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A DSC characterization of sulphur–selenium interaction phenomenology

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Abstract

DSC measurements in the 25–240°C temperature range have been performed on sulphur–selenium physical mixtures (1.99–95.06 mass% of Se) in order to clarify the interaction mechanism. The experimental results can be interpreted on the basis of an interaction model according to which a S/Se copolymerization process takes place in mixtures with Se contents up to 55 mass%. Beyond the 55 mass% Se content the interaction mechanism appears to shift towards an "anomalous melting" behaviour of the two components.

INTRODUCTION

Among the problems affecting the sodium/β-alumina/sulphur cell, some attention has been paid to the issue of molten sulphur transport in the cathodic compartment [1]. For many years the use of additives has been proposed [2] in order to overcome the problem, which has been tentatively ascribed to both the high viscosity and the poor electrical conductivity of sulphur.

Both organic compounds (e.g. tetracyanoethylene) and inorganic substances (e.g boron sulphide, selenium and halogens) have been used quite successfully as additives, although the reasons for their effect in easing the problem have been little investigated. Differential scanning calorimetry (DSC) is a valuable tool which can be used to provide information on the sulphur–additive system. Indeed, in previous works we have reported the results concerning the sulphur–tetracyanoethylene [3] and sulphur–boron sulphide [4] systems.

This paper deals with a DSC investigation on the possible modes of interaction in the sulphur–selenium system. The rather obscure phase relationships in this system were investigated many years ago [5] by means of thermal and dilatometric methods. More recently, Boctor and Kullerud [6] established the equilibrium phase relationships and showed that sulphur

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and selenium exhibit complete liquid miscibility. Anyway, as it is known that the effect of an additive in enhancing cell performance falls off during the life of the cell, it could be that such an effect is tied up with the presence of some product, possibly metastable, of sulphur–selenium interaction that is formed during the first heating of a physical mixture. For this reason, the present study has been focused on the phenomenology of sulphur–selenium mixing, as revealed by DSC evidence obtained during the initial heating.

EXPERIMENTAL

Products

The sample mixtures (1.99–95.06% of selenium by mass) were prepared by weighing a fixed amount of sulphur (0.500 g) with the appropriate amount of selenium and thorough dry mixing in an agate mortar.

The sulphur (99.999%) and selenium (99.9%) were both purchased from Fluka AG.

Apparatus and procedures

The DSC measurements were performed by means of a Du Pont Model 910 Heat Flux DSC cell connected to a Du Pont 1090 Thermal Analysis System. Samples for DSC, weighing 13–18 mg, were sealed in aluminium cups to avoid loss of selenium by evaporation, and then scanned under a nitrogen flow (30 ml $\mathrm{min^{-1}}$) at 5 K $\mathrm{min^{-1}}$ between room temperature and 240°C, which is just above the melting point of selenium.

RESULTS AND DISCUSSION

Pure components

Several runs were performed on pure samples. With regard to sulphur the following thermal effects were found on heating: an endothermic peak ($T_{\mathrm{max}} = 105$°C) which can be attributed to the phase transition from rhombic to monoclinic sulphur ($\Delta H = 12.1$ J $\mathrm{g^{-1}}$; 0.39 kJ $\mathrm{mol^{-1}}$); an endothermic peak ($T_{\mathrm{max}} = 120$°C) marking the melting of monoclinic sulphur ($\Delta H =$ 54.0 J $\mathrm{g^{-1}}$; 1.73 kJ $\mathrm{mol^{-1}}$); and an endothermic peak ($T_{\mathrm{max}} = 164$–166°C; $\Delta H = 8.2$ J $\mathrm{g^{-1}}$; 0.26 kJ $\mathrm{mol^{-1}}$) indicating a liquid-phase phenomenon by which the eight atom rings start to join each other, forming increasingly long chains by a polymerization process [6].

The first heating of a selenium sample shows only the melting endotherm ($T_{\mathrm{max}} = 224$°C; $\Delta H = 73.6$ J $\mathrm{g^{-1}}$; 5.81 kJ $\mathrm{mol^{-1}}$).

