Thermochimica Acta, 22 (1978) 157–162
© Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

EMANATION THERMAL ANALYSIS FOR CHARACTERIZING DIFFUSION PROPERTIES OF Ba-PHTHALATE, -ISOPHTHALATE AND -TEREPHTHALATE

V. BALEK
Nuclear Research Institute, 250 68 Řež (Czechoslovakia)

J. KROUPA
Research Institute of Organic Syntheses, 530 00 Pardubice (Czechoslovakia)

(Received 31 January 1977)

ABSTRACT

Emanation thermal analysis (ETA) is used for characterizing Ba-salts of phthalic, isophthalic and terephthalic acids. It is shown that the emanation thermal characteristics measured in the temperature range between 298 and 373 K are suitable for estimating diffusion properties of studied organic solids. The ETA results are supplied by TG/DTG and DTA curves and surface area measurements. An apparatus for determining emanation-thermal characteristics is proposed.

INTRODUCTION

Many investigators of organic solids and polymers are interested in the study of their diffusion properties. One of the methods that may be utilized for determining these properties is the emanation thermal analysis (ETA), enabling their estimation on the basis of inert gas diffusion[1, 2].

This article presents the emanation-thermal characteristics of barium salts of phthalic, isophthalic and terephthalic acids in the temperature interval between 298 and 373 K. In this series of Ba-salts of dicarboxylic acids, the effect of positional isomerism on the diffusion properties of organic solids is studied.

EXPERIMENTAL

Sample preparation

Barium salts of organic acids used for the ETA measurements were prepared by the following way: The corresponding amounts of organic acids were dissolved in an equivalent volume of 6-n KOH solution. 0.5 ml of aqueous solution containing ^{228}Th and ^{224}Ra radionuclides was added to the formed potassium salt of the organic acid soluble in water. Barium salt of the acid was then prepared by means of

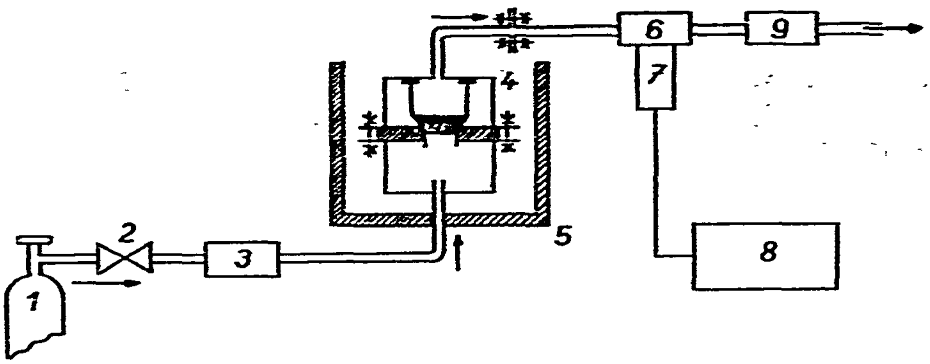


Fig. 1. Apparatus for measurement of emanation thermal characteristics of solids. 1 = gas supply; 2 = flow stabilizer; 3 = flow meter; 4 = throw-flow sample holder; 5 = thermostat; 6 = measuring chamber; 7 = scintillation detector; 8 = counts-meter; 9 = flow meter.

adding an equivalent amount of aqueous solution of $BaCl_2$ to the potassium salt and the solubility of the formed salt was lowered by adding 10 ml of ethylalcohol. The crystalline precipitate was separated by filtration on porous glass filter, washed with water, alcohol, and ether.

This method of labelling leads to a homogeneous distribution of the radionuclides in barium salts of organic compounds. Samples of salts not labelled by radioactive nuclide and prepared for additional determination of surface area and for DTA and TG were prepared in an analogical way.

Apparatus

An equipment schematically shown in Fig. 1 was designed for the ETA measurement of the prepared crystalline precipitates of barium salts of organic acids. The prepared sample on a porous glass filter is placed in a through-flow holder (4) placed into the thermostat (5). Pre-dried nitrogen from storage vessel (1) at a flow-rate of 100 ml min^{-1}, stabilized by a flow stabilizer (2) and measured by flowmeters (3) and (9) is sucked through the sample. The stream of nitrogen carries the atoms of the radioactive gas resulting from ^{228}Th and ^{224}Ra decay into the chamber (6) of the scintillation detector (7). The amount of released radon is determined by a counts-meter (8).

