Journal of Thermal Analysis, Vol. 35 (1989) 1959–1963

THE MELTING BEHAVIOUR OF CONCENTRATED SULPHURIC ACID INVESTIGATED BY DSC

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(Received August 2, 1988)

The DSC-investigation of different concentrated sulphuric acid solutions shows that the results of this dynamic measurement method are in good agreement with those of steady state methods [1]. The diverse DSC-melting peaks can be interpreted by using the known behaviour of the system SO_3/H_2O [1] as the melting of different congruent melting phases or eutecties, respectively. The observed melting enthalpies are in the correct order.

The steady state phase diagram of the system sulphur trioxide/water is well known, especially through the investigations made by Gable et al. [1] with the equilibrium solubility method. The authors found that in the high concentration range of sulphuric acid (~ 70 to ~ 85 wt. percent SO_3, i.e. ~ 83 wt. percent sulphuric acid to ~ 18 wt. percent fuming acid) there are two congruent melting phases ($H_2SO_4 \cdot H_2O$ at 8.56° and H_2SO_4 at 10.371°). Between these congruent melting points an eutectic exists with a melting temperature of $-34.86°$ ($H_2SO_4 \cdot H_2O$ and H_2SO_4). A further eutectic in this range (H_2SO_4 and $H_2S_2O_7$) has a melting temperature of $-10.16°$. The phase diagram in this concentration range is shown in Fig. 1.

The melting enthalpies of these concentrated sulphuric acid solutions are about 100 J/g [2]. The aim of our work was to investigate the influence of kinetic factors on the melting behaviour of concentrated sulphuric acid solutions. The results of the investigations are the basis of further studies on the melting behaviour of the acids in polymer-concentrated sulphuric acid systems [3].

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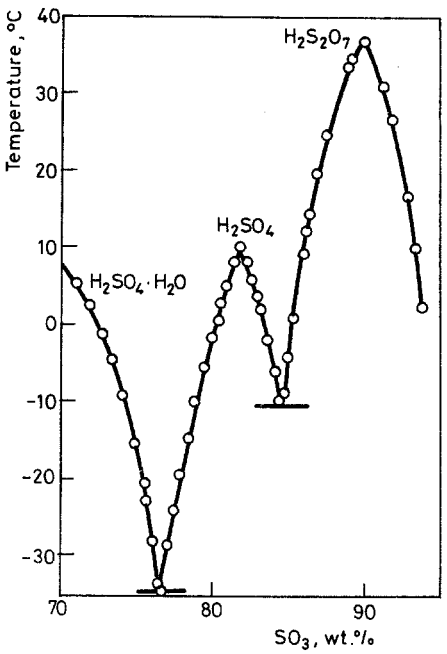

Fig. 1 Phase diagram of the system sulphur-trioxide—water in the concentration range above 70 wt. percent SO_3 according to Gable et al. [1]

Experimental

We have studied seven different acid solutions: 92.3; 95.2; 98.7; and 99.6 wt. percent sulphuric acid, 2 and 5 wt. percent fuming acid respectively. The concentration was checked by titration.

The DSC investigations were carried out with a Perkin–Elmer DSC 1b. The samples were filled in gold capsules and then cooled to the temperature of liquid nitrogen ($\sim -192°$).

On heating some of the samples (95.2, 96.5 wt. percent H_2SO_4) showed a cold crystallization below the melting peak of the acid. To reach high crystallinity of the acids these samples were treated for 30 min at the cold crystallization temperature.

The actual investigations were done with a heating rate of 8 deg/min from $-80°$ to room temperature.

Results and discussion

Figures 2 and 3 show the DSC-traces of the investigated acids. The quantitative results are summarized in Table 1. With the thermal treatment used the 92.3 wt. percent sulphuric acid did not crystallize and no melting peak could be observed upon heating this acid.

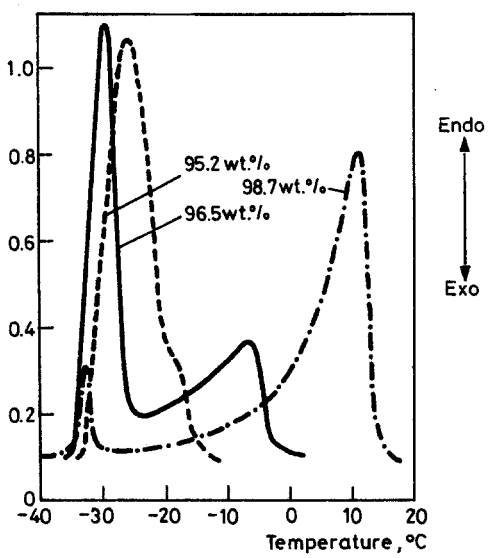

Fig. 2 DSC-traces of the sulphuric acid solutions with concentrations: 95.2 wt. percent (– – –), 96.5 wt. percent (——) and 98.7 wt. percent (–.–.–), respectively