In a subsequent heating run, quite a sharp exothermic peak was detectable ($T_{\mathrm{max}} = 170$°C; $\Delta H = 66.0$ J $\mathrm{g^{-1}}$ of selenium; 5.21 kJ $\mathrm{mol^{-1}}$) followed by the melting peak, which well reproduces that of the initial heating as regards both size and shape. Such thermal behaviour can be explained by allowing for the presence of a glassy phase which forms after the first melting and, upon a second heating, crystallizes to give again metallic selenium, which undergoes normal melting.

Sulphur–selenium mixtures

The heating of sample mixtures typically shows the following effects (see for example Fig. 1): endothermic peaks in the temperature range 100–130°C (sulphur transition and melting region); an endothermic peak in the temperature range of sulphur polymerization ($T = 150–170°\mathrm{C}$).

Table 1 reports the enthalpy values ($\Delta_{\mathrm{trs}}H$ for transition, $\Delta_{\mathrm{fus}}H$ for fusion, $\Delta_{\mathrm{trs+fus}}H$ for transition plus fusion, in J g^{-1} of sulphur) for the peaks in the sulphur melting region. It can be noted that, for mixtures containing up to 40.15 mass% of selenium, both peaks show enthalpic changes that are in fair agreement with those for pure sulphur. With further increase in the Se content, the thermal phenomenology of sulphur in the melting region is no longer the same. The data show that, beyond 40.15 mass% of Se, the transition peak area (in enthalpic units) diminishes, indicating that some type of interaction occurs which modifies the behaviour of sulphur during the transition process. As a matter of fact, by comparing the $\Delta_{\mathrm{trs+fus}}H$ values with the expected value (66.1 J g^{-1} of sulphur), it can be seen that the agreement is fair also for some of the mixtures with Se contents higher than 40.15%. The main evidence of interaction in the sulphur melting region

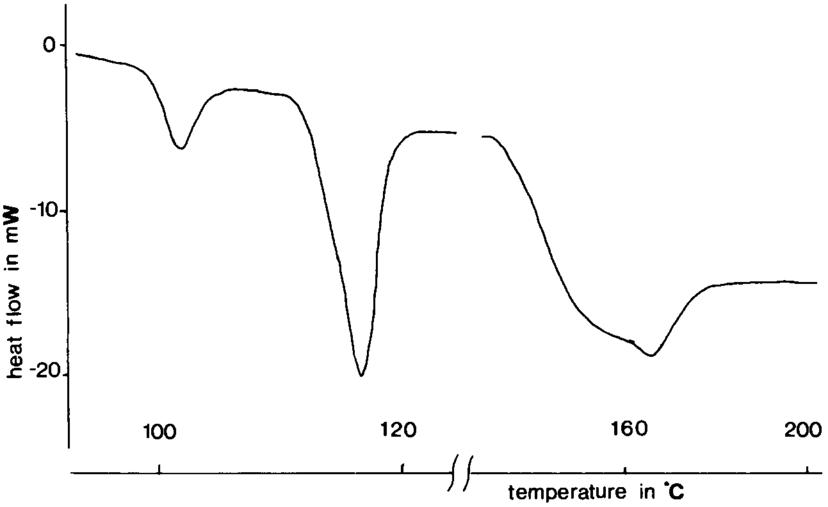

Fig. 1. DSC scan for a sulphur–selenium mixture containing 19.93% by mass of Se.

