

# Gelled $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ with amylose-g-sodium acrylate: heat storage performance, heat capacity and heat of fusion

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Received: 18 September 2007 / Accepted: 19 March 2009 / Published online: 10 June 2009  
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**Abstract** A novel gelling method was studied to stabilize phase change material  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  with amylose grafted sodium acrylate. Gelled  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  shows stable heat storage performance prepared at optimized conditions: 2.7 mass/mass% sodium acrylate, 0.4 mass/mass% amylose, 0.05–0.09 mass/mass% *N, N'*-methylene-bisacrylamide, 0.05–0.09 mass/mass%  $\text{K}_2\text{S}_2\text{O}_8$  and  $\text{Na}_2\text{SO}_3$  (mass ratio 1:1), at 50 °C.  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  was dispersed in gel network as tiny crystals less than 0.1 mm. Melting points were in the range  $35.4 \pm 2$  °C. Short-term thermal cycling proves the effectiveness of the novel method for eliminating phase separation in the gelled salt. Adiabatic calorimetric measurement of heat capacities shows two phase transitions, which correspond to melting of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and freezable bond water in gel, respectively. Heat of fusion of pure  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  was determined as  $260.9 \text{ J g}^{-1}$ . Distribution of extra water is: free water:freezable water:nonfreezing water = 0:0.85:0.15.

**Keywords** Gelling method ·  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  · Phase change material · Phase separation

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## Introduction

Phase change materials (PCMs) have been extensively studied for solar energy heating, peak-shift of electrical demand and heat recovery [1–7] since ‘Sun Queen’ Dr. Maria Telkes designed the first solar-heated house in 1948 [8]. These materials include the inorganic, the organic, metals or the composites, which may take action in gas–liquid, liquid–solid and solid–solid phase transitions. As is known to this field, organic PCMs usually show stable thermal energy capacities but with poor thermal conductivity and small volumetric heat storage densities. Inorganic PCMs, which are mainly salt hydrates, have no those drawbacks of organic PCMs, while often show phase separation for those most incongruent and semi-congruent melting salts [1]. Once this problem is solved, salt hydrates can be used in latent heat storage system. However, up to now only several kinds of salt hydrates PCMs are available as commercial products, among which modified  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is probably the most successful one. Thickener at-pulgite, nucleator borax and habit modifier  $(\text{Na}_2\text{PO}_3)_6$  are found to be the crucial additives for long-term  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  latent heat storage system, which spent about 20 years to be optimized under efforts of Maria Telkes and S. B. Marks [9–12]. Perhaps it is difficult and time-consuming process to select proper thickener and especially habit modifier which limit the development of salt hydrates PCMs with various melting points.

$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  has almost the largest mass heat storage capacity among low temperature phase change materials [1]. However, when heating, it melts incongruently because of the precipitation of hepta hydrate, which leads to a quick decrease in heat stored during thermal cycling [13, 14]. Some thickeners were added to promote performance such as starch, sodium alginate, cellulose

derivates, silica gel, attapulgite and cross-linked water-absorbing polymer [1, 14]. But the effects are not ideal in view of practical use [13, 14].

Gelling by in-situ synthesizing water-absorbing polymer, cross-linked sodium polyacrylate, in the molten salt has been reported for prevention of phase segregation [15, 16]. But the method showed poor reproducibility in our experiments no matter how carefully the reaction conditions were controlled: only about 30% the optimized possess fairly stable heat storage performance [13, 14]. The phenomenon implies that sodium polyacrylate cross-linked to  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  is more of a gel medium but not an effective habit modifier to keep the very small size of crystals in thermal cycling. So we tried to introduce other component, amylose, into sodium polyacrylate gel network, which contains  $-\text{OH}$  and  $-\text{COOH}$  in the chain not merely  $-\text{COOH}$  for the latter. As a result, the novel gelled sample showed stable heat storage performance in a 100-cycle thermal test [17].

This paper presents another novel gelling method by polymerizing amylose grafted sodium acrylate to stabilize  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , including synthesis optimization, short term testing and low temperature heat capacity measurement with adiabatic calorimeter.