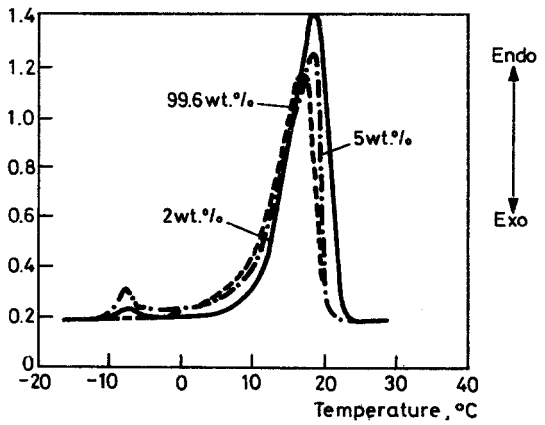

Fig. 3 DSC-traces of 99.6 wt. percent sulphuric acid and of the fuming acids with 2 wt. percent and 5 wt. percent free SO_3, respectively

Table 1 Melting temperatures and melting enthalpies of concentrated sulphuric acid solutions

Concentration wt. percent (sulphuric acids or fuming acids, respectively)	Temperatures, °C		Enthalpy, ΔH_m, J/g
	T_{trans}	T_{max}	
95.2	−33	−26	97.0
96.5	−34	−30.5	
		− 6.5	98.4
98.7	−35	−33	
	− 0.5	10.5	84.6
99.6	8.5	17.5	91.6
2		− 8.5	
	8.5	17.5	103.0
5	−10.5	− 8.0	
	8.0	17.0	102.6

Upon heating the acid solutions, containing with 95.2; 96.5 and 98.7 wt. percent of H_2SO_4 the melting peaks were observed in the region around $-30°$. The lower the concentration of the acid, the greater is the area of this peak. The process which produced these melting peaks in the region around $-30°$ should be the melting of the eutectic of $H_2SO_4 \cdot H_2O$ and H_2SO_4.

The shoulder on the high temperature side of the peak for the 95.2 wt. percent sulphuric acid solution and the main peaks of the other acids can be interpreted as the melting of the pure sulphuric acid component. The small peaks appearing around $-10°$ upon heating the fuming acids result from the melting of the eutectic of H_2SO_4 and $H_2S_2O_7$.

The temperatures of the different melting peaks observed upon heating are generally in good agreement with the equilibrium data of Gable et al. [1]. Only the melting temperature of the eutectic $H_2SO_4 \cdot H_2O$ and H_2SO_4 is about ten degrees lower than the value reported by Gable [1]. In our opinion this shift is the result of an imperfect crystallization of this eutectic during the thermal treatment of the samples.

The melting enthalpies of the different acids are in the order of 100 J/g. For the 100 wt. percent H_2SO_4 the literature gives also different values in the order of 100 J/g (see [2]).

References

1 C. M. Gable, H. F. Betz and S. H. Maron, J. Amer. Chem. Soc., 72 (1950) 4, 1445.

2 Gmelin, System-Nr. 9, Schwefel, Bd. B2 (1060) p. 613.

3 H. Schelle, J.-P. Melior and P. Weigel, Acta Polymerica, 40 (1989) 520.

Zusammenfassung — DSC-Untersuchungen an Schwefelsäurelösungen verschiedener Konzentration zeigten, daß die Ergebnisse dieses dynamischen Meßverfahrens mit den Ergebnissen von Gleichgewichtsverfahren in guter Übereinstimmung stehen. Die verschiedenen DSC-Schmelzpeaks können unter Zuhilfenahme des bekannten Verhaltens des Systemes SO_3/H_2O, nämlich mit dem Schmelzen unterschiedlicher kongruenter Schmelzphasen bzw. Eutektika erklärt werden. Die ermittelten Schmelzenthalpien liegen in der richtigen Größenordnung.

Резюме — ДЗС исследование растворов серной кислоты с различной концентрацией показало, что результаты этого динамического метода измерения хорошо согласуются с таковыми, измеренными установившимися методами. Разнообразные ДСК пики плавления могут быть интерпретированы, используя такое известное поведение системы SO_3/H_2O, как плавление различных конгруэнтно плавящих фаз или эвтектик. Найденные энтальпии плавления корректно располагаются в ряд.