TABLE 1

Thermal phenomenology in the sulphur melting region. $\Delta_{trs}H$: sulphur rhombic–monoclinic transition enthalpy; $\Delta_{fus}H$: sulphur melting enthalpy; $\Delta_{trs+fus}H$: sulphur transition + melting enthalpy

Se content/ wt%	$\Delta_{trs}H/(\mathrm{J\ g^{-1}\ S})$	$\Delta_{fus}H/(\mathrm{J\ g^{-1}\ S})$	$\Delta_{trs+fus}H/(\mathrm{J\ g^{-1}\ S})$
1.99	12.0	52.7	64.7
5.12	12.1	53.4	65.5
8.14	11.4	50.3	61.7
9.80	12.1	48.7	60.8
10.27	12.1	48.1	60.2
14.97	12.1	53.1	65.2
19.93	12.1	51.7	63.8
25.24	12.5	54.3	66.8
35.46	12.4	54.3	66.7
40.15	12.3	54.1	66.4
49.93	10.6	47.3	57.9
55.19	10.8	51.8	63.9
64.94	10.9	47.0	57.9
70.16	9.6	56.8	66.4
75.09	–	–	62.1
79.30	–	–	63.8
84.92	4.0	55.8	59.8
90.13	1.4	45.0	46.4
95.06	2.9	53.0	55.9

could thus be the "freezing" of part of the sulphur into its rhombic form, which then would undergo melting [3].

An interaction process undoubtedly takes place over the entire range of composition, as is clearly indicated by the fact that none of the mixtures examined shows the selenium melting endotherm. The nature of such an interaction process could be understood by analysing the peak which occurs within the sulphur polymerization region, the relevant temperature and energetic data for which are reported in Table 2. From the table it appears that:

1. From a comparison of the peak enthalpic changes (expressed as J g^{-1} of sulphur) with the value for pure sulphur (8.2 J g^{-1}), sulphur polymerization alone can be ruled out as the origin of the peak;
2. The peak enthalpy values, when expressed as J g^{-1} of Se, tend to be more or less constant over a wide compositional range;
3. Such values, for all but the 90.13 and 95.06% mixtures, largely exceed the value to be expected if the peak were to be due to Se fusion (73.6 J g^{-1} of Se).

Thus some phenomenon other than polymerization of S or melting of Se has to be considered to account for the peak enthalpy values. From

TABLE 2

Temperature and enthalpic data for the peak in the sulphur polymerization region. T_{max} peak maximum temperature; $\Delta_{pol}H$: peak enthalpy value

Se content/ wt%	T_{max}/°C	$\Delta_{pol}H/(\mathrm{J\,g^{-1}}$ mix)	$\Delta_{pol}H/(\mathrm{J\,g^{-1}\,S})$	$\Delta_{pol}H/(\mathrm{J\,g^{-1}\,Se})$
1.99	163.5	2.5	2.6	125.6
5.12	164.9	5.5	5.8	101.6
8.14	163.7	9.9	10.8	121.6
9.80	160.1	11.2	12.4	114.3
10.27	161.2	12.0	13.4	116.8
14.97	163.7	16.7	19.6	111.6
19.93	164.1	21.6	27.0	108.4
25.24	163.9	25.0	33.4	100.0
35.46	159.7	40.2	62.3	113.4
40.15	161.7	45.7	76.4	113.8
49.93	161.4	61.8	123.4	123.8
55.19	161.8	66.5	148.4	97.8
64.94	164.9	77.1	220.0	118.8
70.16	162.4	74.5	249.7	106.2
75.09	163.5	76.7	307.9	102.2
79.30	163.0	77.9	376.3	98.2
84.92	162.0	75.2	498.7	88.6
90.13	163.0	68.9	698.1	76.4
95.06	200.7	71.4	1445.0	75.1

Table 2, the peak mean enthalpy can be calculated as 110.0 J g^{-1} of Se. This value agrees fairly well with that estimated by Ward and Myers [7] (120.0 J g^{-1} of Se) as the enthalpy of chain propagation during the polymerization process of pure Se. The hypothesis could be made that the peak is related with polymerization of Se occurring in the same temperature range as that of sulphur. This would represent quite an unexpected finding if one recalls that no evidence of polymerization was observed for pure Se samples.

