



ELSEVIER

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Chemical Engineering Thermodynamics

Investigation on specific heat capacity and thermal behavior of sodium hydroxyethyl sulfonate

Hongying Hao^{1,2}, Yadong Zhang^{1,*}, Xiaoya Chen¹¹ School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, China² Medical School, HuangHe Science and Technology College, Zhengzhou 450063, China

ARTICLE INFO

Article history:

Received 19 September 2016

Received in revised form 1 November 2016

Accepted 19 November 2016

Available online 13 December 2016

Keywords:

Sodium hydroxyethyl sulfonate

Melting temperature

Specific heat capacity

Thermal decomposition

ABSTRACT

The thermal decomposition process was studied by the TG–DTA analyzer. The results show that the decomposition process of sodium hydroxyethyl sulfonate consisted of three stages: the mass loss for the first, the second and third stages may be about the groups of $\text{CH}_3\text{CH}_2\text{OH}$, CH_3CHO and SO_2 volatilized, respectively. The decomposition residuum of three stages was analyzed by FT-IR, and the results of FT-IR agreed with the decomposition process predicted by theoretical weight loss. The specific heat capacity of sodium hydroxyethyl sulfonate was determined by differential scanning calorimetry (DSC). The melting temperature and melting enthalpy were obtained to be 465.41 K and 25.69 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. The molar specific heat capacity of sodium hydroxyethyl sulfonate was determined from 310.15 K to 365.15 K and expressed as a function of temperature.

© 2016 The Chemical Industry and Engineering Society of China, and Chemical Industry Press. All rights reserved.

1. Introduction

The sodium hydroxyethyl sulfonate (2-hydroxyethanesulfonic acid sodium salt, to abbreviate it into SHES, CASRN 1562-00-1) is an important organic intermediate [1–3]. The chemical formula of SHES is $\text{C}_2\text{H}_5\text{NaO}_4\text{S}$, and the relative molecular mass is $148.11\text{ g}\cdot\text{mol}^{-1}$. SHES is easily dissolve in water, but hardly dissolve in ethanol, acetone or other organic solvents. Different researchers [4–9] have studied the synthesis and pharmacological effects of SHES. However, its thermostability has not been reported. Therefore, we have undertaken the investigation of the thermal decomposition process and the thermodynamic properties, such as specific heat capacity and thermal stability. These thermodynamic data may be helpful for further study and application of SHES.

2. Experimental

2.1. Materials and experiment apparatus

$\alpha\text{-Al}_2\text{O}_3$ was used as standard material in the thermal analysis process, provided by Shimadzu Company, Japan. Benzoic acid and ethanol used in the experiment were of AR grade with mass fraction purity of over 99.5%, purchased from Shanghai Chemical Reagent Company. SHES (mass fraction purity of 98%) was purchased from Aladdin Chemistry Co. Ltd. (Shanghai), China. The TG–DTA analyzer (type DTG-60, Shimadzu Company, Japan) was used to determine the TG–DTA curves of the sample. The differential scanning calorimetry (type DSC-60,

Shimadzu Company in Japan) was used to determine the melting temperature and melting enthalpy of the sample. SPN-500 nitrogen generator (the HP analysis technology research institute in Beijing, China) provided nitrogen atmosphere for the experiment of thermal analysis. Thermo FT-IR200 (Thermo Electron Corporation in America) was used to analyze the structure of the intermediate and final product. Elemental analyzer FLASH EA 1112 (Thermo Electron Corporation in America) was used to determine the purity of the sample.

2.2. Purification of SHES

SHES was purified by recrystallized method three times at least in ethanol in order to obtain the content of more than 99%, and then placed in oven at 383.15 K until it was dried. The dried sample was analyzed by elemental analyzer to determine the purity of sample. The elemental analysis results of SHES in Table 1 show that there was an excellent agreement between the theoretical and experimental values.

