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ON THE THERMAL CHARACTERIZATION OF THE SYSTEM SULFUR–TETRACYANOETHYLENE

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ABSTRACT

A DSC characterization of the sulfur–tetracyanoethylene (TCE) system was performed, and the thermal traces obtained quantitatively analyzed. It was shown that (a) some type of solid state interaction takes place between sulfur and TCE, which forces part of the sulfur to be "frozen" into its rhombic form; (b) variable amounts of sulfur and TCE fail to melt at their expected melting temperatures; and (c) a much higher than expected enthalpy change is associated with sulfur polymerization.

A phenomenological model is proposed according to which the sulfur and TCE that fail to melt at their melting temperatures undergo fusion in the wake of the liquid-phase sulfur polymerization process. It is shown that the model proposed is valid in the entire composition range studied.

INTRODUCTION

In the development of the sodium–sulfur battery many problems have been noted that arise from various factors such as the chemical/electrochemical stability of the ceramic electrolyte, cell design and performance and battery engineering [1]. Among the problems which affect the cell behavior, some attention has been focused on the issue of molten sulfur transport in the cathode compartment [2]. The use of additives [3], both organic and inorganic, has proved to have some effectiveness by increasing the electrical conductivity of sulfur and/or reducing its high viscosity. Tetracyanoethylene (referred to below as TCE) has been used as an additive to the molten sulfur electrode [4] with encouraging results as regards both

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conductivity improvement and lowering of viscosity, although its mechanism of action has not yet been completely clarified. A characterization of the sulfur–TCE system would thus be useful in order to gain knowledge on the interactions taking place and with the final aim to optimize the addition process. In this regard a DSC study of the sulfur–TCE system has been undertaken in order both to understand the effect of TCE on the thermal behavior of sulfur and to attempt to investigate the thermal phenomenology, if any, of the sulfur–TCE interactions.

EXPERIMENTAL

Products

Both sulfur (99.999%) and TCE (98%) were obtained from Fluka AG. TCE was purified by sublimation under reduced pressure (140 ° C, 1 Torr).

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. The mixtures (0.6–80% of TCE by weight) were prepared by weighing a fixed amount of sulfur, namely 500 mg, and the corresponding quantity of TCE. The reactants were then thoroughly dry mixed by co-grinding with a pestle in an agate mortar. The DSC samples (8–12 mg) were sealed into hermetic aluminum cups in order to avoid TCE sublimation and scanned (scan rate 5 ° C min^{-1}) from room temperature up to 215 ° C under a flow of dry nitrogen (30 ml min^{-1}). The upper temperature limit of 215 ° C is imposed by the boiling point of TCE, which is about 230 ° C.

RESULTS AND DISCUSSION

Pure components

Sulfur

As regards sulfur, the following thermal effects were found on heating (Fig. 1a):

- an endothermic peak at 106 ° C ($T_{\max}$), $\Delta H = 12.1$ J g^{-1}, which is due to the rhombic to monoclinic conversion;
- an endothermic peak at 122° C ($T_{\max}$), $\Delta H = 54.0$ J g^{-1}, marking the melting of monoclinic sulfur;
- an endothermic peak at 164–166 ° C ($T_{\max}$), $\Delta H = 8.2$ J g^{-1}, indicating a liquid-phase transition where the eight atom rings start to join each other,

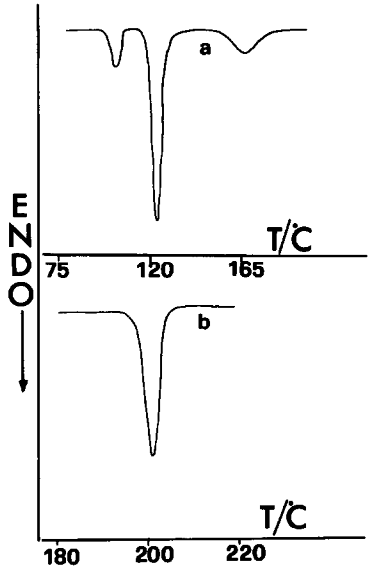

Fig. 1. (a) DSC trace obtained for a pure sulfur sample; (b) DSC trace obtained for a pure TCE sample.

forming increasingly long chains by a polymerization process (sulfur polymerization threshold [5]).

TCE

Only the sharp melting peak was detected at 202 °C (T_{max}), $\Delta H = 185.0$ J g^{-1} (Fig. 1b). It may be noted, from the area of the TCE melting peak on further heating runs, that losses of TCE by sublimation or evaporation can definitely be ruled out.

Sulfur–TCE mixtures

Figure 2 shows, as an example, the DSC traces of samples of different composition, and is representative of the thermal behavior of all the mixtures analyzed. A comparison with Fig. 1 allows one to see at a glance the qualitative differences between the thermal behavior of the mixtures and that of the pure components.

