Radiokinetic Investigation on the Crystallization Process from Aqueous Solutions using β-rays Backscattering

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The paper deals with a study on the nucleation and growth of the crystals from the aqueous solutions, using a radiometric method based on the β-rays backscattering. The experimental data obtained, plotted as the intensity of the β-rays backscattered vs. time, led to curves of sinusoidal shape. To the maximum point of each studied system corresponds the beginning of the nucleation process while the minimum one can be assimilated with the appearance of the solid crystal at a maximum concentration of the crystallization germs. From experimental data the global rate constants of nucleation process and the diffusion coefficients of hydrated ions through germs were established.

Keywords: backscattering, nucleation process

The complex process of the crystallization from solutions or molten salts was studied detailed by several authors [1-5]. According to these studies, the crystals turn up from the solutions through the slow evaporation of the solvent, the change of the solution' composition by adding an extra solvent, or varying the given medium as result of some slow chemical processes etc. The crystal growth from molten salts can be achieved through the slow decreasing of the temperature of the foundry, by means of spontaneous nucleation or inducted one from outside, by crystallization at a constant temperature as well as with the extraction of the crystal from that system, the slow solidification with a constant gradient of temperature of a fluid salt etc. Using such as techniques, some crystals of iron, cooper, zinc, zirconium, tin,... oxides or salts were prepared .

This paper is a continuity of some previous studies regarding the radiokinetic investigation of crystals growth in gels [6-8]. In this case, it was developed a new radiokinetic method based on the β-rays backscattering [9] in the investigation of the nucleation process and the growing of simple and double crystals (as chlorides and sulfates) of some cations from the aqueous solutions.

Experimental part

Firstly the following double salts crystals (potassium and cadmium chloride, ammonium and cooper chloride, ammonium and cobalt sulfate and potassium and nickel sulfate) were synthesized by reactions between the proper reactants, in aqueous concentrated solutions, as described in literature [10-11].

The X-rays diffraction patterns both of the reactants and to the reaction products, confirmed the appearance of the double salts.

Then, in cylindrical glass-flasks (ϕ=5 cm), equal volumes of 10 ml aqueous saturated solutions were poured, taking into account the values of the simple/ double salts solubility [12]. These samples were thermostated at 21.5±0.5 °C to achieve a slow evaporation of the solvent. At given time intervals the intensity of the backscattered β-rays was measured for each solution. As a β-rays source, the ^{90}Sr radionuclide (Λ= 5.6 x 10^{7} Bq) well screened upside with a lead shield, was used. The 5 GM-CMC beta-detectors, put in parallel-horizontal position up to radioactive source, were connected to a decimal scalar VA-M-14. The device was described in a previous study [8].

Results and discussion

The achieved experimental results were plotted as the intensity of backscattered β-rays vs. time (fig. 1-4).

The shape of these curves, the same with those found by other authors[13-16] (when were graphically drawn the evolution in time of the concentration, or number of crystallisation germs, or the rate of solid phase appearance, or the decreasing of solute concentration...), can be explained in following way :

Within the framework of crystals nucleation and growth from the aqueous solutions, the chemical species from the systems create crowds of individual particles more and more dense, through the evaporation of the solvent, covering the following sequences: hydrolysis→ polymerization → nucleation → crystal well defined geometrically.

However, the intimate process of crystallization starts in the same time, during the continuous increasing of the concentration of solved substance by the evaporation of the solvent and reaches a point which corresponds to the appearance of the first crystalline germs in the all colloidal viscous mass. This point was assimilated with the maximum of every curve shown in figures 1A-4A where the intensity of backscattered β-rays has the highest value; in this point, the crystallization germs concentration is the smallest. This given point corresponds to the beginning time of nucleation process.

Going on with the evaporation of the solvent, from this maximum point, the concentration of the crystallization germs increases, by crowding, through diffusion until they turn into the final solid crystal (as simple or double salts). As a result, the measured radioactivity of backscattered β-rays begins to decrease up to a minimum value. At this point, the crystal is considered as being formed, through the condensation of the proper germs. As a result, the β-rays lost a part of their initial energy, after they touched and penetrated in that solid surface; these rays will no more be able to succeed, by scattering, at the detection system.

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If the resulted crystal is hygroscopic, it is observed that the radioactivity of the backscattered β-rays begins to increase again, providing a second nucleation.

From kinetic point of view [16], as far as the solvent evaporates, the variation in time of the concentration of solved substance can be expressed through the relation:

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

where "C_S" is the concentration where the first crystallization germs appear and "*C*" is the concentration of the same solution at a given time interval „*t*"; „*k*" is the global rate constant of the nucleation process. „*k*" means also the diffusion rate constant of ions in the solution to new appeared crystallisation germs.