2.3. The determination procedure of melting temperature and melting enthalpy

In order to determine the melting temperature and melting enthalpy, the samples were cooled to room temperature when it was melted for the first time, and then reheated at a rate of $10\text{ K}\cdot\text{min}^{-1}$ until complete melting, or quenched to 20 K and reheated at $10\text{ K}\cdot\text{min}^{-1}$ to a temperature higher than the melting temperature. The method of melting temperature was used for SHES, which is described in detail in ISO 11357-3:2011 [10]. The melting temperature was obtained by multiple measurement and averaging.

* Corresponding author.

E-mail address: zzuzhangyadong@126.com (Y.D. Zhang).

Table 1
Elemental analysis of SHES ($C_2H_5NaO_4S$)

Elements	Theoretical/%	Experimental/%
Carbon	16.22	16.14
Hydrogen	3.40	3.39
Sulfur	21.65	21.52

2.4. The specific heat measurement principle

The measuring methods of the specific heat capacity from DSC are described in the literature [11–15]. The relationship between the specific heat capacity and heat flow rate at constant pressure can be expressed by Eq. (1) [16].

$$C_p = \left(\frac{dQ}{dT} \right)_p \cdot \frac{1}{m} \quad (1)$$

where m is the mass of the tested sample, g; C_p is the specific heat capacity, $J \cdot K^{-1} \cdot g^{-1}$, subscript p indicates an isobaric process; T is Kelvin temperature, K; Q is the quantity of heat.

The absolute value of $\left(\frac{dQ}{dT} \right)_p$ cannot be determined accurately because of the instrument itself and the operating conditions [17]. So the indirect measurement method is used in the experiment. This indirect procedure can be done in two ways, which are continuous-scanning method and the stepwise-scanning method [18]. The continuous-scanning method was used for sodium isethionate, which is described in detail in ASTM norm E1269-11 [19]. The specific heat capacity C_p can be calculated by Eq. (2) [19].

$$C_p(s) = C_p(st) \cdot \frac{D_s \cdot W_{st}}{D_{st} \cdot W_s} \quad (2)$$

where $C_p(s)$ and $C_p(st)$ are the constant-pressure specific heat capacities of both a tested sample and a calibration material, $\alpha-Al_2O_3$ is used as the calibration material and the values of $C_p(st)$ are extracted from ISO 11357-4 [16]; W_s and W_{st} are the mass of the tested sample and $\alpha-Al_2O_3$, respectively; D_s is the vertical displacement between the empty crucible and the test sample on DSC thermal curves at a given temperature; D_{st} is the same as D_s which is between the empty crucible and $\alpha-Al_2O_3$.

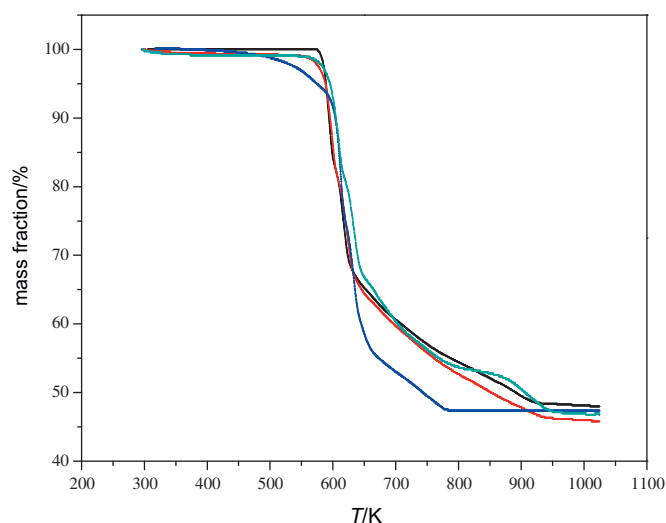


Fig. 1. The TG curves of SHES at different rate under nitrogen atmosphere. $\beta/K \cdot min^{-1}$: — 8; — 12; — 16; — 20.