100–400 mg of the sample were used for single determinations. The temperature in the thermostat was stepwise elevated by 15 K h^{-1} in the temperature interval between 298 and 373 K. The amounts of ^{228}Th and ^{224}Ra isotopes were determined by measuring gamma-activity of these samples. These determinations were carried out on the porous glass filter by a G.M.-tube conserving the same geometry. From the obtained values of the alpha- and beta-activities of the sample and a standard (Ba-palmitate), the values of the emanating power were determined according to the relation:

$$E\,\% = \frac{(A_\alpha)_{\text{sample}}}{(A_\gamma)_{\text{sample}}} \cdot \frac{(A_\gamma)_{\text{stand}}}{(A_\alpha)_{\text{stand}}} \cdot \frac{100}{E_{\text{stand}}} \tag{1}$$

where $E_{\text{stand}} = 98\,\%$.

Before measuring, the prepared samples were stored in a dessicator for 30 days in order to reach radioactive equilibrium.

Surface area was determined by argon sorption at the boiling point of liquid nitrogen according to Nelsen and Eggertsen[3]. The additional DTA and TG were accomplished on Mettler thermoanalyzer at linear heating rate of 8 K min^{-1} in air sucked through the sample.

Results and discussion

Emanation-thermal characteristics of Ba salts of dicarboxylic acids — phthalic, isophthalic, and terephthalic — are presented in Table 1 and Fig. 2.

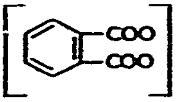
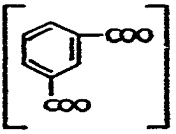
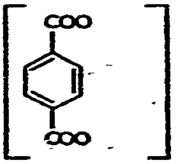
The values of emanating power corresponding to the temperature of 298 K, surface area S, and the ratio E/S characterizing the diffusional properties of a compound at the given temperature are given in Table 1.

The emanating power of crystallites of solids may be expressed as

$$E = \text{const.} + (D/\lambda)^{1/2} \cdot \rho \cdot S \tag{2}$$

TABLE 1

CHARACTERISTICS OF BARIUM-PHTHALATE ISOMERS

Sample No.	*Barium salt*	*Formula*	*Emanation power E_{298} (%)*	*Surface area S ($m^2\,g^{-1}$)*	*$\frac{E_{298}}{S}$ (%)*
1	phthalate	 Ba	11.11	3.6	3.1
2	isophthalate	 Ba	11.43	1.0	11.4
3	terephthalate	 Ba	9.87	8.1	1.2

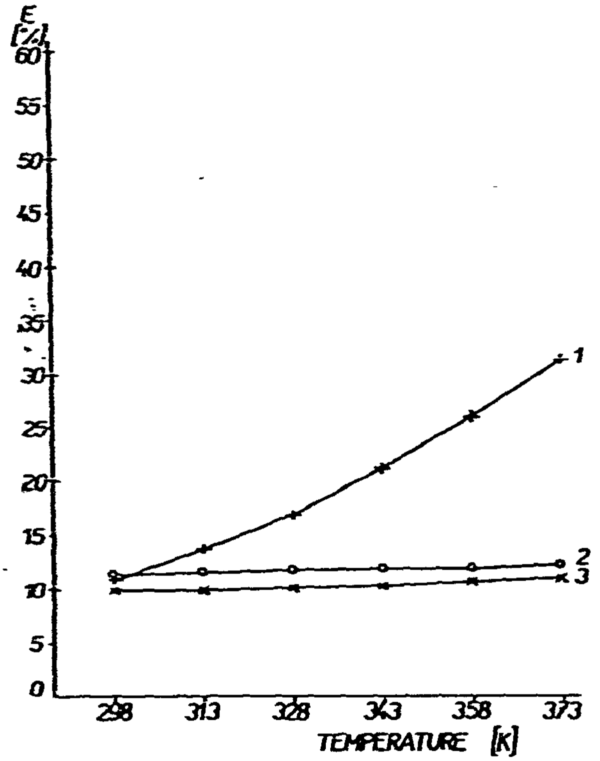


Fig. 2. Emanation-thermal characteristics of barium phthalate (curve 1), isophthalate (curve 2) and terephthalate (curve 3) in the temperature range between 298 and 373 K.

