Thermochimica Acta, 158 (1990) 71–77
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE ENTHALPY OF CRYSTALLISATION OF ASPHALTS

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(Received 28 June 1989)

ABSTRACT

Exothermic heat contents ($-\Delta H$) of asphalts were determined using a Perkin–Elmer DSC-4 and a TADS data station. The size of an obtainable peak was dependent in all instances solely on the prior cooling time rather than on the thermal history introduced by heating the samples to 130 °C and 180 °C. The enthalpies associated with the exothermic peaks of asphalts have been measured under a variety of controlled conditions. Exothermic transformations were noted at about −10 °C. The most obvious difference between the runs was the occurrence of lower ΔH values when the sample was kept in the DSC for 2.5 h as compared with 30 min, and when the thermograms were obtained by heating the samples from −33 °C to 32 °C at a scan rate of 10 °C min^{-1}. The *t*-test values of the two types of runs, conditioning in the DSC for 30 min or for 2.5 h at −33 °C and then scanning at 10 °C min^{-1}, were shown to be significantly different. These results show that the enthalpy of crystallisation was dependent on the duration of the prior cooling.

INTRODUCTION

Asphalts are complex mixtures of hydrocarbons with a range of relative molecular mass which varies widely from less than 150 to several thousand. They contain paraffins, naphthenes, aromatic hydrocarbons and other compounds. The proportion of the various compounds varies from asphalt to asphalt depending on the crude source and method of processing. Asphalts contain 80–85% carbon and 9–10% hydrogen. In addition, there are varying amounts of oxygen, sulphur and nitrogen present. The oxygen content ranges from 2% to 8%, depending on the origin of the petroleum and on the asphalt production methods. The relationship between the composition of asphalts and their glass transition temperatures (T_g) has been reported by many workers [1–5]. The presence of waxes in the oily fraction, which tend to crystallise and cause a phase separation, has been reported by Manheimer [6]. Exothermic transformations (of a crystalline type) at temperatures between −30 and 5 °C have been reported by Brule et al. [7]. The crystalline phases in asphalts have also been studied by Noel and Corbett [8]. Enthalpy values calculated from experimental data are discussed in this paper.

0040-6031/90/$03.50

EXPERIMENTAL

The study materials used in this research were asphalts from Ohio (C-8533 and C-8525), Michigan (C-8843) and Utah (C-8566).

A Perkin–Elmer differential scanning calorimeter, model DSC-4 with intracooler 1, was used for the thermal determinations. The standard aluminium pan with lid was used as a reference. A slow current of nitrogen (20 lbf in^{-2}) was passed over the sample holder during the experiment. The energy measurements were calibrated using distilled water, taken to have a heat of fusion of 78.36 cal g^{-1}. The sample weights for each DSC run ranged from 17 mg to 27 mg. The samples were weighed into the aluminium pans at ambient temperature.

The asphalt samples were placed in a DSC sample cell and the temperature of the system was brought to −33 °C. After the cells reached this equilibration temperature, they were kept at −33 °C for an additional 30 min. The thermogram was obtained as the sample was heated from −33 °C to 32 °C at a scan rate of 10 °C min^{-1}. The same sample was run twice in the same manner. The sample was then heated to 130 °C at a heating rate of 10 °C min^{-1}, cooled to room temperature, quench-cooled to −33 °C and re-run in a similar manner from −33 °C to 32 °C. This sample was then left in the DSC for 2.5 h at −33 °C and then scanned at a rate of 10 °C min^{-1} from −33 °C to 32 °C. The sample was heated from 30 °C to 180 °C (heating rate 10 °C min^{-1}) and left in the DSC for an additional 30 min at 180 °C. It was then quench-cooled to 30 °C, and when the temperature reached 30 °C, further quench-cooled to −33 °C and scanned as before. At

TABLE 1

Thermogram parameters and pertinent results for C-8533 (Ohio). Sample weight, 26.60 mg

Run	DSC no.	Temperature range (° C)	Peak minimum (° C)	ΔH (cal g^{-1})	Notes
1	6033	−33– 32	−9.24	−0.40	30 min (−33° C)
2	6034	−33– 32	−9.47	−0.43	30 min (−33° C)
3	6035	−33– 32	−9.67	−0.46	30 min (−33° C)
4	6061	30–130	–	–	
5	6063	−33– 32	−9.67	−0.45	30 min (−33° C)
6	6064	−33– 32	−10.60	−0.44	30 min (−33° C)
7	6065	−33– 32	−9.27	−0.32	2.5 h (−33° C)
8	6072	−33– 32	−11.27	−0.49	30 min (−33° C)
9	6073	30–180	–	–	
10	6074	−33– 32	−10.34	−0.43	30 min (−33° C)
11	6075	−33– 32	−11.67	−0.46	30 min (−33° C)

Statistical calculations: mean ΔH (30 min) = −0.445 cal g^{-1} and mean ΔH (2.5 h) = −0.32 cal g^{-1}; standard deviation ΔH (30 min) = −0.0267 cal g^{-1}; and *t*-test value (comparison of above data) = 4.4169.