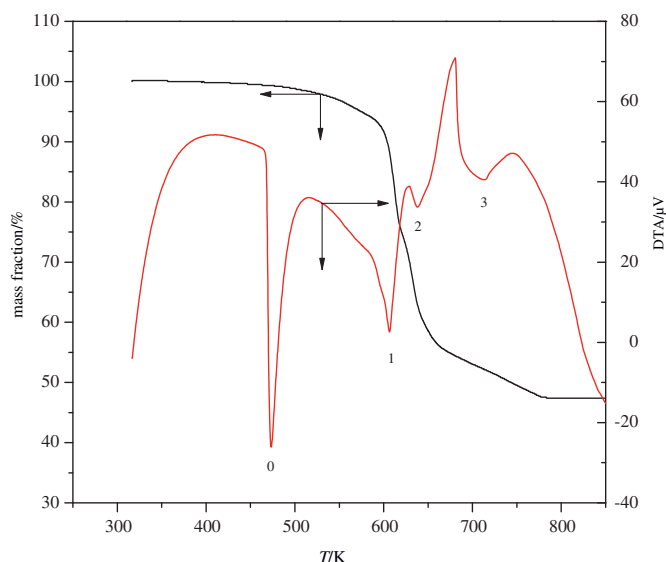


Fig. 2. The TG-DTA curves of SHES at heating rate of $16 K \cdot min^{-1}$ under nitrogen atmosphere.

3. Results and Discussion

3.1. Thermal decomposition behavior of sodium isethionate

TG and DTA curves of sodium isethionate sample are shown in Figs. 1 and 2. The results indicate that the process of thermal decomposition has three stages (1–3 stages). The signature of them can be divided successively into the first endothermic peak, the second endothermic peak, and the third endothermic peak. The total mass loss (mass%) of decomposition was less than 51.98% as the maximum temperature was lower than 1123.15 K. The zero endothermic peak is a melting process between 463.14 K and 468.23 K so that the onset melting temperature of the SHES sample could be considered as 465.41 K, the melting temperature presented in literature was 465.15–467.15 K [20], so the experimental value of the melting point determined by DSC was reliable. The melting enthalpy was $25.69 kJ \cdot mol^{-1}$ calculated by TA-60WS workstation. The result is consistent with DSC in Fig. 3.

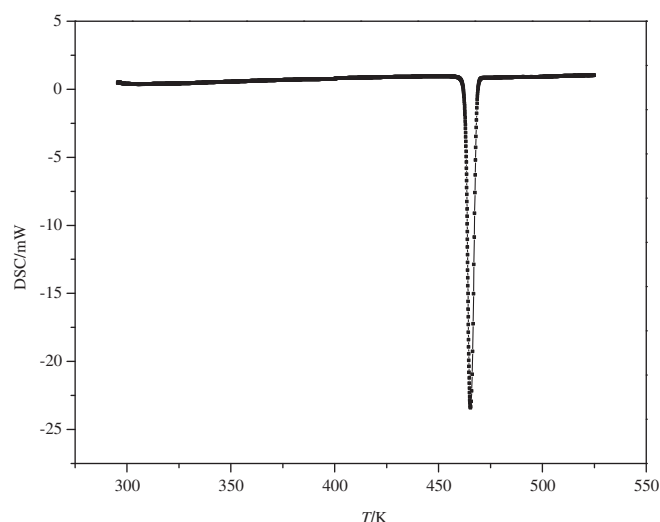
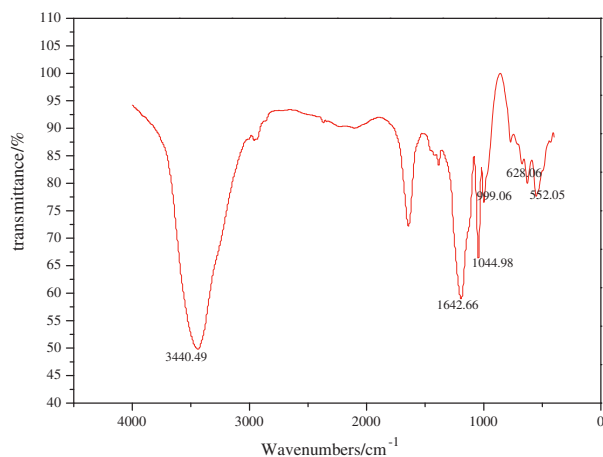


Fig. 3. The DSC curves of SHES under nitrogen atmosphere.