## Experimental

All inorganic salts, amylose and *N, N'*-methylenebis-acrylamide (MBA) (Shanghai Chemical Reagents Co.) were of analytical grade. Acrylic acid (CP) was purified through reduced pressure distillation and prepared as a storage solution of 20 mass/mass% with  $\text{pH} = 7.0$ .  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  was prepared by cooling a solution of 40 g  $\text{Na}_2\text{HPO}_4$  and 100 g  $\text{H}_2\text{O}$  below  $35^\circ\text{C}$  [18]. The large crystals were filtered out and dried before use.

Gelled  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  with different water absorbing components was prepared by adjusting the amount of monomer, cross-linking agent, initiators and reaction temperatures. A typical synthesis method was as follows: 13.5 g  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and 1.5 g  $\text{H}_2\text{O}$  mixed in a closed vial and stirred at  $50^\circ\text{C}$  till a clear solution was obtained. Then 0.085 g amylose was introduced and stirred for 30 min. After that, under helium atmosphere, an aqueous sodium acrylate solution 2.5 g, 0.017 g of MBA and 0.01 g potassium peroxydisulfate were added and dissolved sequentially; 15 min later, 0.010 g of sodium sulfite dissolved in 0.67 g water was dropped into the solution. A jelly-like product was obtained in a few minutes and was cooled down after 2 h (Scheme 1). Acrylate was not detected in the product by FT-IR since  $\text{C}=\text{C}$  stretching ions  $1,640\text{ cm}^{-1}$  in sodium acrylate and  $1,660\text{ cm}^{-1}$  in MBA were not observed (figure not shown).

Evaluation of heat storage performance of the products was performed on a DSC (141, SETARAM, France, calibrated with indium, aluminum, tin, of standard material, 99.999% pure) under nitrogen atmosphere, in the temperature range  $0\text{--}50^\circ\text{C}$ . 3–5 mg sample was sealed in a  $30\ \mu\text{L}$  aluminum crucible used for TG analysis (Setsys 16/18, Setaram, France). FT-IR analysis was conducted on a spectrophotometer (Nicolet Impact 400D, ThermoNicolet, USA). The size of the tiny crystals in gelled  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  was measured by a reading microscope with a resolving power of  $0.001\text{ mm}$  (JC4-10, Shanghai Precision Instruments Co., China).

Heat capacity measurements were carried out by an adiabatic calorimeter described in detail elsewhere [19, 20]. Prior to the heat capacity measurements, the calorimeter was calibrated with standard material  $\alpha\text{-Al}_2\text{O}_3$  (1.6382 g, 0.016 mol). The deviations of our calibration results from the recommended values by NIST [21] are within  $\pm 0.2\%$  in the range from 80 to 350 K.