where E is the emanating power,

const. includes the range of recoil atoms in the organic compound,

D is the diffusion coefficient of radon in the substance,

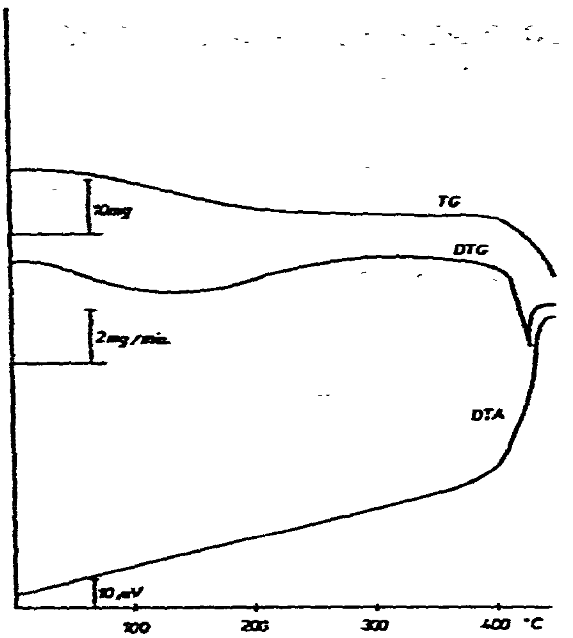
λ is the decay constant of radon,

ρ is the density, and

S is surface area.

The ratio E/S may, therefore, be considered as the characteristic of the diffusional properties of the substances. As evident from Table 1, the E/S values of Ba-salts of organic acids decrease in the following sequence: isophthalate, phthalate, and terephthalate. The values of the diffusion coefficient of radon in the studied substances decrease in the same sequence.

The course of the thermal dependence of emanating power of these salts in the temperature interval between 298 and 373 K is presented in Fig. 2. Whereas the emanating power of Ba-phthalate (curve 1) increases exponentially with increasing temperature, it remains practically unchanged with isophthalate (curve 2) and terephthalate (curve 3) at the identical temperature increase rate. The increase in emanating power of Ba-phthalate may be explained as a result of both the temperature increase of the diffusion coefficient of this substance between 298 and 327 K (the activation enthalpy ΔH of ^{220}Rn-diffusion equals 20.1 kJ mol^{-1}), and the partial release of



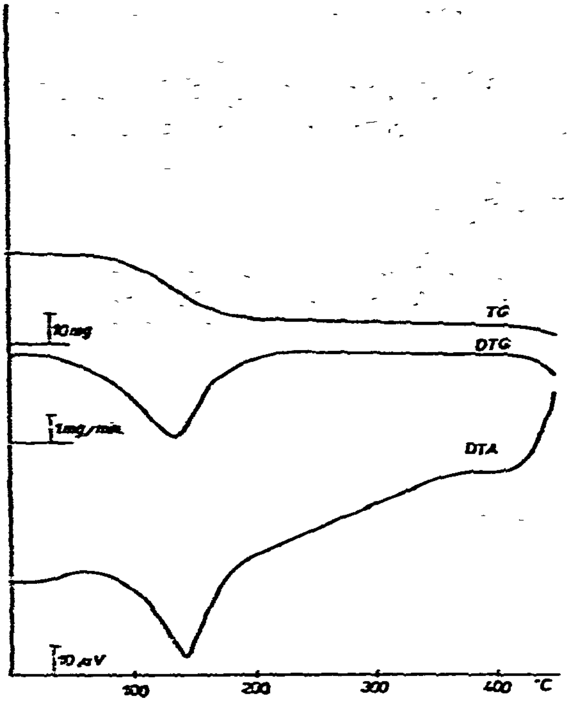


Fig. 3. TG/DTG and DTA curves of barium-phthalate.

Fig. 4. TG/DTG and DTA curves of barium isophthalate.

water contained in the sample (above 327 K). The decrease in the mass of the sample heated at linearly increasing temperature (see TG curve in Fig. 3) indicated that Ba-phthalate contained 1.5 molecules of H_2O. It is interesting that no increase in emanating power at increasing temperature, was observed with Ba-isophthalate (containing up to 2.5 molecules of H_2O), even though a partial dehydration may proceed in this range of temperatures (according to the TG/DTG and DTA results in Fig. 4).

Ba-terephthalate was prepared as an anhydrous substance. No visible effects are evident on DTA and TG/DTG curves in the temperature interval between 273 and 773 K (the curves are not presented).

CONCLUSIONS

Emanation-thermal analysis has been proved to be suitable for estimating diffusional properties of Ba-phthalate, -isophthalate and -terephthalate.

Diffusion characteristics of Ba-phthalate, -isophthalate and -terephthalate determined in the range between 298 and 373 K indicate that positional isomerism of these salts markedly affects their diffusion properties in the solid state. The proposed apparatus enables to perform the determination of emanation-thermal characteristics with minimum handling of the radioactive substances.

ACKNOWLEDGMENT

The authors wish to acknowledge Mr. M. Prachař, Nuclear Research Institute, Řež for the technical assistance in evaluating results.

REFERENCES

1 V. Balek, *Anal. Chem.*, 42 (1970) 16A.
2 V. Balek, *Thermochim. Acta*, 22 (1978) 1.
3 F. M. Nelsen and F. T. G. Eggertsen, *Anal. Chem.*, 30 (1958) 1387.