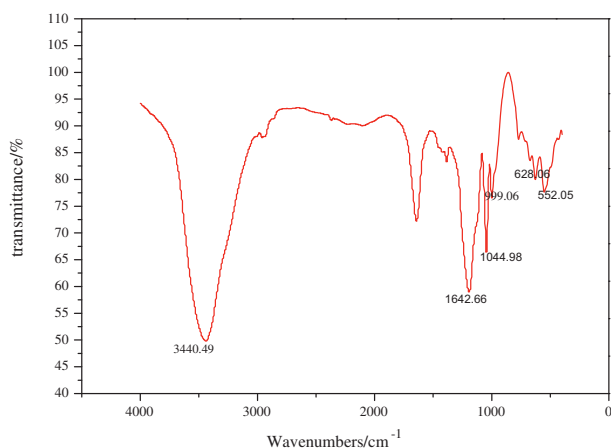
Table 2

The basic results based on the TG–DTA curves

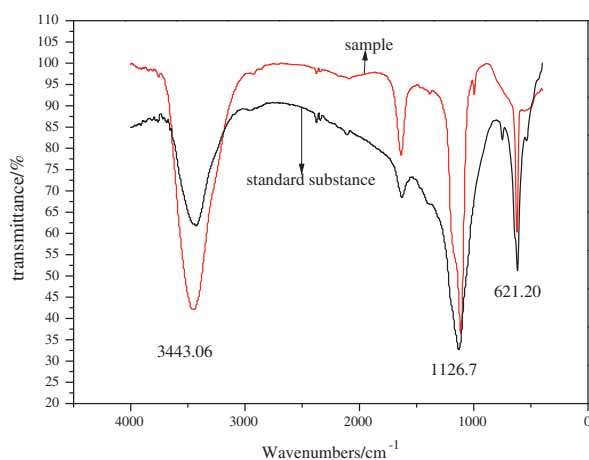
Stage number	Loss mass (exp)/%	Weightlessness group	Loss mass (theory)/%	Error/%	Phenomenon	T_p/K	T_b/K	T_f/K
The first stage	15.56	$\text{CH}_3\text{CH}_2\text{OH}$	15.53	0.19	Endothermic	333.45	313.00	344.92
The second stage	15.39	CH_3CHO	14.85	3.64	Endothermic	355.76	344.92	376.11
The third stage	21.41	SO_2	21.60	0.88	Endothermic	407.64	376.11	653.23



(a)



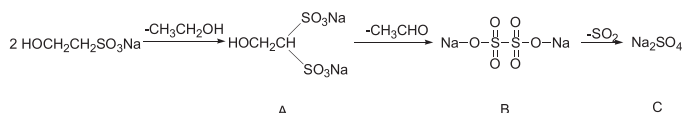
(b)



(c)

Fig. 4. FT-IR spectrum of the decomposition products. (a): the decomposition product A at the first stage. (b): the decomposition product B at the second stage. (c): the decomposition product C at the third stage.

From Table 2, Figs. 2 and 4, the results show that the thermal behavior is as follows:



In the first stage between 586.15 K and 618.07 K, the experimental data of mass loss is 15.56%, and there is an obvious endothermic peak. The infrared spectrum of the residue A is shown in Fig. 4(a). FTIR data ($\nu_{\text{max}}, \text{cm}^{-1}$): $\nu(\text{O}-\text{H}) = 3436$, $\beta(\text{O}-\text{H}) = 1386$, $\nu(-\text{CH}_2) = 2924$, $\nu(\text{C}-\text{S}) = 627$, and the characteristic peaks of sulfonate are 1123 and 967 [12]. The results demonstrate that the most possible group loss in this stage may be $\text{CH}_3\text{CH}_2\text{OH}$. On the other hand, the mass loss of the group $\text{CH}_3\text{CH}_2\text{OH}$ in thermal decomposition process is 15.53%. Compared the experimental value with the theoretical value, the relative error is 0.19%.