The integral form of the differential equation (1) is:

$$\ln\frac{C_s - C_0}{C_s - C} = kt \qquad (2)$$

For very diluted initial solutions, $C_0 \longrightarrow 0$, so:

$$\ln\frac{C_s}{C_s - C} = kt \quad , \text{or } \ln\frac{R_s}{R_s - R} = kt \quad ,(3)$$

taking into account that the activity of the backscattered β-rays is proportional to the concentration of solution of a given time. Plotting equation (3) as: ln R =f(t) with the experimental values corresponding to the first part of each crystallization curve (until the maximum is reached), straight lines are obtained (figs. 1B-4B). From the slopes of these lines, the values of „*k*" can be evaluated.

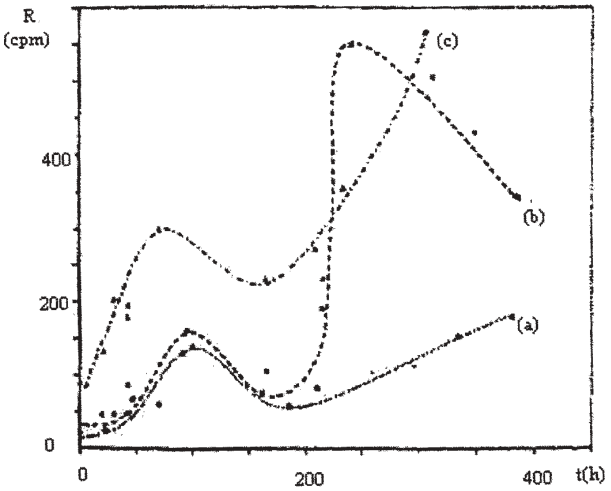

Fig. 1A. The diagrams for the crystalization studies:
(a) KCl; (b) $CdCl_2$. KCl . H_2O; (c) $CdCl_2$. $2H_2O$

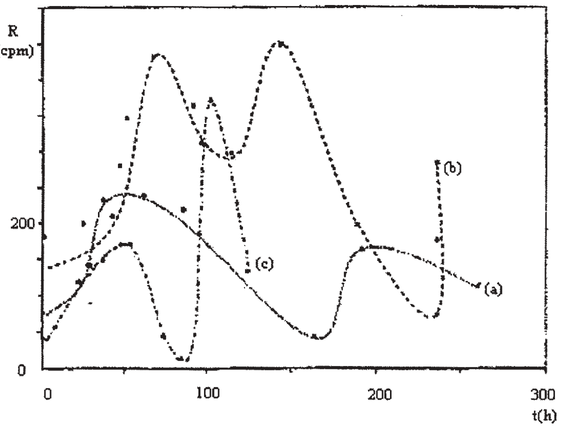

Fig. 2A. The diagrams for the crystalization studies:
(a) $2NH_4Cl$. $CuCl_2$. $2H_2O$; (b) $CuCl_2$. H_2O; (c) NH_4Cl

Meanwhile, concerning the first diffusion relation of Fick, the evolution in time of the ions' concentration passed from solution in to the crystallization germs is proportional with the concentration gradient:

$$\frac{dC}{dt} = A\cdot D\left(\frac{\Delta C}{\Delta x}\right)_t \qquad (4)$$

where "*D*" means the diffusion coefficient of hydrated ions in colloidal mass inside the germs and "*A*" represents the liquid/ solid interface area respectively.

If we consider:

$$\left(\frac{\Delta C}{\Delta x}\right)_t = \frac{C_s - C}{\delta} \qquad (5)$$

where "δ" is the infinitesimal thickness of the diffusion layer, the equation:

$$\frac{dC}{dt} = \frac{A\cdot D}{\delta}(C_s - C) \qquad (6)$$

is obtained.

From the relations (1) and (6), results, $k = \frac{A\cdot D}{\delta}$ which follows

$$\ln\frac{R_s}{R_s - R} = D\cdot t \qquad (7)$$

for "A" and "δ" considered as constant in a given experimental device .They can not be direct determined ,but only by absolute methods, as mentioned in literature[18].