(1) Mixtures with a low TCE content do not show the TCE melting peak (Fig. 2a).

(2) A thermal effect is present in the mixtures at a temperature ($T_{max} \simeq$ 177 °C) where no peaks appear in the thermograms of either pure sulfur or pure TCE.

(3) Mixtures (TCE content > 3.63%) show a double peak in the thermal region of sulfur melting (T_{max} about 115 °C and 122 °C); the area of the first part gradually overcomes that of the second on increasing the TCE content of the mixture (Fig. 2b–d).

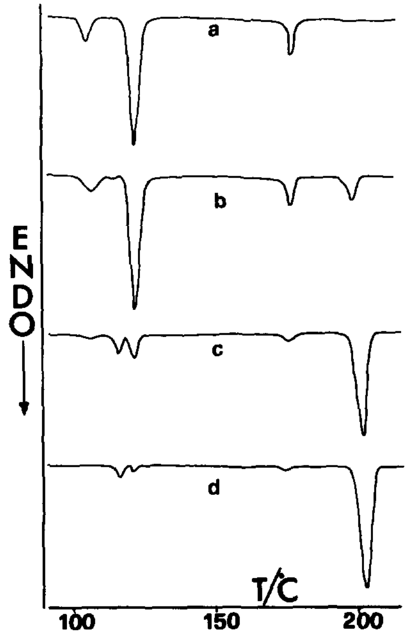

Fig. 2. DSC traces obtained for different sulfur–TCE mixtures (the composition is expressed in percentage of TCE by weight): (a) $\%TCE^{mix} = 2.58$; (b) $\%TCE^{mix} = 7.65$; (c) $\%TCE^{mix} = 50.18$; (d) $\%TCE^{mix} = 79.93$.

Before quantitative analysis of the thermal behavior of the mixture can be undertaken, some comment is necessary on points (2) and (3).

Because the "sulfur polymerization threshold" is known to range between ca. 160 and 190 ° C [6], the peak discussed under point (2) may be thought of as originating from the sulfur polymerization process.

Because 115 ° C (T_{max}) can be taken as the melting point of the sulfur rhombic phase [7], the double peak discussed under point (3) may be attributed to the melting of rhombic and monoclinic sulfur phases.

The presence of a double peak in the thermal region of sulfur melting indicates that some type of solid state interaction takes place in the mixtures which "freezes" part of the sulfur into its rhombic form. If this is the case, lower than expected enthalpy changes should be obtained for the transition from rhombic to monoclinic sulfur. Moreover, the relative amount of frozen rhombic sulfur could be quite easily obtained from a knowledge of the experimental and expected transition enthalpies.

The expected enthalpy changes can be obtained by the relationship

$$\Delta H_{t,exd} = \Delta H_t^{\star}(\%S^{mix}/100) \qquad (1)$$

where $\Delta H_{t,exd}$ is the expected enthalpy change, expressed in J g^{-1} of mixture, and represents the enthalpy change that should be obtained if all the sulfur present in the mixture were to undergo the rhombic to monoclinic transi-

TABLE 1

Experimental (ΔH_t) and expected ($\Delta H_{t,exd}$) enthalpy changes for sulfur solid state transition

%TCE^{mix}	ΔH_t	$\Delta H_{t,exd}$	%S$_{rh}^{mix}$
0.59	10.9	12.0	9.1
2.58	11.2	11.8	5.0
2.58	11.3	11.8	4.1
3.63	11.2	11.7	4.1
5.14	10.7	11.5	6.6
7.65	11.2	11.2	0.0
9.79	10.3	10.9	5.0
11.29	10.2	10.7	4.1
14.89	9.4	10.3	7.4
14.89	9.2	10.3	9.1
19.92	9.2	9.7	4.1
24.84	8.2	9.1	7.4
30.07	7.4	8.5	9.1
30.17	5.3	8.5	26.4
30.17	6.9	8.5	13.2
34.74	6.7	7.9	9.9
34.74	4.6	7.9	27.3
50.18	1.5	6.0	37.2
79.93	0.0	2.4	20.1

%S$_{rh}^{mix}$ represents the percentage (calculated with respect to the total mass of the mixture) of sulfur that does not undergo transition.

tion; $\Delta H_t^\star$ is the transition enthalpy of pure sulfur expressed in J g^{-1} of S; and %S^{mix} is the percentage of sulfur in the mixture.

The amount of rhombic sulfur can be calculated by the relationship

$$\%S_{rh}^{mix} = \left[(\Delta H_{t,exd} - \Delta H_t)100/\Delta H_t^\star\right] \qquad (2)$$

where %S$_{rh}^{mix}$ is the percentage, calculated with respect to the total mass of the mixture, of sulfur frozen in the rhombic form; and ΔH_t is the experimental value (expressed in J g^{-1} of mixture) of the enthalpy change associated with the sulfur transition.

