqrt{\sum_{i=1}^{5}(x_i - \bar{x})^2/n(n-1)}$, in which n is the experimental number; x_i, a single value in a set of dissolution measurements; $\bar{x}$, the mean value of a set of measurement results.

ical components and physicochemical properties between the two solutions.

4. Conclusions

(1) This paper reports low temperature heat capacities measured by adiabatic calorimetry and the dissolution enthalpies of the reactants and the products of the liquid phase reaction of sodium acetate with benzoic acid by isoperibol solution calorimetry. Furthermore, the thermodynamic functions and standard molar enthalpy of formation of the product C_6H_5COONa (s) were derived from these experimental results.

(2) The enthalpy change of the liquid phase reaction (1) obtained by solution calorimetry was determined to be $\Delta_r H^\circ{}_m = -(30.38 \pm 0.15)\,\mathrm{kJ\,mol^{-1}}$, which was an exothermic reaction. Based on thermodynamic theory, the reaction was an enthalpy-driven process. What is more, all of the reactants were solid, and the products included one solid and one volatile liquid. It was concluded from an increase of degree of chaos or disorder in the reaction that the entropy change of the liquid phase reaction was more than zero according to the statistical explanation of the entropy of the system in statistical thermodynamics, and the entropy function of the system was really a measure of “degree of disorder or chaos of the system”. Therefore, this reaction should also be an entropy-driven process.

(3) The standard molar enthalpy of formation of sodium benzoate is negative with a larger absolute value, which showed that it has lower energy and more stable structure in comparison with the stabile elementary substance which it was made up from. The uncertainty of the standard molar enthalpy of formation obtained by isoperibol solution calorimetry was estimated to be between 0.3 and 0.5%, chiefly considering the measurements of voltage changes ΔE_s and ΔE_e, the duration time of electric calibration t_e, final data processing and so on.

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References

[1] H.J. Tsay, Y.H. Wang, W.L. Chen, M.Y. Huang, Y.H. Chen, Neurotoxicol. Teratol. 29 (2007) 562–569.
[2] B. Nair, Int. J. Toxicol. 20 (S3) (2001) 23–50.
[3] Z.Y. Zeng, China Pharm. 16 (6) (2007) 64.
[4] Y.B. Lin, L. Wang, D. Wang, Shandong Sci. 4 (1) (1991) 68–69.
[5] Y.Y. Di, J.T. Chen, Z.C. Tan, Thermochim. Acta 471 (1–2) (2008) 70–73.
[6] Y.Y. Di, Y.C. Cui, Z.C. Tan, J. Chem. Eng. Data 51 (2006) 1551–1555.
[7] D.A. Ditmars, S. Ishihara, S.S. Chang, G. Bernstein, E.D. West, J. Res. Natl. Bur. Stand. 87 (1982) 159–163.
[8] Y.Y. Di, Z.C. Tan, S.L. Gao, S.X. Wang, J. Chem. Eng. Data 49 (2004) 965–969.
[9] R. Rychly, V. Pekarek, J. Chem. Thermodyn. 9 (1977) 391–396.
[10] L.B. Corral, Rev. R. Acad. Cienc. 54 (1960) 365–403.
[11] Y.B. Yao, T. Xie, Y.M. Gao, Hand Book of Physics and Chemistry, Press of Science and Technology, [M] Shanghai, 1985, p. 894.
[12] W.V. Steele, R.D. Chirico, A.B. Cowell, S.E. Knipmeyer, A. Nguyen, J. Chem. Eng. Data 42 (1997) 1052–1066.