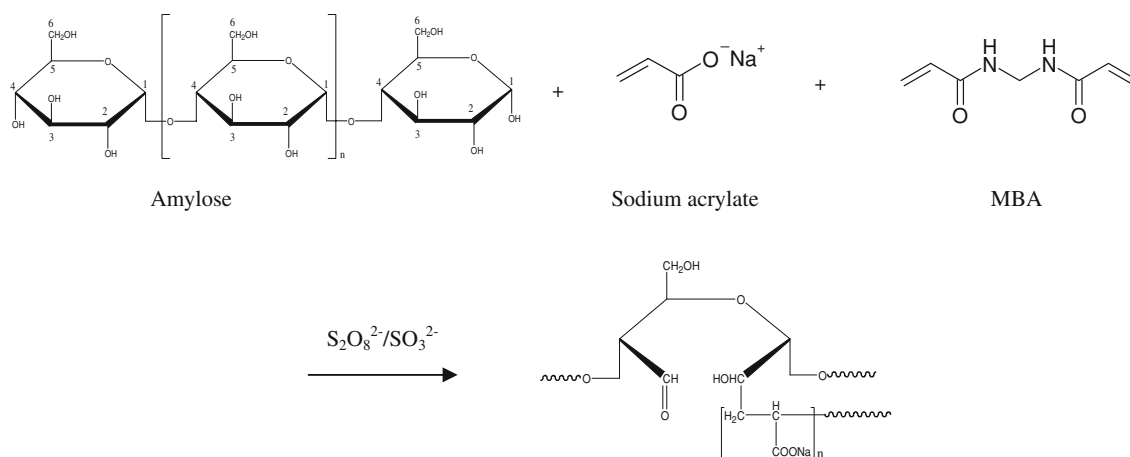
## Results and discussions

Extra water is introduced to dissolve  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  on melting, to reproduce  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  on cooling [1]. This is important for stabilization of incongruent melting inorganic PCMs though inevitably to sacrifice energy storage density. A molar ratio of  $\text{Na}_2\text{HPO}_4:\text{H}_2\text{O} = 1:18$  was adopted in the experiments, which may be varied in the range 1:16–20 [15, 16].

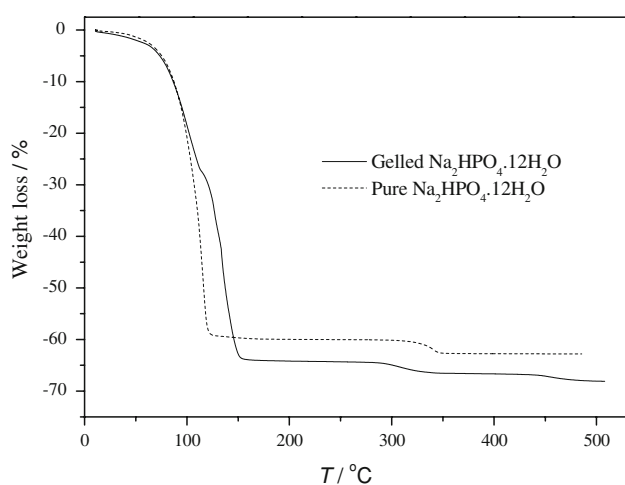
According to TG curves in Fig. 1,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  lost lattice water in the first stage (close to theoretically 60.3%); it transformed to pyrophosphoric acid,  $(\text{NaPO}_3)_x$  at about  $348^\circ\text{C}$  [22]. From room temperature to  $157^\circ\text{C}$ , the gelled salt lost the freezable water in gel network and lattice water in crystals,  $\sim 64\%$  of the total mass;  $282^\circ\text{C} \rightarrow 340^\circ\text{C}$ , it transformed to  $(\text{NaPO}_3)_x$ ;  $426^\circ\text{C} \rightarrow 491^\circ\text{C}$ , probably loss of nonfreezing water in gel network.

Influence of sodium acrylate has already been studied in  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ /sodium polyacrylate system in our previous work [13, 14]:  $\sim 3\text{ mass/mass\%}$  is desirable. More sodium acrylate leads to a very short gelation time,  $<30\text{ s}$ , which may cause inhomogeneity in the gel network; if less, the reaction solution does not gel.  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  then dispersed in sodium polyacrylate in sizes about 1 mm or more (occasional  $<1\text{ mm}$ ) when cooled down.

Figure 2a–d show effects of amylose, MBA,  $\text{K}_2\text{S}_2\text{O}_8/\text{Na}_2\text{SO}_3$  and reaction temperature on heat storage performance and initial  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  sizes (expressed as length  $\times$  width,  $a \times b$ , mm) measured with microscope. Interestingly, heat storage performance may be adjusted by different composition gel network, sometime sensitive to this change. Synthesis conditions were thus optimized



**Scheme 1** Radical polymerization for synthesizing water-absorbing polymer



**Fig. 1** TG curves of pure and gelled  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . The dashed and solid curve correspond to the pure and the gelled salt, respectively

(mass/mass%): 2.7% sodium acrylate, 0.4% amylose 0.05–0.09% MBA, 0.05–0.09%  $\text{K}_2\text{S}_2\text{O}_8$  and  $\text{Na}_2\text{SO}_3$ , reaction temperature  $50^\circ\text{C}$ . In addition, initial mean particle size relates to heat storage performance of gelled salt: the smaller size, the more stable heat storage performance. The particle size of most crystals in gelled salt with stable heat storage performance were found to be less than 0.1 mm, which were much smaller than that gelled by sodium polyacrylate only.