Experimental and expected enthalpy changes associated with the sulfur solid state transition are reported in Table 1, together with the calculated amount of sulfur frozen in the rhombic form. It can be seen that the experimental enthalpy changes are systematically lower than those expected, confirming that part of the sulfur does not undergo the rhombic to monoclinic transition. The amount of this sulfur, however, does not seem to be in any regular relationship with the TCE content of the mixture: it shows quite similar, even if scattered, values up to a mixted TCE content of about 30%, whereas it seems to increase noticeably at higher TCE contents. Moreover the reproducibility of these frozen rhombic sulfur values appears quite uncertain and it may happen that samples obtained from the same mixture and analyzed independently from each other give results that are reasonably similar (Table 1, $\%\mathrm{TCE}^{\mathrm{mix}} = 2.58$ and 14.89), or quite different (Table 1; $\%\mathrm{TCE}^{\mathrm{mix}} = 30.17$ and 34.74).

It might be thought at this point that, whenever the analysis of the thermal region of sulfur solid state transition indicates that some sulfur has frozen into its rhombic form, a double peak should be obtained in the thermal region of sulfur melting. However, despite evidence that frozen rhombic sulfur was obtained in the whole composition range (Table 1), formation of a double melting peak was detected only for mixtures with TCE contents higher than 3.63%. This should indicate that in mixtures of low TCE content ($\%\mathrm{TCE}^{\mathrm{mix}} \leq 3.63$) part of the sulfur, namely the frozen rhombic sulfur, fails to melt.

To confirm this hypothesis and to test if part of the sulfur fails to melt also in mixtures of higher TCE content, a quantitative analysis of the sulfur melting endotherm has to be performed. The expected values of the enthalpy changes associated with the melting of monoclinic and rhombic sulfur ($\Delta H_{\mathrm{mo,exd}}$, $\Delta H_{\mathrm{rh,exd}}$) respectively can be obtained by the relationships

$$\Delta H_{\mathrm{mo,exd}} = \Delta H^{\star}_{\mathrm{mo}}(\%\mathrm{S}^{\mathrm{mix}}_{\mathrm{mo}}/100) \tag{3}$$

$$\Delta H_{\mathrm{rh,exd}} = \Delta H^{\star}_{\mathrm{rh}}(\%\mathrm{S}^{\mathrm{mix}}_{\mathrm{rh}}/100) \tag{3'}$$

where $\Delta H^{\star}_{\mathrm{mo}}$ and $\Delta H^{\star}_{\mathrm{rh}}$ are enthalpy changes (expressed in J g^{-1} of S) associated with the melting of pure monoclinic and rhombic sulfur, respectively, and $\%\mathrm{S}^{\mathrm{mix}}_{\mathrm{mo}}$ and $\%\mathrm{S}^{\mathrm{mix}}_{\mathrm{rh}}$ are the percentages, calculated with respect to the total mass of the mixture, of monoclinic and rhombic sulfur respectively.

The amount of sulfur that does not undergo melting ($\%\mathrm{S}^{\mathrm{mix}}_{\mathrm{n,m}}$) could be obtained, in complete analogy with that previously seen for the amount of sulfur frozen in the rhombic form, from the following relationship

$$\begin{aligned}\%\mathrm{S}^{\mathrm{mix}}_{\mathrm{n,m}} &= \%\mathrm{S}^{\mathrm{mix}}_{\mathrm{mo,n,m}} + \%\mathrm{S}^{\mathrm{mix}}_{\mathrm{rh,n,m}} \\ &= \left[(\Delta H_{\mathrm{mo,exd}} - \Delta H_{\mathrm{mo}})100/\Delta H^{\star}_{\mathrm{mo}}\right] + \left[(\Delta H_{\mathrm{rh,exd}} - \Delta H_{\mathrm{rh}})100/\Delta H^{\star}_{\mathrm{rh}}\right]\end{aligned} \tag{4}$$

where $\%\mathrm{S}^{\mathrm{mix}}_{\mathrm{mo,n,m}}$ and $\%\mathrm{S}^{\mathrm{mix}}_{\mathrm{rh,n,m}}$ are the percentages (calculated with respect to the total mass of the mixture) of monoclinic and rhombic sulfur, respectively, which do not undergo melting, and ΔH_{mo} and ΔH_{rh} are the experimental values (expressed in J g^{-1} of mix) of the enthalpy changes associated with the melting of monoclinic and rhombic sulfur respectively.

In contrast to $\Delta H^{\star}_{\mathrm{mo}}$, the $\Delta H^{\star}_{\mathrm{rh}}$ value cannot be experimentally determined, but it can reliably be taken as the sum of the sulfur transition and monoclinic-phase melting enthalpies.

This notwithstanding, the use of relationship (4) presents two problems: a formal problem and a substantial problem.

