

RADIOCHEMICAL METHOD BASED ON THE BACKSCATTERED β -RAYS FOR THE STUDY OF NUCLEATION PROCESS

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This paper deals with a study on the complex process of nucleation of crystals by using a radiochemical method based on the backscattering of β -rays. From experimental data were calculated the values of the global rate constant of the nucleation process and the starting time of crystallization germs appearance, respectively, in concentrated water solutions. Hence the nucleation of two double sulfates and five complex compounds with oxalate anions was studied.

INTRODUCTION

There are known some of monographs¹⁻³ in which there are described the complex processes of appearance and growth of crystals either in water solutions or from foundry, in different experimental solutions. Crystals may be formed by slow evaporation of solvent, by changing solvent composition or slow variation of the given medium temperature, by solidification of a molten mass with a constant gradient of temperature etc.

Kinetic study of crystal growth can be achieved by using marked ions, which migrate in concentrated solutions to crystallisation germs or diffuse by such solid incipient conglomerates^{4,5} under a gradient of mass, concentration or temperature, or by means of backscattered β -rays by solid surface, etc.

EXPERIMENTAL

Firstly there were prepared two double sulfates: $KAl(SO_4)_2 \cdot 12H_2O$ and $NH_4Al(SO_4)_2 \cdot 12H_2O$ and also five complex compounds with oxalate anions: $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$; $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$; $Na_3[Cr(C_2O_4)_3] \cdot 3H_2O$; $(NH_4)_3[Cr(C_2O_4)_3] \cdot 3H_2O$ and $(NH_4)_3[Tl(C_2O_4)_3] \cdot 3H_2O$, in solid states, following the literature indications.^{6,8} Confirmation of the structures of new prepared substances structure were established by X – rays diffraction.

From the synthesized solid compounds there were prepared saturated water solutions. Afterwards from these solutions 15 mL were taken out and were put in cylindrical glass vials ($\varnothing = 5$ cm) with a capacity of 50 mL. In thermostatic conditions, at a temperature of 21.5°C it was started the slow evaporation of the solvent. At certain intervals of time there were measured the backscattered β -rays radioactivity, under the same conditions of geometry, using a device known in radioanalytical chemistry.⁹

The principle of the used method is suggested in Fig. 1

While evaporating the solvent from the crystallization device with saturated solution (1), the activity of backscattered β -rays increases up to a maximum (2). To that point there appear the first crystallization germs in a colloidal viscous mass; that means the starting of nucleation process. Then, by going on with water evaporation (3), the measured activity will decrease reaching a minimum, where the crystal is already geometrically formed (4). Here β -rays, after touching and partially penetrating the surface of the crystal, gradually lost energy and hence will not be able to return to detectors by backscattering. But, if the crystal is hygroscopic the process can be repeated by the track: dilution \rightarrow appearing of crystallization germs \rightarrow crystal growth....

RESULTS AND DISCUSSION

The experimental results are presented in Figures 2a and 3a.

There is to mention that similar results were reported by other authors¹⁰⁻¹⁴ who studied the variation in time of the formation rate of solid phase or the crystallization germs number, etc.

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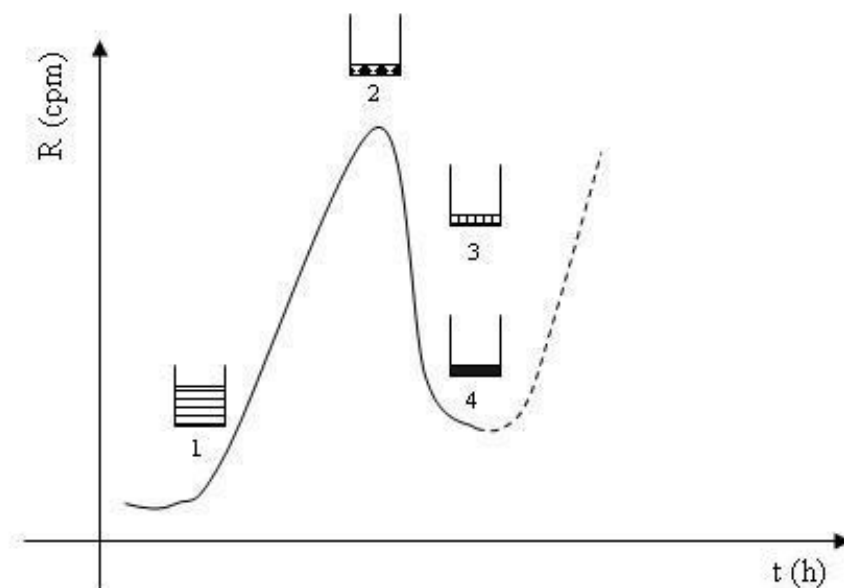


