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THERMAL DEKRYPTONATION CHARACTERIZATION OF SOME SOLID MATERIALS

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ABSTRACT

A simple device for dekryptonation thermal analysis /DkTA/ using a flow-type GM detector is described and results on DkTA of three inorganic /$CuSO_4.5H_2O$; $ZnSO_4.7H_2O$; $CaCO_3$/ and one organic /polyvinylchloride/ materials are presented.

INTRODUCTION

Dekryptonation analysis /radiometric emanation analysis using radioactive Kryptonates/ have found important applications in the field of physical chemistry, chemical physics, analytical chemistry and technology. The recently increased interest in these methods is due to their high versatility and sensitivity in comparison with other chemical and physical methods [1].

Dekryptonation thermal analysis /DkTA/ is based on incorporation of ^{85}Kr atoms into a solid sample and measurement of the ^{85}Kr released during isothermal heating of the Kryptonate.

The most common techniques of the incorporation of ^{85}Kr atoms into solid materials are based on

1/ the diffusion of ^{85}Kr atoms into solid under high pressure,
2/ the inclusion of ^{85}Kr atoms by sample during its preparation or phase transitions in the inert gas atmosphere, and
3/ the bombardment of the sample surface by accelerated ^{85}Kr ions.

In this paper a simple device for dekryptonation thermal analysis using a flow-type GM detector is described and results on DkTA of three inorganic and one organic materials are presented.

EXPERIMENTAL

The studied solid materials were: $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$, $CaCO_3$ and polyvinylchloride.

Incorporation of ^{85}Kr into investigated materials was accomplished by the microdiffusion technique [2] in a thick-wall capillary.

The dekryptonation thermal analysis was carried out with a sim-

ple device using a flow-type GM tube [3]. The diagram of the device is in Fig.1. The carrier gas which is also the counting gas of the GM-tube flows from a pressure tank /1/ through a reduction valve /2/ and manometer to the dekryptomatipn chamber /3/ containing the kryptonated material. The released ^{85}Kr is carried from the dekryptonation chamber by carrier gas to a flow-type GM-tube /4/ and then to a flow-meter /5/. The plotter /7/ joined to the rate-meter /6/ records the radioactivity detected by a GM-tube. The flow-type GM-tube consists of a brass tube /negative electrode/ in the middle of which is a positive electrode wire. The carrier gas had the same composition as the counting gas for the GM-tube. The choosing of this gas is limited because for this purpose can be used only a gas resistant to higher temperature. Our experiments showed that more suitable gas is a mixture of argon and ethanol mixed at 0 °C. The flow-type GM-tube is six times more efficient than the end-window one.

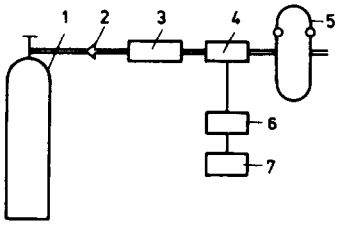

Fig.1
The diagram of device for DkTA /1 - pressure tank, 2 - reduction valve, 3 - dekryptonation chamber, 4 - flow-type GM tube, 5 - flow-meter, 6 - rate-meter, 7 - plotter/

RESULTS

In Figs 2 - 4 some examples of DkTA curves are given.

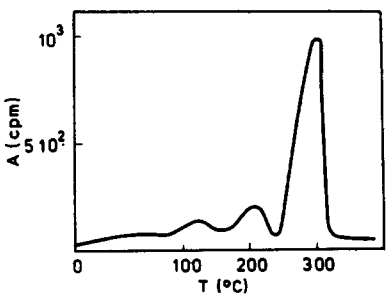

Fig.2
DkTA curve of $CuSO_4 \cdot 5\ H_2O$

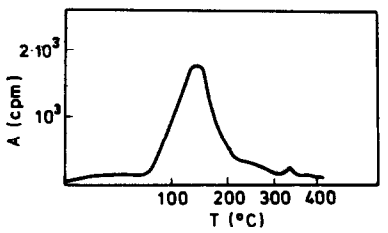

Fig.3
DkTA curve of $ZnSO_4 \cdot 7\ H_2O$

Fig.2 represents DkTA curve for $CuSO_4 \cdot 5H_2O$, Fig.3 for $ZnSO_4 \cdot 7H_2O$ and Fig.4 for $CaCO_3$. On curves in Figs 2 and 3 peaks correspond to the loss of water. In Fig.4 the greatest peak represents the total decomposition of the sample.

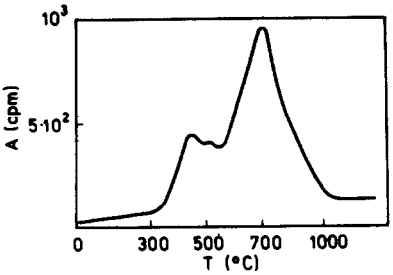

Fig.4
DkTA curve of $CaCO_3$

Dekryptonation thermal analysis was used for the determination of the glass transition temperature of polyvinylchloride [4].

At sufficiently low temperatures solid polymers exist in a glassy state and with the altering temperature their properties vary only slightly. When a certain temperature is reached /glass transition temperature, T_g/, characteristic of each polymer of certain molecular weight, the polymers become elastic.

Dekryptonation thermal analysis of eight fractions of PVC has been carried out /m.w. $1x10^4$ - $2.2x10^5$/. As a demonstrative example Fig.5 shows this curve obtained from the sample having a m.w. of 88.000 recorded 24 h after kryptonation. The activity

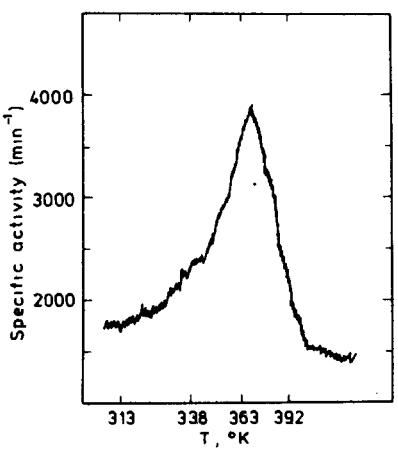

Fig.5
DkTA run 24 h after the kryptonation

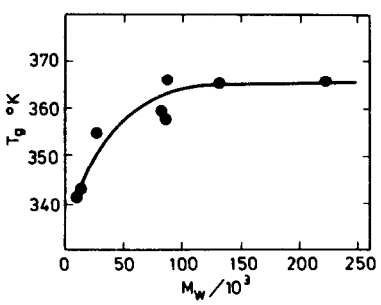

Fig.6
The dependence of T_g of PVC upon its relative molecular weight

of the carrier gas produced during the measurement is the result of the releasing of ^{85}Kr from sites of which the energetic state /the possibility of performing rotation and vibration movements, above all/ is given by the value of absolute intrinsic temperature. The position of such emanation peaks, or their maxima, on the axis of temperature is well reproducible under constant gas-dynamic and thermal conditions of DkTA.

The glass transition temperature values /T_g/ against the relative molecular weights are given in Fig.6. By comparing the obtained T_g with those given in literature for PVC, a very good agreement was found.

REFERENCES

1 V. Balek, J. Tölgyessy, Emanation Thermal Analysis and other Radiometric Emanation Methods, Elsevier, Amsterdam 1984
2 V. Jesenák, Š. Varga, J.Tölgyessy, Atompraxis, 14 /1968/ 204
3 P. Lukáč, Radiochem.Radioanal.Lett., 28 /1977/ 323
4 P. Lukáč, L. Lapčík, Radiochem.Radioanal.Lett., 29 /1977/ 227