The first problem relates to the knowledge of $\Delta H_{\mathrm{mo,exd}}$ and $\Delta H_{\mathrm{rh,exd}}$ which, in turn, requires knowledge of the relative amounts of monoclinic

TABLE 2

$\Delta H_{\text{mo,exd}}$ and $\Delta H_{\text{rh,exd}}$ were calculated by relations (3) and (3′) utilizing the $\%S_{\text{rh}}^{\text{mix}}$ values reported in Table 1

$\%\text{TCE}^{\text{mix}}$	$\Delta H_{\text{mo,exd}}$	ΔH_{mo}	$\Delta H_{\text{rh,exd}}$	ΔH_{rh}	$\%S_{\text{rh,n,m}}^{\text{mix}}$	$\%S_{\text{n,m}}^{\text{mix}}$
0.59	48.8	48.7	6.0	0.0	9.1	9.3
2.58	49.9	49.7	3.3	0.0	5.0	5.4
2.58	50.4	48.9	2.7	0.0	4.1	6.9
3.63	49.8	49.8	2.7	0.0	4.1	4.1
5.14	47.7	47.2	4.4	0.4	6.0	6.9
7.65	49.9	48.8	0.0	0.4	−0.6	1.4
9.79	46.0	45.4	3.3	0.7	3.9	5.0
11.29	45.7	44.9	2.7	0.3	3.6	5.1
14.89	42.0	42.6	4.9	1.1	5.7	4.6
14.89	41.0	42.2	6.0	0.8	7.9	5.7
19.92	41.0	41.5	2.7	1.2	2.3	1.4
24.84	36.6	37.3	4.9	1.5	5.1	3.8
30.07	32.8	34.3	6.0	2.5	5.3	2.5
30.17	23.4	33.9	17.4	5.5	18.0	−1.4
30.17	30.6	34.5	8.7	3.5	7.9	0.7
34.74	29.9	35.3	6.5	4.2	3.5	−6.5
34.74	20.5	29.2	18.0	6.2	17.8	1.7
50.18	6.8	14.4	24.6	13.2	17.2	3.1
79.93	0.0	3.2	13.3	8.9	6.6	0.7

ΔH_{mo} and ΔH_{rh} were obtained by separating the two sulfur melting peaks by a straight line parallel to the ordinate axis. $\%S_{\text{rh,n,m}}^{\text{mix}}$ and $\%S_{\text{n,m}}^{\text{mix}}$ were calculated by eqn. (4).

and rhombic sulfur present in the mixture immediately before melting. Such information can be obtained only from the solid state transition peak. In other words, to determine $\Delta H_{\text{mo,exd}}$ and $\Delta H_{\text{rh,exd}}$ it is necessary to utilize the percentages of monoclinic and rhombic sulfur obtained by the quantitative analysis of the solid state transition peak. The values obtained in this way for $\Delta H_{\text{mo,exd}}$, $\Delta H_{\text{rh,exd}}$, $\%S_{\text{rh,n,m}}^{\text{mix}}$ and $\%S_{\text{n,m}}^{\text{mix}}$ are reported, together with the experimental values ΔH_{mo} and ΔH_{rh}, in Table 2. First of all it is interesting to compare the $\%S_{\text{rh,n,m}}^{\text{mix}}$ values with $\%S_{\text{rh}}^{\text{mix}}$ values reported in Table 1 (such a comparison is obviously meaningful only when a double sulfur melting peak is present, i.e. for mixtures with $\%\text{TCE}^{\text{mix}} > 3.63$). It can be seen that the former values are always lower (for mixtures with high TCE content, much lower) than the latter, meaning that only part of the sulfur which has frozen in the rhombic form undergoes melting as rhombic sulfur.

A comparison between the $\%S_{\text{rh,n,m}}^{\text{mix}}$ and $\%S_{\text{n,m}}^{\text{mix}}$ values is also quite instructive. It can be seen that the former values are slightly lower than the latter up to the composition $\%\text{TCE}^{\text{mix}} = 11.29$, indicating that in these mixtures not only the rhombic sulfur, but a small part of the monoclinic sulfur also, fails to melt.