In the second stage, there is an endothermic peak. The theoretical mass loss of the sample is 14.85%, and the mass loss of the group CH_3CHO in thermal decomposition process is 15.39%. Compared experimental value with the theoretical value, the relative error of the experimental value is 3.64%. The infrared spectrum of the residue B is in Fig. 4(b). FTIR data: the characteristic peaks of $-\text{SO}_3\text{Na}$ are 1192 and 1044 cm^{-1} .

In the third stage, the most possible lose group is SO_2 because the lost mass in the stage is 21.41% in accordance with the lost mass (21.60% in theory) of SO_2 . The result demonstrates that the last residue substance may be Na_2SO_4 . The infrared spectrum of the residue C is shown in Fig. 4(c). FTIR data (cm^{-1}): 1126 and $621(\text{SO}_4^{2-})$ are in good agreement with the standard sodium sulfate.

3.2. The constant-pressure specific heat capacity of the sample

The accuracy of experimental results may be influenced by several material parameters. In order to eliminate the influence of the factors and obtain precise measurements, the specific heat capacity of $\alpha\text{-Al}_2\text{O}_3$ was determined firstly, and compared with the literature values of $\alpha\text{-Al}_2\text{O}_3$ [5,16]. The results are shown in Table 3. The relative error between the measured values and the literature values were within 1%. The relationship between the specific heat capacity and temperature of $\alpha\text{-Al}_2\text{O}_3$ was obtained with the least square

Table 3Experimental values and the literature values of specific heat capacity of $\alpha\text{-Al}_2\text{O}_3$

T/K	$C_p (\text{Exp})/\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$	$C_p (\text{Lit.})/\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$	$RD/\%$
328.15	0.8388	0.8434	0.55
333.15	0.8473	0.8536	0.74
338.15	0.8590	0.8536	0.63
343.15	0.8684	0.8729	0.52
348.15	0.8774	0.8820	0.52
353.15	0.8944	0.8907	0.42
358.15	0.9035	0.8990	0.50
363.15	0.9104	0.9071	0.36
ARD/%			0.53

Table 4
Experimental values and the literature values of specific heat capacity of benzoic acid

<i>T</i> /K	$C_p/\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ Exptl.	$C_p/\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ Lit.	<i>RD</i> /%
298.15	1.2592	1.2506	0.68
300.15	1.2689	1.2576	0.89
303.15	1.2796	1.2681	0.91
313.15	1.3148	1.3027	0.93
318.15	1.3350	1.3198	1.15
333.15	1.3840	1.3707	0.96
343.15	1.4182	1.4042	0.99
358.15	1.4687	1.4538	1.03
363.15	1.4854	1.4701	1.04
370.15	1.5087	1.4929	1.06
380.15	1.5367	1.5250	0.76
385.15	1.5551	1.5409	0.92
<i>ARD</i> /%			0.94

method and represented by Eq. (3), where the linear correlation coefficient (R^2) was 0.9959.

$$C_p(\alpha\text{-Al}_2\text{O}_3) = 45.77 + 0.39395T + 1.15 \times 10^{-3}T^2 - 1 \times 10^{-6}T^3 \quad (3)$$

In order to further verify the reliability of the method, the specific heat capacity of benzoic acid was measured by DSC [17], and the results are expressed in Table 4. The relationship between the specific heat capacity and temperature of benzoic acid could be expressed by Eq. (4). The linear correlation coefficient (R^2) of Eq. (4) was 0.9998.

$$C_p(\text{benzoic acid}) = -0.55973 + 9.42 \times 10^{-3}T - 1 \times 10^{-5}T^2 + 1 \times 10^{-8}T^3 \quad (4)$$

The constant-pressure specific heat capacity of SHES is expressed in Table 5 and Fig. 5. The relationship between the specific heat capacity and temperature at solid phase state could be derived using the least square method and be represented by Eq. (5). The linear correlation coefficient (R^2) of Eq. (4) was 0.9949.