TABLE 2

Thermogram parameters and pertinent results for C-8525 (Ohio). Sample weight, 20.80 mg

Run	DSC no.	Temperature range (°C)	Peak minimum (°C)	ΔH (cal g^{-1})	Notes
1	6092	−33– 32	−9.47	−0.47	30 min (−33°C)
2	6093	−33– 32	−9.74	−0.53	30 min (−33°C)
3	6094	−33– 32	−10.00	−0.55	30 min (−33°C)
4	6137	30–130	–	–	
5	6147	−33– 32	−10.63	−0.56	30 min (−33°C)
6	6148	−33– 32	−10.63	−0.56	30 min (−33°C)
7	6153	−33– 32	−9.28	−0.39	2.5 h (−33°C)
8	6157	−33– 32	−10.49	−0.58	30 min (−33°C)
9	6161	30–180	–	–	
10	6202	−33– 32	−9.20	−0.45	30 min (−33°C)
11	6203	−33– 32	−10.00	−0.62	30 min (−33°C)

Statistical calculations: mean ΔH (30 min) = −0.540 cal g^{-1} and mean ΔH (2.5 h) = −0.39 cal g^{-1}; standard deviation ΔH (30 min) = −0.0560 cal g^{-1}; and *t*-test value (comparison of above data) = 2.5256.

this point, the sample was again scanned twice from −33°C to 32°C in a similar manner to that previously described.

Details of the thermogram parameters used in the DSC measurements and the results obtained are given in Tables 1–4. Peak minima and ΔH values were measured using a TADS (thermal analysis data station).

TABLE 3

Thermogram parameters and pertinent results for C-8843 (Michigan). Sample weight, 17.60 mg

Run	DSC no.	Temperature range (°C)	Peak minimum (°C)	ΔH (cal g^{-1})	Notes
1	6082	−33– 32	−8.81	−0.71	30 min (−33°C)
2	6083	−33– 32	−8.81	−0.71	30 min (−33°C)
3	6084	−33– 32	−9.47	−0.78	30 min (−33°C)
4	6131	30–130	–	–	
5	6133	−33– 32	−9.55	−0.81	30 min (−33°C)
6	6134	−33– 32	−9.95	−0.80	30 min (−33°C)
7	6135	−33– 32	−9.21	−0.67	2.5 h (−33°C)
8	6142	−33– 32	−8.96	−0.73	30 min (−33°C)
9	6143	30–180	–	–	
10	6144	−33– 32	−9.40	−0.80	30 min (−33°C)
11	6145	−33– 32	−9.80	0.80	30 min (−33°C)

Statistical calculations: mean ΔH (30 min) = −0.7675 cal g^{-1} and mean ΔH (2.5 h) = −0.67 cal g^{-1}; standard deviation ΔH (30 min) = −0.0433 cal g^{-1}; and *t*-test value (comparison of above data) = 2.1123.

TABLE 4

Thermogram parameters and pertinent results for C-8566 (Utah). Sample weight, 20.70 mg

Run	DSC no.	Temperature range (°C)	Peak minimum (°C)	ΔH (cal g^{-1})	Notes
1	6101	−33– 32	−11.87	−0.43	30 min (−33°C)
2	6102	−33– 32	−11.60	−0.40	30 min (−33°C)
3	6103	−33– 32	−11.07	−0.44	30 min (−33°C)
4	6137	30–130	–	–	
5	6209	−33– 32	−12.05	−0.41	30 min (−33°C)
6	6210	−33– 32	−11.74	−0.39	30 min (−33°C)
7	6211	−33– 32	−6.81	−0.24	2.5 h (−33°C)
8	6242	−33– 32	−11.47	−0.43	30 min (−33°C)
9	6244	30–180	–	–	
10	6245	−33– 32	−11.47	−0.43	30 min (−33°C)
11	6246	−33– 32	−12.10	−0.47	30 min (−33°C)

Statistical calculations: mean ΔH (30 min) = −0.425 cal g^{-1} and mean ΔH (2.5 h) = −0.24 cal g^{-1}; standard deviation ΔH (30 min) = −0.0250 cal g^{-1}; and t-test value (comparison of above data) = 6.978.