The $\%S_{\text{rh,n,m}}^{\text{mix}}$ values of mixtures with $\%\text{TCE}^{\text{mix}} > 11.29$ are always higher (often much higher) than the $\%S_{n,m}^{mix}$ values. This can be interpreted only by accepting that an appreciable part of the frozen rhombic sulfur undergoes melting as monoclinic sulfur, thus undergoing solid state transition in the thermal region of sulfur melting. Besides providing interesting indications on the interaction phenomenology, the calculation procedure described does not introduce any error in the evaluation of $\%S_{n,m}^{mix}$. In fact it is easy to show that, with eqns. (3) and (3′), eqn. (4) can be written as

$$\%S_{n,m}^{mix} = \%S^{mix} - \left[(\Delta H_{mo}/\Delta H_{mo}^{\star})100\right] - \left[(\Delta H_{rh}/\Delta H_{rh}^{\star})100\right] \qquad (4')$$

This equation obviously does not depend at all on the relative values of $\Delta H_{mo,exd}$ and $\Delta H_{rh,exd}$. In other words, $\%S_{n,m}^{mix}$ does not depend on the relative values of $\%S_{mo}^{mix}$ and $\%S_{rh}^{mix}$, but only on their sum, $\%S_{mo}^{mix} + \%S_{rh}^{mix} = \%S^{mix}$; i.e. it depends only on the total percentage of sulfur in the mixture. This is the reason that the use of the monoclinic and rhombic sulfur percentages obtained from the solid state transition peak constitutes only a formal problem. A substantial problem is however constituted by the fact that both eqns. (4) and (4′) require separate knowledge of the experimental values of both monoclinic and rhombic heats of fusion (ΔH_{mo} and ΔH_{rh}). In other words, the calculation of $\%S_{n,m}^{mix}$ requires the resolution of the double peak obtained in the thermal region of sulfur melting. The ΔH_{mo} and ΔH_{rh} values reported in Table 2 have been obtained by separating the two parts of the double peak by a straight line parallel to the ordinate axis.

However, as each graphical separation criterion is an arbitrary one, the proportion of rhombic and monoclinic melting enthalpies obtained is also arbitrary, and the values calculated for the amount of sulfur that does not undergo melting may not be reliable.

The problem can be overcome by extending the quantitative analysis to the entire thermal region of sulfur solid state transition and melting. It can be easily shown that the amount of sulfur that does not undergo either transition or melting can be unambiguously obtained by the relationship

$$\%S_{n,t,m}^{mix} = \frac{(\Delta H_{t,exd} + \Delta H_{m,exd}) - (\Delta H_t + \Delta H_m)}{\Delta H_t^{\star} + \Delta H_{mo}^{\star}} \times 100 \qquad (5)$$

where $\%S_{n,t,m}^{mix}$ is the percentage (calculated with respect to the total mass of the mixture) of sulfur that does not undergo either solid state transition or melting; $\Delta H_{m,exd} = \Delta H_{mo}^{\star}(\%S^{mix}/100)$ is the expected enthalpy change expressed in J g^{-1} of mixture, and represents the enthalpy change that should be obtained if all the sulfur present in the mixture were to undergo melting as monoclinic sulfur; and $\Delta H_m = \Delta H_{mo} + \Delta H_{rh}$ is the overall experimental enthalpy change, expressed in J g^{-1} of mix, associated with sulfur melting.

The values of $(\Delta H_{t,exd} + \Delta H_{m,exd})$ and $(\Delta H_t + \Delta H_m)$ are reported, together with those of $\%S_{n,t,m}^{mix}$, in Table 3. As just seen these last parameters represent more reliable values for the amount of sulfur that fails to melt than do the $\%S_{n,m}^{mix}$ values of Table 2. However, the conclusions which can be

TABLE 3

Experimental ($\Delta H_t + \Delta H_m$) and expected ($\Delta H_{t,exd} + \Delta H_{m,exd}$) enthalpy changes for sulfur solid state transition and melting

%TCE^{mix}	($\Delta H_t + \Delta H_m$)	($\Delta H_{t,exd} + \Delta H_{m,exd}$)	%S$^{mix}_{n,t,m}$
0.59	59.6	65.7	9.2
2.58	60.9	64.4	5.3
2.58	60.2	64.4	6.3
3.63	61.0	63.7	4.1
5.14	58.3	62.7	6.6
7.65	60.4	61.1	1.0
9.79	56.4	59.6	4.8
11.29	55.4	58.6	4.8
14.89	53.1	56.2	4.7
14.89	52.2	56.2	6.0
19.92	51.9	52.9	1.5
24.84	47.0	49.7	4.1
30.07	44.2	46.3	3.2
30.17	44.7	46.2	2.3
30.17	44.9	46.2	2.0
34.74	46.2	43.1	−4.7
34.74	40.0	43.1	4.7
50.18	29.1	32.9	5.7
79.93	12.1	13.2	1.7

%S$^{mix}_{n,t,m}$ represents the percentage (calculated with respect to the total mass of the mixture) of rhombic sulfur that does not undergo either solid state transition or melting.

drawn from a comparison of each of these parameters with the %S$^{mix}_{rh}$ values of Table 1 are substantially the same, and they will not be discussed further.