Now, to attempt to clarify the thermal phenomenology shown by the mixtures, a comparison will be made between experimental and calculated values of the overall enthalpy change of each DSC trace. The total experimental enthalpy change will be simply the sum of the enthalpy changes measured for each thermal effect shown by the DSC trace, namely

$$\Delta H_{exp} = \Delta_{trs+fus}H + \Delta_{pol}H$$

The relevant values are reported in Table 3. Different hypotheses can now be put forward as to what happens during heating of the mixtures in order to calculate the total expected enthalpy change. The first hypothesis is that the overall enthalpy change is the sum of the enthalpy changes expected for the solid state transition and melting of sulphur [$\Delta_{trs+fus}H_{exd}$ (1)], the

TABLE 3

Comparison between the experimental enthalpy changes of the overall DSC trace and those calculated under different hypotheses explained in the text. All enthalpy values are expressed in J g^{-1} for the mixture. $\Delta_{trs+fus}H$: experimental values of the sulphur transition + melting enthalpy; $\Delta_{trs+fus}H_{exd}$: expected values of sulphur transition + melting enthalpy; $\Delta_{pol}H$: enthalpy changes of the peak in the sulphur polymerization region; $\Delta_{pol}H_{S,exd}$: expected values of the S polymerization enthalpy; $\Delta_{pol}H_{Se,exd}$: expected values of the Se polymerization enthalpy; ΔH_{exp}: $\Delta_{trs+fus}H + \Delta_{pol}H$; $\Delta_{fus}H_{Se,exd}$: expected values of the selenium melting enthalpy

Se content/ wt%	$\Delta_{trs+fus}H$	$\Delta_{pol}H$	ΔH_{exp}	$\Delta_{trs+fus}H_{exd}$ [1]	$\Delta_{pol}H_{S,exd}$ [2]	$\Delta_{pol}H_{Se,exd}$ [3]	$\Delta_{fus}H_{Se,exd}$ [4]	[1 + 2 + 3]	[1 + 2 + 4]	[1 + 3]
1.99	63.5	2.5	66.0	64.8	8.0	2.4	1.5	75.2	74.3	67.2
5.12	62.1	5.5	67.6	62.7	7.8	6.1	3.8	76.6	74.3	68.8
8.14	61.7	9.9	71.6	60.7	7.5	9.8	6.0	78.0	74.2	70.5
9.80	59.6	11.2	70.8	59.6	7.4	11.8	7.2	78.8	74.2	71.4
10.27	59.0	12.0	71.0	59.3	7.3	12.4	7.6	79.0	74.2	71.7
14.97	55.5	16.7	72.2	56.2	7.0	18.0	11.0	81.2	74.2	74.2
19.93	51.1	21.6	72.7	52.9	6.6	24.0	14.7	83.5	74.2	76.9
25.24	50.0	25.0	75.0	49.4	6.1	30.4	18.6	85.9	74.1	79.8
35.46	43.0	40.2	83.2	42.7	5.3	42.7	26.1	90.7	74.1	85.4
40.15	39.8	45.7	85.5	39.6	4.9	48.3	29.6	92.8	74.1	87.9
49.93	29.0	61.8	90.8	33.1	4.1	60.1	36.7	97.3	73.9	93.2
55.19	28.0	66.5	94.5	29.6	3.7	66.4	40.6	99.7	73.9	96.0
64.94	20.3	77.1	97.4	23.2	2.9	78.1	47.8	104.2	73.9	101.3
70.16	19.8	74.5	94.3	19.7	2.4	84.4	51.6	106.5	73.7	104.1
75.09	15.5	76.7	92.2	16.5	2.0	90.3	55.3	108.8	73.8	106.8
79.30	13.2	77.9	91.1	13.7	1.7	95.4	58.4	110.8	73.8	109.1
84.92	9.0	75.2	84.2	10.0	1.2	102.2	62.5	113.4	73.7	112.2
90.13	4.6	68.9	73.5	6.5	0.8	108.4	66.3	115.7	73.6	114.9
95.06	2.8	71.4	74.2	3.3	0.4	114.4	70.0	118.1	73.7	117.7

polymerization of sulphur [$\Delta_{\mathrm{pol}}H_{\mathrm{S,exd}}$ (2)] and the melting of selenium [$\Delta_{\mathrm{fus}}H_{\mathrm{Se,exd}}$ (4)]. Such a hypothesis implies a phenomenological model according to which:

(a) any selenium or sulphur that fails to melt at its melting temperatures undergoes melting within the sulphur polymerization region;

(b) all the sulphur contained in the mixtures undergoes its normal polymerization process.