RESULTS AND DISCUSSION

A typical thermogram is shown in Fig. 1. All of the tested asphalts showed one broad peak in the DSC curve. In all the curves this broad exothermic peak occurs between −19°C and 0°C. There is an exothermic transformation at approximately −10°C. Thermograms of samples kept at −33°C for 30 min and 2.5 h, obtained with a scanning rate of 10°C min^{-1}, are shown in Fig. 2. The most obvious difference noted between two concurrent runs of the same sample is the lowering of the ΔH values when the sample is kept at −33°C for 2.5 h as compared with the same sample kept in the DSC for 30 min at −33°C and scanned at the same rate. The exothermic heat contents ($-\Delta H$) of the asphalts decreased drastically from −0.445 to −0.32 (C-8533, Ohio), −0.540 to −0.39 (C-8525, Ohio), −0.767 to −0.67 (C-8843, Michigan) and −0.425 to −0.24 (C-8566, Utah) cal g^{-1}. The t-test values [9–11] for comparisons of the above are 4.4169 (C-8533, Ohio), 2.5256 (C-8525, Ohio), 2.1123 (C-8843, Michigan) and 6.978 (C-8566, Utah) (statistically, t-tests are used to determine significant differences in the mean values taking into account the number of items and also the variances of their departures from the derived mean). The critical t-value for seven degrees of freedom, found from a t-table [10,11], was $t_{0.050} = 1.895$.

The samples were heated from 30°C to 130°C and 180°C (introduction of thermal history) and run in the manner described in Tables 1–4. The position of the exothermic peak and the heat content does not appear to be markedly dependent on the thermal history of the sample, the ΔH values

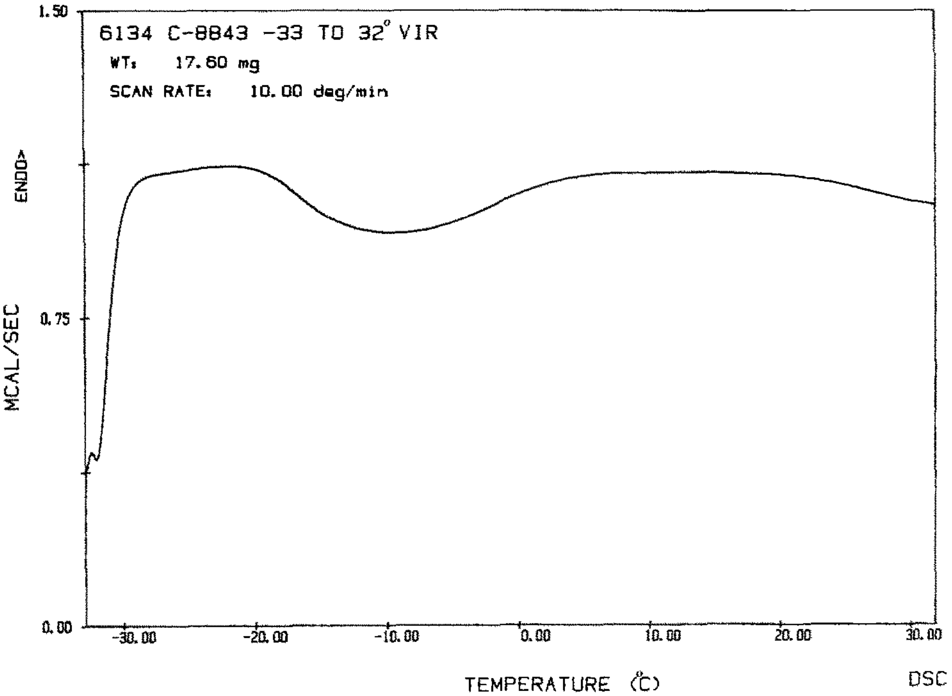

Fig. 1. A typical thermogram of sample C-8843 obtained with a scan rate of 10 °C $\min^{-1}$.

being almost the same. Prime et al. [12] have reported that the crystallinity decreases with time. In our experiment, the ΔH value decreased when the sample was kept in the DSC at -33 °C for 2.5 hr. This means that some of the asphaltic material was crystallised during the 2.5 h at -33 °C, the rest of the material crystallising when it was heated from -33 °C to 32 °C. Much less crystallisation occurs when the sample is kept in the DSC for only 30 min prior to heating from -33 °C to 32 °C. This indicates that the peak size is dependent on the prior cooling time. Rodriques [13] has mentioned that if a polymer is quenched rapidly to a temperature below the T_g a metastable glass may be obtained. Warming the sample above T_g can increase crystallinity, making the sample more viscous. The maximum rate of crystallisation occurs at a temperature between T_m (the melting temperature) and T_g.