It was noted, when discussing the qualitative differences between the thermal behavior of the pure components and the mixtures, that TCE fails to melt in mixtures of very low TCE content. It seems at this point useful to verify whether, when a TCE melting peak is present, its area corresponds to the melting of all the TCE contained in the sample. The expected enthalpy change for the melting of all the TCE contained in a sample ($\Delta H_{TCE,exd}$) can be obtained by the following relationship (completely analogous to eqn. (1))

$$\Delta H_{TCE,exd} = \Delta H^{\star}_{TCE}(\%TCE^{mix}/100) \qquad (6)$$

where $\Delta H^{\star}_{TCE}$ is the melting enthalpy of pure TCE expressed in J g^{-1} of TCE, and %TCE^{mix} is the percentage of TCE in the sample.

On the other hand, the amount of TCE that does not undergo melting can be obtained by the relationship (completely analogous to eqn. (2))

$$\%TCE^{mix}_{n,m} = \left[(\Delta H_{TCE,exd} - \Delta H_{TCE})100/\Delta H^{\star}_{TCE}\right] \qquad (7)$$

where %TCE$^{mix}_{n,m}$ is the percentage, calculated with respect to the total mass of the sample, of TCE that does not undergo melting, and ΔH_{TCE} is the experimental value (expressed in J g^{-1} of mix) of the enthalpy change associated with TCE melting.

TABLE 4

Experimental (ΔH_{TCE}) and expected ($\Delta H_{\mathrm{TCE,exd}}$) enthalpy changes for TCE melting

$\%\mathrm{TCE}^{\mathrm{mix}}$	ΔH_{TCE}	$\Delta H_{\mathrm{TCE,exd}}$	$\%\mathrm{TCE}^{\mathrm{mix}}_{\mathrm{n,m}}$
0.59	0.0	1.1	0.6
2.58	0.0	4.8	2.6
2.58	0.0	4.8	2.6
3.63	0.7	6.7	3.2
5.14	4.8	9.5	2.5
7.65	5.4	14.1	4.7
9.79	15.0	18.1	1.7
11.29	17.6	20.9	1.8
14.89	23.6	27.5	2.1
14.89	23.5	27.5	2.2
19.92	29.4	36.8	4.0
24.84	39.7	45.9	3.3
30.07	51.4	55.6	2.3
30.17	52.6	55.8	1.7
30.17	51.4	55.8	2.4
34.74	56.0	64.3	4.5
34.74	63.7	64.3	0.3
50.18	96.0	92.8	−1.7
79.93	147.0	147.9	0.5

$\%\mathrm{TCE}^{\mathrm{mix}}_{\mathrm{n,m}}$ represents the percentage of TCE (calculated with respect to the total mass of the mixture) that does not undergo melting (see text).

The $\Delta H_{\mathrm{TCE,exd}}$ and ΔH_{TCE} values are reported, together with the $\%\mathrm{TCE}^{\mathrm{mix}}_{\mathrm{n,m}}$ values, in Table 4. It can be seen that the experimental enthalpy changes are systematically lower (except in one case) than the expected ones, meaning that some TCE fails to melt in all the samples analyzed. Moreover, the amount of this TCE does not seem to bear any reasonable relationship to sample composition.

One more thermal region has now to be analyzed to produce a complete picture of the energetic differences that mixtures present relative to pure components. This is the region of sulfur liquid state transition or sulfur polymerization. The expected values for the enthalpy changes associated with this process ($\Delta H_{\mathrm{p,exd}}$) can be obtained, by analogy with eqn. (1), by the relationship

$$\Delta H_{\mathrm{p,exd}} = \Delta H^{\star}_{\mathrm{p}} (\%\mathrm{S}^{\mathrm{mix}}/100) \tag{8}$$

where $\Delta H^{\star}_{\mathrm{p}}$ is the polymerization enthalpy of pure sulfur expressed in J g^{-1} of S.

The expected values are reported together with the experimental ones in Table 5. It can be seen that, in contrast to what was previously observed with respect to sulfur solid state transition and melting and TCE melting, the experimental values are now considerably higher (except in one case)