Fig. 1 – Graphical explanation of the studied crystal appearance and growth.

From a kinetic point of view, the increase of the concentration of saturated solution by solvent evaporation can be expressed by equation:

$$\frac{dC}{dt} = k(C_s - C) \quad (1)$$

Here C_s is the concentration when the first crystallization germs appear, while C represents the concentration at a given time t .

By integration, it is obtained:

$$\ln \frac{C_s}{C_s - C} = k.t, \text{ or } \ln \frac{R_s}{R_s - R} = k.t \quad (2)$$

taking into account that the activity of backscattered β -rays (R) is proportional to the concentration of solution at a given time.

If plotting the last relation (2) in coordinates of $\ln R = f(t)$ considering only the values of backscattered β -rays radioactivity up to reaching the maximum point of each curve from Figs. 2a and 3a, corresponding to the starting time of crystallization germs, straight lines result as observed in Figs. 2b and 3b. From the slopes of these straight lines the global rate constant of the nucleation process can be determined.

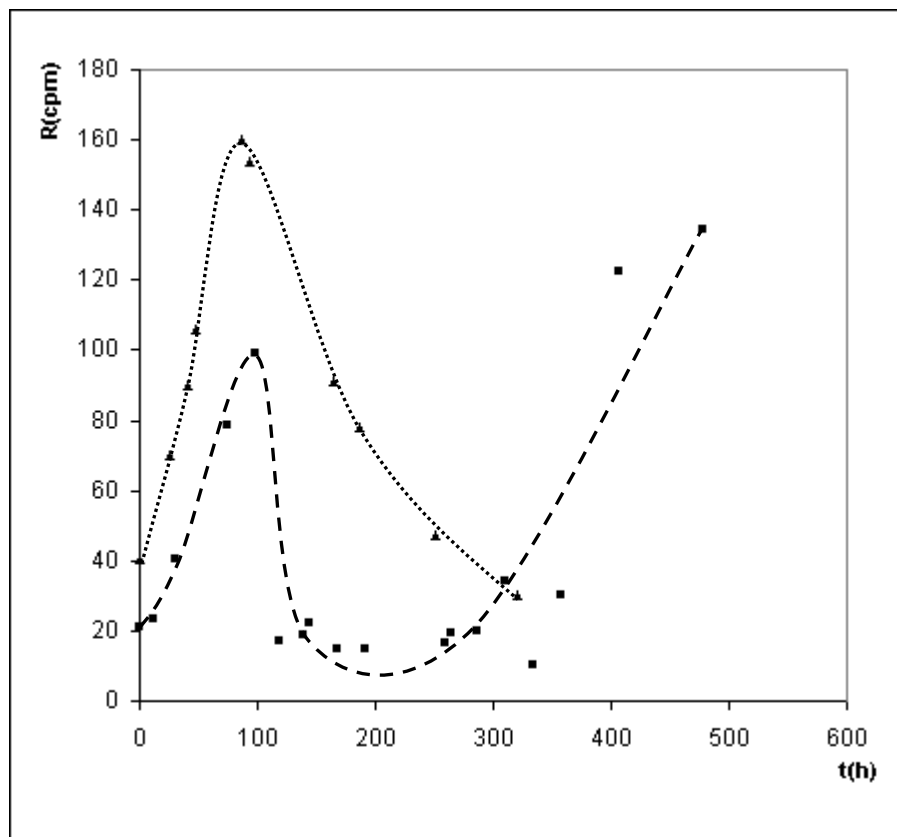
Kinetic data obtained are presented in Table 1.