$$C_p(\text{SHES}) = 48.41118 - 0.43356T + 0.00131T^2 - 1.30619 \times 10^{-6}T^3 \quad (5)$$

Compared the values calculated by Eqs. (3) and (4) with the literature values [21] examined the relative deviation *RD* and average relative deviation *ARD* are listed in Tables 3 and 4. And average relative deviation is defined as:

$$ARD = \frac{1}{n} \sum \left(\frac{|C_{p_i} - C_{p_i, \text{cal}}|}{C_{p_i}} \right) \quad (6)$$

The results show that *ARD* is respectively 0.53 and 0.94 for $\alpha\text{-Al}_2\text{O}_3$ and benzoic acid and there are good agreement between the experimental and calculated results for the specific heat capacity.

Table 5
Experimental values of specific heat capacity for SHES

<i>T</i> /K	$C_p(\text{Exp})/\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$	<i>T</i> /K	$C_p(\text{Exp})/\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$
310.15	0.8027	340.15	0.8715
315.15	0.8079	345.15	0.8916
320.15	0.8189	350.15	0.9081
325.15	0.8343	355.15	0.9119
330.15	0.8451	360.15	0.9122
335.15	0.8665	365.15	0.9169

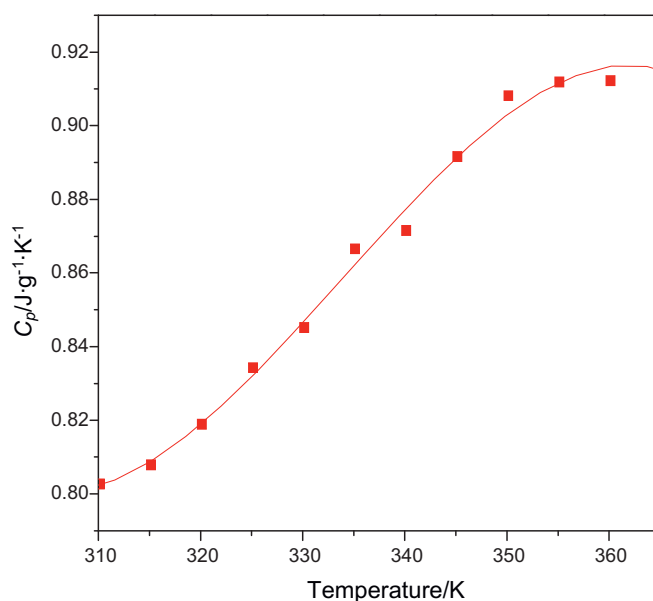


Fig. 5. The specific heat capacity of SHES.

4. Conclusions

From the thermal analysis of the differential thermal analysis (DTA) and thermogravimetric analysis (TGA), the decomposition process of SHES was divided into three stages: (1) the mass loss in the first stage and the second stage may be $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3CHO ; (2) the third stage may lose SO_2 . The residue sample of every stage was analyzed by FT-IR, and the results of FT-IR match well with the predicted structure. In addition, the thermodynamic data, the specific heat capacity, melting temperature, and melting enthalpy of SHES were determined using differential scanning calorimetry (DSC). The relationship between the specific heat capacity and temperature was obtained at the temperature range of 310.15–365.15 K. The equation was $C_p = 48.41118 - 0.43356T + 0.00131T^2 - 1.30619 \times 10^{-6}T^3$. The melting temperature and melting enthalpy were obtained to be 465.41 K and 25.69 $\text{kJ}\cdot\text{mol}^{-1}$, respectively.