TABLE 5

Enthalpy changes for sulfur polymerization

$\%\mathrm{TCE}^{\mathrm{mix}}$	ΔH_p	$\Delta H_{p,\mathrm{exd}}$	$(\Delta\,\Delta H)$	$(\Delta\,\Delta H)\%$	$\Delta H_{p,\mathrm{mod}}$	$(\Delta\,\Delta H)_{\mathrm{mod}}$	$(\Delta\,\Delta H)_{\mathrm{mod}}\%$
0.59	14.5	8.1	6.4	78.8	15.3	−0.8	−5.2
2.58	17.3	8.0	9.3	117.6	16.3	1.0	+6.1
2.58	16.1	8.0	8.1	102.5	17.0	−0.9	−5.3
3.63	17.2	7.9	9.3	118.8	16.6	0.6	+3.6
5.14	17.7	7.8	9.9	126.9	16.9	0.8	+4.7
7.65	18.2	7.6	10.6	139.5	17.0	1.2	+7.1
9.79	13.6	7.4	6.2	84.8	13.7	−0.1	−0.7
11.29	14.6	7.3	7.3	100.0	13.8	0.8	+5.8
14.89	14.0	7.0	7.0	100.0	14.0	0.0	0.0
14.89	14.7	7.0	7.7	110.0	15.0	−0.3	−2.0
19.92	14.6	6.6	8.0	121.2	15.0	−0.4	−2.7
24.84	12.7	6.2	6.5	104.8	15.1	−2.4	−15.9
30.07	10.8	5.7	5.1	89.1	12.0	−1.2	−10.0
30.17	12.5	5.7	6.8	119.3	10.4	2.1	+20.2
30.17	11.0	5.7	5.3	93.0	11.4	−0.4	−3.5
34.74	11.7	5.3	6.4	119.9	10.5	1.2	+11.4
34.74	8.9	5.3	3.6	67.3	9.0	−0.1	−1.1
50.18	3.2	4.1	−0.9	−21.2	4.7	−1.5	−31.9
79.93	5.2	1.6	3.6	217.1	3.7	1.5	+40.5

ΔH_p = experimental enthalpy change; $\Delta H_{p,\mathrm{exd}}$ = expected enthalpy change (see text); $\Delta H_{p,\mathrm{mod}}$ = enthalpy change calculated on the basis of the phenomenological model proposed (see text). $(\Delta\ \Delta H) = (\Delta H_p - \Delta H_{p,\mathrm{exd}})$; $(\Delta\ \Delta H)\% = [(\Delta H_p - \Delta H_{p,\mathrm{exd}})100/\Delta H_{p,\mathrm{exd}}]$; $(\Delta\,\Delta H)_{\mathrm{mod}} = \Delta H_p - \Delta H_{\mathrm{mod}}$; $(\Delta\,\Delta H)_{\mathrm{mod}}\% = [(\Delta H_p - \Delta H_{\mathrm{mod}})100/\Delta H_{\mathrm{mod}}]$.

than the expected ones. However, as in those cases, it seems that the differences between the experimental and expected enthalpy changes constitute a random function of sample composition.

It is now useful to summarize the results obtained by the quantitative analysis of the DSC traces of sulfur–TCE mixtures, and to analyze their meaning, in order to describe correctly the phenomenology of sulfur–TCE interaction.

Some type of solid state interaction takes place between sulfur and TCE, the phenomenological effect of which is to freeze some sulfur into its rhombic form, as indicated by the fact that lower than expected rhombic to monoclinic transition enthalpies are obtained.

All this rhombic sulfur (in some cases), or a greater or lesser part of it (in others), fails to melt at its melting temperature, as indicated by the fact that lower than expected values are obtained for the overall enthalpy change associated with sulfur solid state transition and melting.

A widely variable part of the TCE contained in the mixtures fails to melt at its melting temperature, as indicated by the fact that lower than expected values are obtained for the TCE melting enthalpy. However, there does not seem to be any reasonable relationship between the amounts of TCE and rhombic sulfur that fail to melt at their melting temperatures.

In general, higher than expected values are obtained for the sulfur polymerization enthalpy, as if the energy that was not absorbed in the thermal regions of sulfur and TCE melting is being absorbed in the intermediate region of sulfur polymerization.

This last hypothesis implies a phenomenological model according to which (a) all the rhombic sulfur and TCE that fail to melt at their melting temperatures undergo melting in the thermal region of sulfur polymerization; and (b) all the sulfur contained in the mixture undergoes its normal polymerization process (as if no TCE were present).

On the basis of such a model, the enthalpy change associated with the thermal region of sulfur polymerization ($\Delta H_{\mathrm{p,mod}}$) would be

$$\Delta H_{\mathrm{p,mod}} = (\Delta H_{\mathrm{t,exd}} + \Delta H_{\mathrm{m,exd}}) - (\Delta H_{\mathrm{t}} + \Delta H_{\mathrm{m}}) + (\Delta H_{\mathrm{TCE,exd}} - \Delta H_{\mathrm{TCE}}) + \Delta H_{\mathrm{p,exd}} \tag{9}$$

The $\Delta H_{\mathrm{p,mod}}$ values are reported in Table 5. It can be seen that there is quite good agreement between these values and the experimental ones (also reported in Table 5), indicating that the phenomenological model proposed constitutes a good explanation of the experimental results.