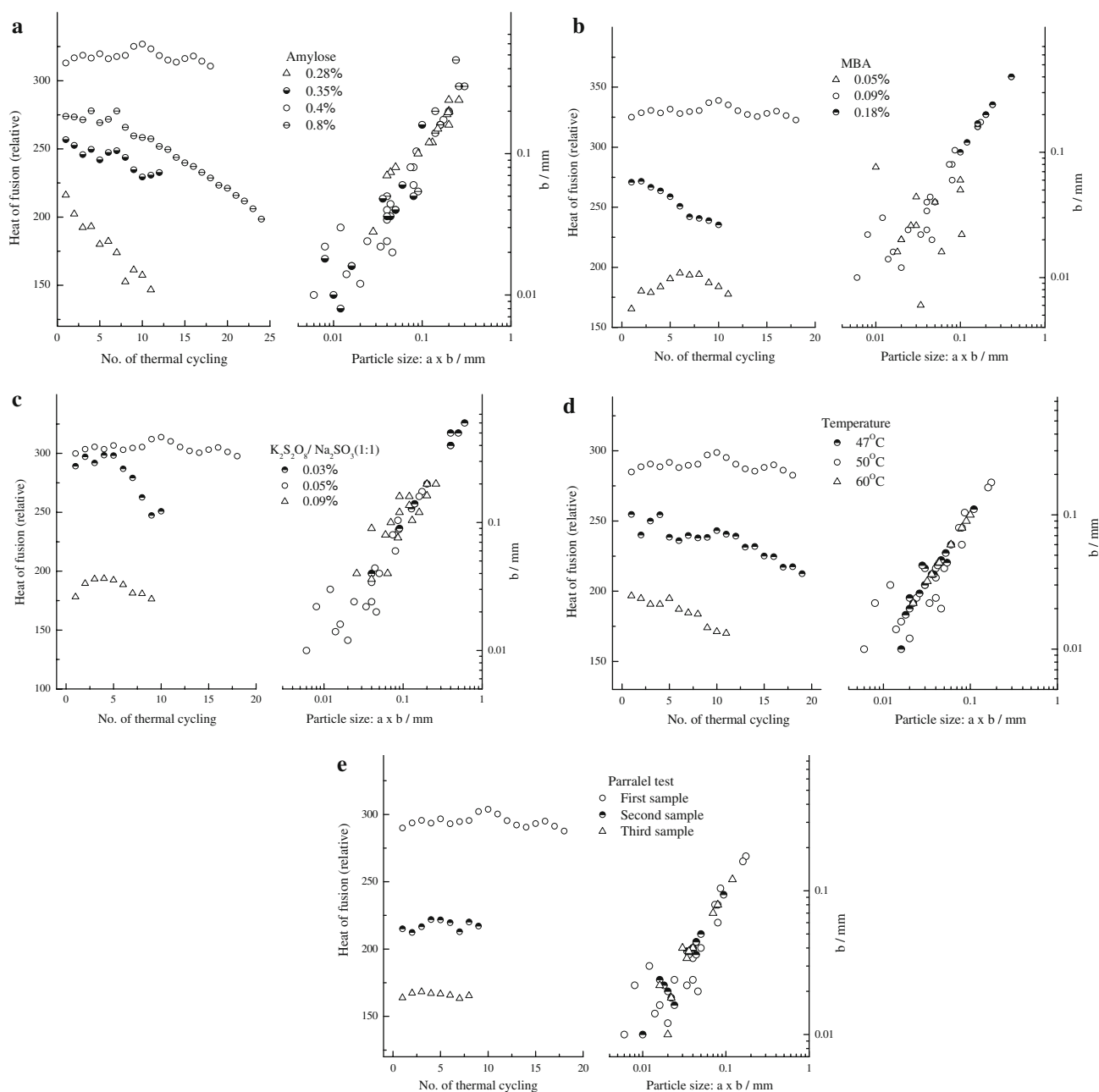
Reproducibility of the synthesis method was confirmed by three parallel tests shown in Fig. 2e. All the three samples exhibit stable heat storage performance, small initial mean particle size ( $\leq 0.1$  mm for the most part) and small variations of melting points ( $35.4 \pm 2^\circ\text{C}$ ) during thermal cycling.