Nomenclature

<i>ARD</i>	The average relative deviation
C_p	The constant-pressure specific heat capacity, $\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$
<i>D</i>	The signal value of DSC for sample, mW
<i>m</i>	Mass of the tested sample, kg
<i>Q</i>	Quantity of heat, $\text{J}\cdot\text{mol}^{-1}$
<i>RD</i>	The relative deviation
<i>T</i>	Absolute temperature, K
β	Heating rate, $\text{K}\cdot\text{s}^{-1}$
λ	Wavelength, nm

Subscripts

<i>i</i>	Serial number
<i>m</i>	Material
<i>p</i>	Constant pressure
<i>s</i>	Sample
<i>st</i>	Standard sample

References

- [1] K. Kushibe, Process for the production of pure alkanesulfonic acids, U.S. Pat., 1999 5912385.
- [2] D.X. Wei, H. Jiang, H. Gong, Process on synthesis and application of isethionic acid, *Fine Chem. Intermed.* 4 (2012) 16–20.

- [3] J.D. Welty, W.O. Read, E.H. Shaw, Isolation of 2-hydroxyethanesulfonic acid (isethionic acid) from dog heart, *J. Biol. Chem.* 237 (1962) 1160–1161.
- [4] G. Schreyer, Process for the production of alkyl sulfonic acids, U.S. Pat., 1980 4239696.
- [5] E. Dennis, Synthesis of hydroxy sulfonic acids, U.S. Pat., 1991 4987250.
- [6] E. Dennis, Synthesis of sulfonic acids and carboxylic acid ester derivatives thereof, U.S. Pat., 1990 4910330.
- [7] A.R. Sexton, E.C. Britton, Continuous production of salts of hydroxy aliphatic sulfonic acids, U.S. Pat., 1957 2810747.
- [8] K.D. Longley, Preparation of isethionic acid, U.S. Pat., 1985 4499028.
- [9] J.S. Roberts, Preparation of isethionic acid with organic acid, U.S. Pat., 1999 5053530.
- [10] ISO 11357-3, Plastics-Differential Scanning Calorimetry (DSC)—Part 3: Determination of Temperature and Enthalpy of Melting and Crystallization, ISO, 2011.
- [11] X.W. Han, C.R. Zhou, X.H. Shi, Determination of specific heat capacity and standard molar combustion enthalpy of taurine by DSC, *J. Therm. Anal. Calorim.* 109 (2012) 441–446.
- [12] L. Atanasova, G. Baikusheva-Dimitrova, G. Gospodinov, Specific heat capacity and thermodynamic properties of CuTeO_3 and HgTeO_3 , *J. Therm. Anal. Calorim.* 118 (2014) 493–497.
- [13] P. Andreu-Cabedo, R. Mondragon, L. Hernandez, R. Martinez-Cuenca, L. Cabedo, J.E. Julia, Increment of specific heat capacity of solar salt with SiO_2 nanoparticles, *Nano Res. Lett.* 9 (2014) 582–593.
- [14] W.L. Li, C.R. Zhou, L. Zhang, Investigation on the decomposition kinetics of Ivermectin, *J. Therm. Anal. Calorim.* 121 (2015) 797–806.
- [15] X. Yu, C.R. Zhou, X.W. Han, G.P. Li, Study on thermodynamic properties of glyphosate by oxygen-bomb calorimeter and DSC, *J. Therm. Anal. Calorim.* 111 (2013) 943–949.
- [16] ISO 11357-4, Plastics-Differential Scanning Calorimetry (DSC)—Part 4: Determination of Specific Heat Capacity, ISO, 2005.
- [17] C.S. Yang, P.S. Ma, S.Q. Xia, The specific heats of aqueous mixtures of acetic acid with water measured with DSC, *J. Chem. Eng. Chin. Uni.* 16 (2002) 479–483 (in Chinese).
- [18] R. Pilař, P. Honcová, P. Košťál, G. Sádovská, L. Svoboda, Modified stepwise method for determining heat capacity by DSC, *J. Therm. Anal. Calorim.* 118 (2014) 485–491.
- [19] ASTM norm E1269-11, Standard Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry, ASTM Int., Pennsylvania, 2011.
- [20] W.M. Lauer, A. Hill, The addition of sodium bisulfite to alkylene oxides, *J. Am. Chem. Soc.* 58 (10) (1936) 1873–1874.
- [21] C.L. Yaws, Chemical Properties Handbook, McGraw-Hill Education (Asia) Co. and Chemical Industry Press, Beijing, 1999.