The relevant results are reported under the heading [1 + 2 + 4] in Table 3 (the anomalous melting model).

The second phenomenological model takes into consideration the polymerization process of selenium. Indeed, Ward and Myers [7] proposed, in the case of S/Se mixtures, a copolymerization model which states that the Se is not present as Se_8 rings, but, rather, that it enters the sulphur rings substitutionally, forming S_xSe_{8-x} monomer units, which then undergo copolymerization with S_8 units with nearly the same enthalpic change as for pure selenium (120.3 J g^{-1}).

On the other hand, according to Boctor and Kullerud [6], the addition of Se should not suppress the polymerization of sulphur despite lowering its temperature, but no polymerization of sulphur at all is expected if the Se content exceeds a 12% atomic fraction (25% by weight).

Two calculation procedures have been performed to take into account the possible modes of Se polymerization. The results are reported respectively:

- under heading [1 + 2 + 3] of Table 3: these represent the sum of the enthalpy changes expected for sulphur transition plus melting and and for polymerization of S plus Se considered separately [$\Delta_{\mathrm{pol}}H_{\mathrm{Se,exd}}$ (3)];
- under heading [1 + 3] of Table 3: these represent the sum of the enthalpic changes expected for sulphur transition plus melting and for copolymerization of S and Se according to Ward and Myers (the copolymerization model).

The comparison of ΔH_{exp} values with those reported under the different headings of Table 3 shows that the best experimental/calculated agreement is obtained for the mixtures with Se contents up to 55.19%; the values are reported under heading [1 + 3]. It thus seems that the thermal phenomenology of mixing of S and Se, over a wide compositional range, essentially involves a S/Se copolymerization process.

In contrast, no satisfactory agreement is obtained by any kind of calculation procedure for mixtures of higher Se content. A close agreement between calculated and experimental values is again obtained (this time with values under the [1 + 2 + 4] heading) for the mixtures containing 90.13 and 95.06% of Se mixtures. Thus for Se contents higher than 90% in the mixture the interaction model implies sulphur polymerization and melting of selenium, although this last process takes place during sulphur polymerization.

Sulphur transition and melting also occur in this range of composition throughout the whole DSC scan. The thermal behaviour of S/Se mixtures can thus be explained on the basis of an anomalous melting behaviour of the two components. As for the mixtures containing 70.16–84.92% of Se, it can be seen that the experimental values (ΔH_{exp}) decrease with increasing Se content in the mixture. Thus the conclusion could be drawn that the interaction phenomenology is undergoing a shift, with increasing Se content, from the "copolymerization" model to the "anomalous melting" model.

CONCLUSIONS

Two effects of the sulphur–selenium interaction have been demonstrated:

1. the first, which applies only for mixtures with selenium contents greater than ≈50 at%, results in a modification of the sulphur structure, as suggested by the fact that the usual sulphur melting thermal phenomenology is no longer maintained;
2. the second one involves a sulphur/selenium copolymerization process, which has been shown to occur over a fairly wide compositional range.

It is here worth remembering in this context that a Na/S cell has been reported with a cathodic Se content between 50 and 90 at% [8]. At this stage of limited knowledge it is impossible to say whether the benefit of Se as an additive is connected to the modified structure of sulphur or rather to some peculiar property of the S/Se copolymer.

The effect of the additive would in any case be linked to the modified sulphur polymerization, which is thought to result in shorter chains with a consequent reduction in the viscosity of sulphur. Indeed, even a very limited amount of selenium (1 at%) has been proved to be effective in reducing the viscosity of sulphur [9].

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