The higher is the value of global constant rate the smaller is the starting time of nucleation process.

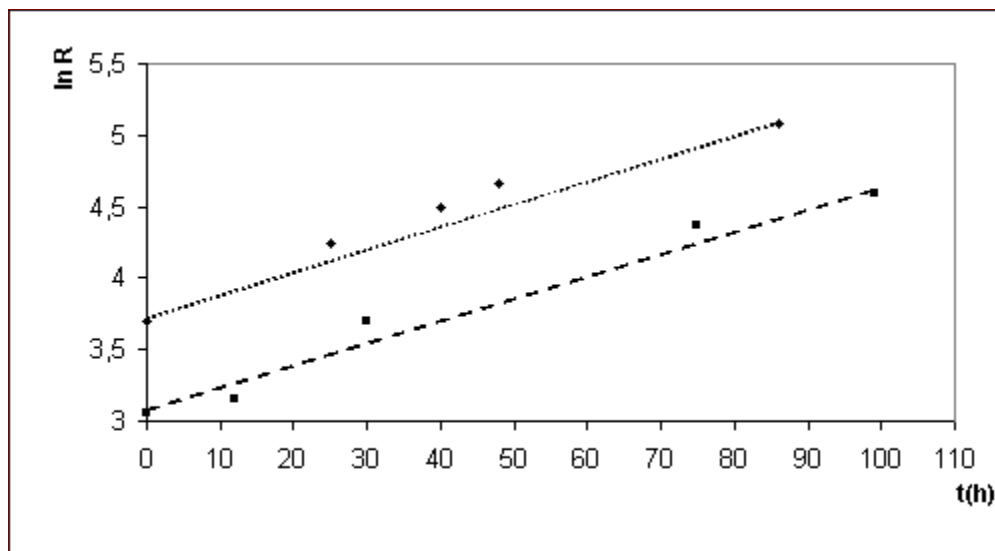
Table 1

Kinetic data characteristic for studied systems

Crystal	Global rate constant $k(\text{h}^{-1})$	Starting time $t(\text{h})$
$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	0.0159	86
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	0.0155	99
$\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	0.0041	205
$\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	0.0081	133
$\text{Na}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	0.0074	143
$(\text{NH}_4)_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	0.0123	112
$(\text{NH}_4)_3[\text{Ti}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	0.0125	105



a



b

Fig. 2 – Time dependence of the measured activity of backscattered β -rays on crystals: $KAl(SO_4)_2 \cdot 12H_2O$ (▲) and $NH_4Al(SO_4)_2 \cdot 12H_2O$ (■).