A short-term thermal cycling test was carried out to further evaluate the novel gelling method. Two samples (each about 30 ml) for the parallel tests were examined,

with the initial heat of fusion of about  $180\text{--}190\text{ J g}^{-1}$ . After a 50-run freeze-thaw cycling, the two samples maintained both homogeneity and heat storage capacities. At the 100th cycle, one sample was homogeneous in appearance and maintained the same heat of fusion. But another sample had about 10% volume out of gel network. The remaining part of the sample still absorbed heat of  $180\text{--}190\text{ J g}^{-1}$ . In addition, melting points varied in the range  $35.4\text{--}37.5^\circ\text{C}$ . The different behavior of the two samples reminds us to be careful during sample preparation. The experimental heat capacities of gelled  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  measured by our adiabatic calorimeter are shown in Fig. 3 and listed in Table 1.

From the phase transition at 308.52 K, heat stored by gelled salt was decided as  $192.53\text{ J g}^{-1}$ . Since  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  has a mass ratio of 73.8% in the mixture, the heat of fusion of pure  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  is thus deduced:  $192.53\text{ J g}^{-1}/73.8\% = 260.9\text{ J g}^{-1}$ , which agrees with reported value  $260\text{--}280\text{ J g}^{-1}$  [2, 3]. Melting point in this gelled salt, 308.52 K, is very close to the pure salt (m.p. 308.40 K,  $\Delta H_{\text{fus}} 181.0\text{ J g}^{-1}$  [14]).

From another phase transition at 271.70 K, the distribution of extra water added can be deduced, which may exist in gel network in the form of free water, freezable bond and nonfreezing water [23]. Apparently, there is no free water in the solid sample otherwise would melt at  $0^\circ\text{C}$  as bulk water. So the proportion of freezable bond water is:  $m_s Q_{\text{fus}}^{\text{fb}}/m_w \Delta H_{\text{fus}}^{\text{fb}} \approx 0.85$  [22], where  $m_s$  (18.3 g) and  $m_w$  (4.17 g) are the mass of sample and extra water,  $Q_{\text{fus}}^{\text{fb}}$  ( $63.51\text{ J g}^{-1}$ ) and  $\Delta H_{\text{fus}}^{\text{fb}}$  ( $329.22\text{ J g}^{-1}$ ) are the heat of fusion of gelled sample and pure ice at 271.70 K [24]. As a result, extra water distributes in gel network as freezable water: nonfreezing water = 0.85: 0.15. All the extra water is in a bonding state, weakly or tightly, and thus disperses uniformly in gel network. This can dissolve  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  efficiently on melting because of large



**Fig. 2** Influence of reaction conditions [a amylose, b MBA, c  $K_2S_2O_8$  and  $Na_2SO_3$ , d reaction temperature] on heat storage performance and the initial particle size of gelled  $Na_2HPO_4 \cdot 12H_2O$  with amylose-g-sodium acrylate: In preparation, reactants and