Mack [14] considered asphalts as sols of asphaltenes in a mixture of asphaltic resins and oily constituents (petrolenes or maltenes). It is generally assumed that asphalt is a system in which the solubility of the dispersed phase (asphaltenes) in the oily continuous phase (petrolenes) is influenced by temperature. At high temperature the solubility is increased, except for free carbon if it is present. As the temperature is progressively lowered, the two phases become more distinct and the colloidal properties of the system become more exaggerated. However, even at low temperatures the system is

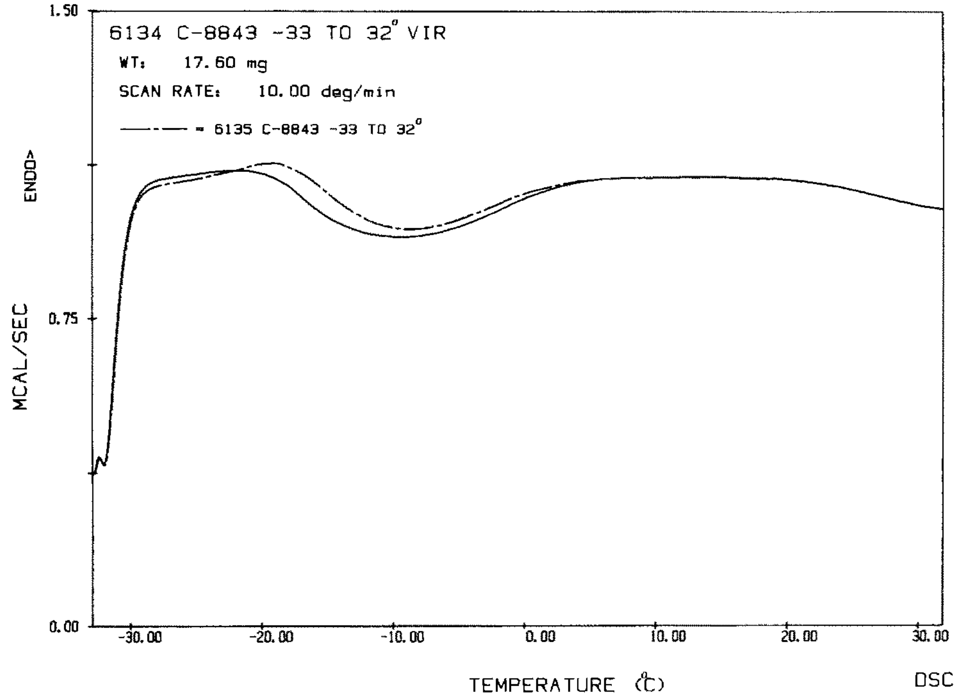

Fig. 2. Thermogram of sample (C-8843) kept at -33 °C for 30 min (———) and for 2.5 h (— - —), obtained with a scan rate of 10 °C min^{-1}.

usually stable, the asphaltenes remaining dispersed owing to the protective action of the asphaltic resins. The transition from the true liquid state to anything approximating the solid state means a change from purely viscous properties to definitely plastic behaviour. Saal [15] has shown that as the temperature is lowered, the asphaltenes gradually separate from the true solution with the petrolenes to give rise to a stable system whose colloidal properties become more pronounced as the temperature decreases.

Gel-type asphalts are formed at low temperatures. A gel is a semi-rigid mass of a lyophilic (solvent attracting) sol in which all the dispersion medium has been absorbed by the sol particles. A gel-type asphalt contains insufficient polar aromatic fractions to fully disperse the micelles. Gel-type asphalt cements exhibit non-Newtonian flow and thixotropy, which are typical of colloidal systems [16,17]. On the other hand sol-type asphalt cement contains sufficient polar aromatic compounds to fully disperse the micelles. The asphaltenes in a sol-type asphalt cement are fully peptized and able to move freely through the remaining maltene fraction. The enthalpy of the exothermic peaks of the asphalts under a variety of controlled conditions is shown in Tables 1–4. The treatments described above indicate that a gel is present at low temperatures and that a sol is present at higher temperatures.

CONCLUSION

Differential scanning calorimetry appears to be an important tool in the investigation of asphalts, both to characterise them and to observe changes at low temperatures with time. It is also a promising tool for the determination of exothermic heat contents of asphaltic material. Our results show that the enthalpy of crystallisation is dependent on the duration of prior cooling. These DSC results have been useful in the investigation into how the asphaltic material changes with time (sol $\rightleftharpoons$ gel) during temperature changes from room temperature to low temperature.

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