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USE OF LUMINESCENCE FOR THERMAL ANALYSIS

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Intensive radiothermoluminescence (RTL) has been observed /1/ in gamma-irradiated (77 K) mixtures of hydrocarbons with chlorine during warm up of these mixtures. The narrow peak of RTL must have resulted from exothermic post-irradiational chemical reaction of hydrocarbons chlorination followed by recombination processes of trapped electrons.

In principle, the endo- and exothermal transitions in irradiated system could be determined by using the RTL of small glass particles which were previously introduced into irradiated system /2/. The use of RTL for study of phase transitions presents an advantage over DTA methods (low inertia, small (1 mg) samples, high (10 K/min) rates of heating). The limited use of RTL in thermal analysis is accounted for by the necessity have sample irradiated at low temperature (usually at 77 K) prior to analysis. Moreover the RTL method is impossible to use in frequent thermal analysis when multiple heating or cooling of sample is needed.

This paper suggests a simple technique registration of phase transitions based on measurements of relative intensity J_o of chemiluminescent additives, made in the process of warming or cooling the sample. In absence of phase transitions and as the temperature rises, the J_o goes up by exponential equation. If we have endothermal transition in the system the temperature of the sample remains constant and the curve of J_o dependence on temperature will have a gap, the so-called endo-peak. In the presence of exothermal transition the sample gets temporary overheated, which leads to appearence of exo-peak in the curve.

This paper presents evidence obtained in our laboratory by the use of the chemiluminescence for study of phase transitions in glasses of aqueous NaOH solutions at low temperature. The glass sample (5 mg) produced by rapid cooling (10 K/s) of 10 M NaOH containing 10^{-3} M of luminole (5-amino-2,3-dihydro-1,4-phtalazindione), 10^{-4} M of $K_3Fe(CN)_6$ and 10^{-4} M of O_2, is placed in luminograph and heated at 1.5 – 5 K/min rate. The luminescence is registered by using photomultiplier FEU-39 (sensitivity in blue range - 10^3 photon/s, ratio of signal to noise about 1.0). Two curves were obtained simultaneously: one shows the changes of J_o as a time function and the other - calorimetric curve of the same sample.

The sharp increasing and subsequent drop of J_o near 210 K coincide with exothermal peak (Q = 25 cal/g) in calorimetric curve and is a result of the crystallization of overcooled liquid. Near 235 K both the second peak of luminescence and the second exothermal peak of less intensity in calorimetric curve were observed. The appearence of a gap at the curve of J_o dependence on temperature near 250 K coincides with the appearance of endothermal peak at calorimetric curve.

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The cooling of the sample (15 mg, rate of cooling - 3 K/min) from 300 to 250 K results in a monotonic decrease of J_o. But at 250 and 235 K two bursts of luminescence appear which confirm the two-stage crystallization process. At lower temperatures (210 K) J_o drops practically to zero value.

Thus the use of luminescence for thermal analysis makes it possible to study phase transitions adn obtain important characteristics of several exo- and endothermal processes including that of hardening high-temperature phases.

This method can be widely used with standard equipment usual for luminescence analysis. It presents certain advantage over the wellknown calorimetric methods (low inertia, small samples, high sensitivity, etc.) and can surely find an application in thermal analysis.

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