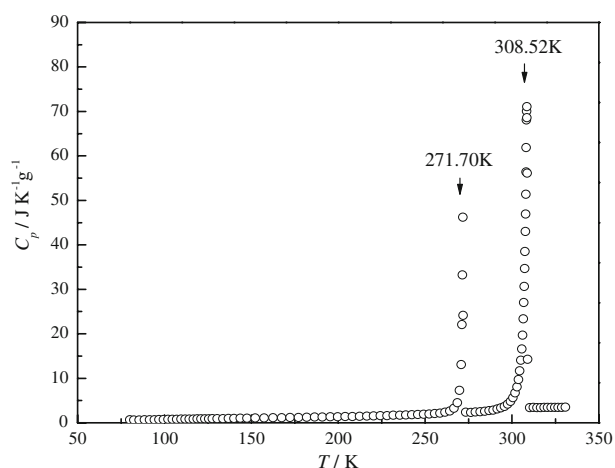
temperature were as follows otherwise specified: sodium acrylate 2.7%, amylose 0.4%, MBA 0.09%,  $K_2S_2O_8$  and  $Na_2SO_3$  0.05%,  $T = 50^\circ C$ ; e is the parallel test

contacting area between them, and further eliminate phase separation.

## Conclusions

In summary, gelling by amylose grafted sodium acrylate can prevent  $Na_2HPO_4 \cdot 12H_2O$  from phase separation. The gelled salts show stable heat storage capacity during 100

freeze-thaw cycles. Their initial particle size is less than 0.1 mm in most part. Melting point kept almost constant in thermal cycling. Amylose grafted sodium acrylate acts as not only a water absorbing medium but an effective crystallization habit modifier, both favorable to stabilize heat storage performance of  $Na_2HPO_4 \cdot 12H_2O$ . Adiabatic calorimetric measurements can provide accurate heat capacities, heat of fusion for both gelled and pure salt, as well as the information of existing state of water in solid sample.



**Fig. 3** Low-temperature heat capacities of gelled Na<sub>2</sub>HPO<sub>4</sub> · 12H<sub>2</sub>O with amylose-g-sodium acrylate. Preparation conditions: 13.5 g Na<sub>2</sub>HPO<sub>4</sub> · 12H<sub>2</sub>O, 0.085 g amylose, 2.17 g H<sub>2</sub>O, 2.5 g sodium acrylate (20 mass/mass%), pH=7, 17 mg MBA, 10 mg K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 10 mg Na<sub>2</sub>SO<sub>3</sub>, *T* = 50°C

**Table 1** Smoothed heat capacities of gelled Na<sub>2</sub>HPO<sub>4</sub> · 12H<sub>2</sub>O

| <i>T</i> /K | <i>C<sub>p</sub></i> /JK <sup>-1</sup> g <sup>-1</sup> | <i>T</i> /K | <i>C<sub>p</sub></i> /JK <sup>-1</sup> g <sup>-1</sup> |
|-------------|--|-------------|--|
| 80          | 0.59   | 195         | 1.32   |
| 85          | 0.63   | 200         | 1.36   |
| 90          | 0.66   | 205         | 1.40   |
| 95          | 0.70   | 210         | 1.44   |
| 100         | 0.74   | 215         | 1.48   |
| 105         | 0.77   | 220         | 1.53   |
| 110         | 0.80   | 225         | 1.58   |
| 115         | 0.84   | 230         | 1.64   |
| 120         | 0.87   | 235         | 1.70   |
| 125         | 0.90   | 240         | 1.77   |
| 130         | 0.93   | 245         | 1.85   |
| 135         | 0.97   | 250         | 1.94   |
| 140         | 1.00   |             |  |
| 145         | 1.03   | 275         | 2.35   |
| 150         | 1.06   | 280         | 2.43   |
| 155         | 1.08   | 285         | 2.63   |
| 160         | 1.11   |             |  |
| 165         | 1.14   | 310         | 3.42   |
| 170         | 1.17   | 315         | 3.44   |
| 175         | 1.20   | 320         | 3.45   |
| 180         | 1.23   | 325         | 3.47   |
| 185         | 1.26   | 330         | 3.49   |
| 190         | 1.29   |             |  |

Preparation conditions: 13.5 g Na<sub>2</sub>HPO<sub>4</sub> · 12H<sub>2</sub>O, 0.085 g amylose, 2.17 g H<sub>2</sub>O, 2.5 g sodium acrylate (20 mass/mass%, pH=7), 17 mg MBA, 10 mg K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 10 mg Na<sub>2</sub>SO<sub>3</sub>, *T* = 50°C

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