It should, however, be noted that, although the differences between the experimental values of the polymerization enthalpy and those calculated according to the model are always quite small, the percentage differences can be quite high (see, for example, Table 5; the mixtures with $\%\mathrm{TCE}^{\mathrm{mix}} = 50.18$ and 79.93). This is a direct consequence of the small absolute values of sulfur polymerization enthalpies. Moreover, it must be taken into account that, owing to the data manipulation procedure followed with the model, the experimental errors of the entire DSC trace are forced into the sulfur polymerization peak. Thus an analysis of the quoted percentage differences would give an incorrect idea of the precision with which the proposed phenomenological model explains the experimental results. In contrast, such precision can be correctly evaluated by a comparison 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 present in the DSC trace, namely

$$\Delta H_{\mathrm{exp}} = \Delta H_{\mathrm{t}} + \Delta H_{\mathrm{m}} + \Delta H_{\mathrm{p}} + \Delta H_{\mathrm{TCE}} \tag{10}$$

The total expected enthalpy change will be given by the sum of the enthalpy changes expected for sulfur solid state transition and melting, sulfur polymerization and TCE melting, namely

$$\Delta H_{\mathrm{exd}} = (\Delta H_{\mathrm{t,exd}} + \Delta H_{\mathrm{m,exd}}) + \Delta H_{\mathrm{p,exd}} + \Delta H_{\mathrm{TCE,exd}} \tag{11}$$

The ΔH_{exp} and ΔH_{exd} values and the differences between the two are reported in Table 6. It can be seen that now not only the differences, but

TABLE 6

Overall enthalpy changes of the DSC traces

$\%TCE^{mix}$	ΔH_{exp}	ΔH_{exd}	$(\Delta\, \Delta H)$	$(\Delta\, \Delta H)\%$
0.59	74.1	74.9	−0.8	−1.1
2.58	78.2	77.2	1.0	1.3
2.58	76.3	77.2	−0.9	−1.2
3.63	78.9	78.3	0.6	0.8
5.14	80.8	80.0	0.8	1.0
7.65	84.0	82.8	1.2	1.4
9.79	85.0	85.1	−0.1	−0.1
11.29	87.6	86.8	0.8	0.9
14.89	90.7	90.7	0.0	0.0
14.89	90.4	90.7	−0.3	−0.3
19.92	95.9	96.3	−0.4	−0.4
24.84	99.4	101.8	−2.4	−2.4
30.07	106.4	107.6	−1.2	−1.1
30.17	109.8	107.7	2.1	1.9
30.17	107.3	107.7	−0.4	−0.4
34.74	113.9	112.7	1.2	1.1
34.74	112.6	112.7	−0.1	−0.1
50.18	128.3	129.8	−1.5	−1.2
79.93	164.3	162.7	1.6	1.0

ΔH_{exp} = experimental enthalpy change; ΔH_{exd} = enthalpy change calculated on the basis of the phenomenological model proposed; $(\Delta\, \Delta H) = (\Delta H_{exp} - \Delta H_{exd})$; $(\Delta\, \Delta H)\% = [(\Delta H_{exp} - \Delta H_{exd})100/\Delta H_{exd}]$.

also the percentage differences between experimental and expected values are quite small (around 1%). As 1–2% can be taken as the experimental error of good thermal measurements, it can be concluded that the proposed phenomenological model agrees fully, within experimental error, with the experimental results.

It was noted, in discussing Tables 3 and 4, that one mixture in each gave experimental enthalpy changes higher than the expected ones and, as a consequence, negative values for the amounts of sulfur and TCE which did not undergo melting in their respective melting regions. No comment was made, however, on these "impossible" results. It can be seen in Table 6 that the percentage difference between the experimental and expected values of the overall enthalpy change associated with these mixtures ($\%TCE^{mix}$ = 34.74 and 50.18) do not show any anomaly. All are around 1%, indicating that the model proposed accounts well for the overall thermal behavior of these mixtures also. If the difference between the expected and experimental values of the pertinent melting enthalpies (deducible from Tables 3 and 4) is compared with the difference between the expected and experimental values of the overall enthalpy change (reported in Table 6), it is found that the first one is more than twice the second for both mixtures. In other words the "impossible" difference between the expected and the experimental melting enthalpy is not within the experimental error. No more than a phenomenological explanation can obviously be given of this discrepancy. From a purely phenomenological point of view, the fact that more sulfur (TCE) than was present undergoes solid state transition and melting (melting) means that some TCE (sulfur) undergoes melting (solid state transition and melting) in the thermal region of sulfur (TCE) melting.

It seems, after all, that the thermal behavior of sulfur–TCE mixtures can be satisfactorily explained, at least from a phenomenological point of view, on the basis of an anomalous melting behavior of the two components. Part of the TCE can undergo melting at temperatures sensibly lower than expected. Conversely, part of the sulfur can undergo melting at temperatures higher than expected.

The understanding of the physical meaning of the proposed phenomenological model needs a much deeper knowledge of the system than can be obtained by thermal measurements alone. To gain a comprehensive view of all the interaction processes in the system, thermal measurements will have to be matched by corresponding microscopic, diffractometric and spectroscopic ones. This study is now in its first stages, and the results will hopefully be reported in a future paper.

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