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Interpretation of Thermal Effects in Differential Scanning Calorimetry Study of Asphalts

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Abstract—The structural and thermal properties of petroleum asphalt and its components have been analyzed using temperature-modulated differential scanning calorimetry (DSC). This technique makes it possible to distinguish processes, such as "order–disorder" and glass transition, ensuring identification of structural-phase transitions that are undetectable or overlapping on conventional DSC curves. The analysis of thermal effects for macro- and microcrystalline paraffins; mono-, bi-, and polycyclic aromatic hydrocarbons; asphaltenes; and benzene and alcohol–benzene resins allows identifying and interpreting effects on DSC thermograms of test asphalts.

Keywords: asphalt, saturated and aromatic hydrocarbons, resins and asphaltenes, temperature-modulated DSC

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The consumer and technological properties of petroleum asphalt are determined by its rheology due to structural-phase transformations and temperature–time conditions of microstructure formation [1–3]. The latter depend on the concentrations and physicochemical features of the composition and structure of asphalt components [4–6]. Petroleum asphalt is a mixture of hydrocarbons (HC), the composition of which (in the simplest form) is usually defined in terms of chromatographic analysis of the saturates, aromatics, resins, and asphaltenes (SARA) fractions [4, 7]. The asphalt microstructure is formed during the course of thermokinetic relaxation processes of glass transition and thermodynamic processes of crystallization [2, 5, 6, 8].

One of the techniques for studying the thermal behavior of asphalts and their components is differential scanning calorimetry (DSC) [9–11]. The identification of thermal effects on DSC curves determines the accuracy of quantitative evaluation of processes responsible for these effects. This problem does not always have a unique solution for asphalt, since the effects can overlap. The use of temperature-modulated DSC (TM-DSC) eliminates this problem [12–14]. The method allows to decompose the signal of the total heat flow (equivalent to that of conventional DSC) into components [15]. The reversing component is a mapping of structural–thermal transformations reaching equilibrium during the thermal-signal modulation period. The heat flow component due to nonequilibrium processes is formed as the difference between the signals of total and reversing heat flows, causing the formation of a nonreversing curve. This approach ensures the separation and independent evaluation of the glass transition and crystallization (melting) processes, allowing their identification.

The capabilities of the TM-DSC technique are illustrated in Fig. 1, which shows how a total heat flow decomposes into the reversing and nonreversing components for the asphalt under study (see Experimental). It is clearly seen that the reversing component determines the general nature of the change in the heat flow, and the nonreversing component details the temperature profile of the signal. The DSC curves of asphalts usually display identifiable glass transition of amorphous fractions and a melting endotherm of crystalline fractions [9–11]. In our case, the identification of thermal effects on the total heat-flow curve (construction of the corresponding baselines) does not have a unique solution. This difficulty is eliminated by a joint analysis of the curves of reversing and nonreversing heat flows (Figs. 1b, 1c).

A clear nonalternative identification of thermal effects on DSC curves is a necessary, but insufficient condition for their interpretation. Correct interpretation of DSC effects requires a comprehensive approach and knowledge of the structural and thermal behavior of asphalt components [2]. Studies on this