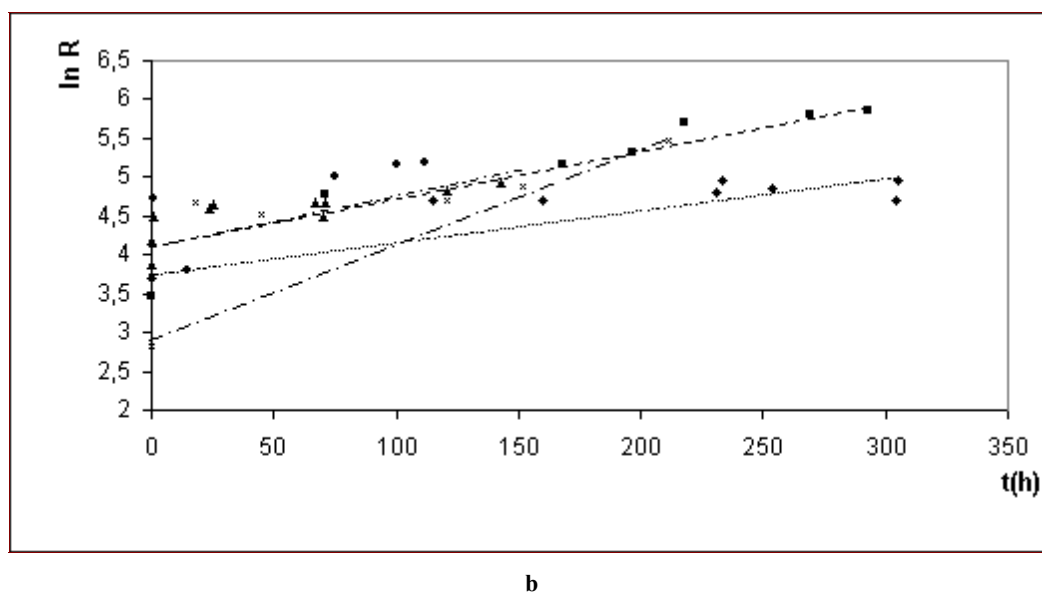
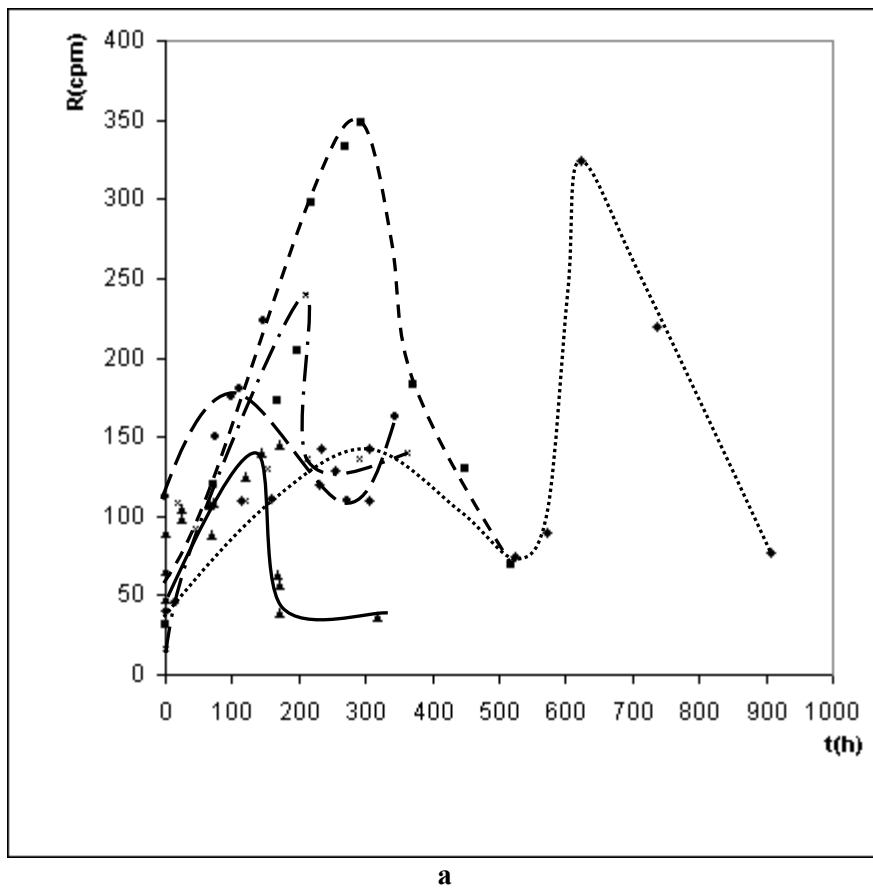


Fig. 3 – The variation in time of the radioactivity of β -rays backscattered on the crystals: $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ (\blacklozenge), $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ (\blacksquare), $Na_3[Cr(C_2O_4)_3] \cdot 3H_2O$ (\blacktriangle), $(NH_4)_3[Cr(C_2O_4)_3] \cdot 3H_2O$ (\bullet), $(NH_4)_3[Tl(C_2O_4)_3] \cdot 3H_2O$ (\times).

CONCLUSIONS

The β -rays backscattering measurements can describe kinetically the nucleation process connected with the appearance and growth of crystals.

There were suggested two kinetic parameters for characterization of nucleation process: the global rate constant and the starting time, depending on the chemical structure of each crystal.

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