By means of the last relation (7), taking into account the initial "*R*" and final (maximum) "R_s" values of the intensity of the backscattered β-rays, as well as the starting moment of the nucleation process (which can be

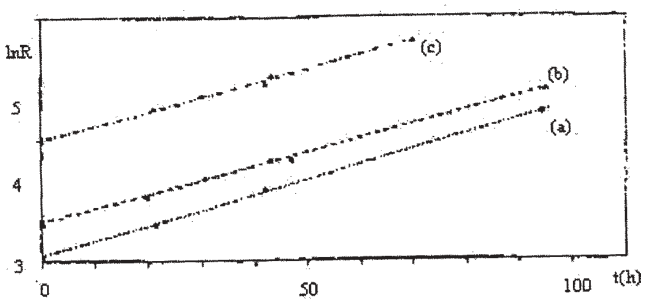

Fig. 1B. The diagrams for the crystalization studies:
(a) tg(α) =0.0182; (b) tg(α) =0.0168; (c) tg(α) = 0.1740

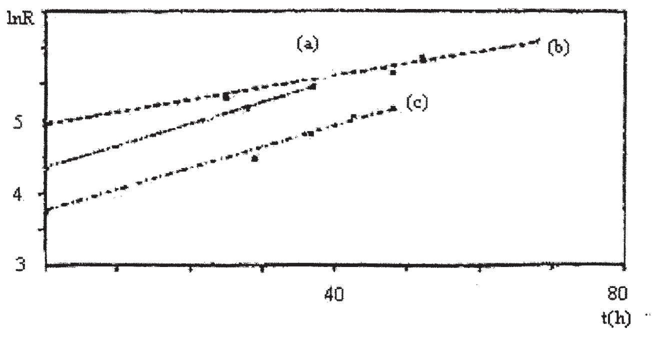

Fig. 2B. The diagrams for the crystalization studies:
(a) tg(α) =0.0302; (b) tg(α) =0.0167; (c) tg(α) = 0.2929

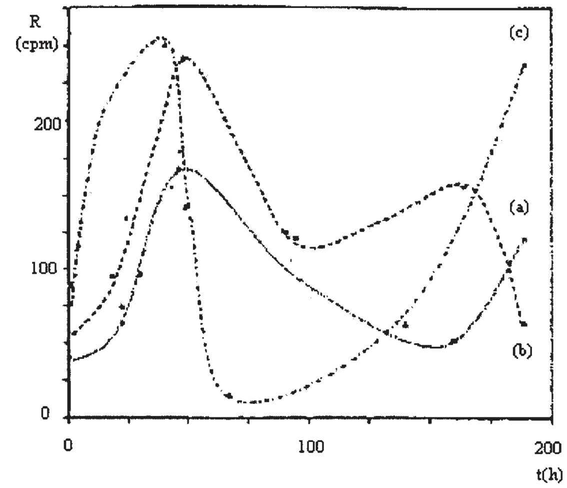

Fig. 3A. The diagrams for the crystalization studies:
(a) $(NH_4)_2SO_4 . CoSO_4 . 6H_2O$, (b) $(NH_4)_2$. (c) $CoSO_4 . 7H_2O$

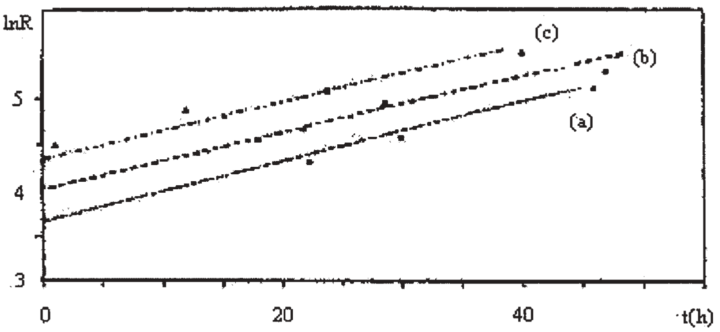

Fig. 3B. The diagrams for the crystalization studies:
(a) tg(α) =0.0310; (b) tg(α) =0.0303; (c) tg(α) = 0.0297

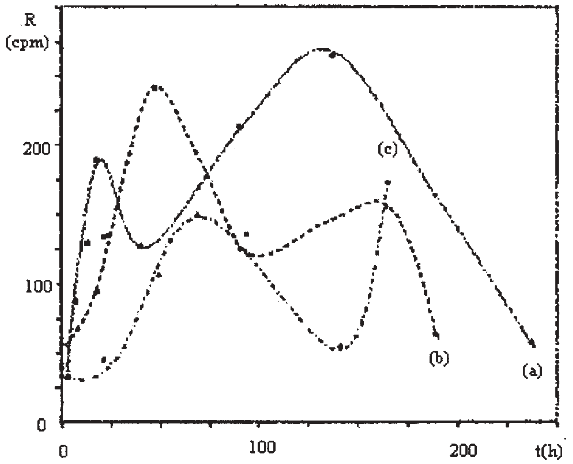

Fig. 4A. The diagrams for the crystalization studies:
(a) $K_2SO_4 . NiSO_4 . 6H_2O$; (b) $K_2 SO_4$; (c) $NiSO_4 . 7H_2O$

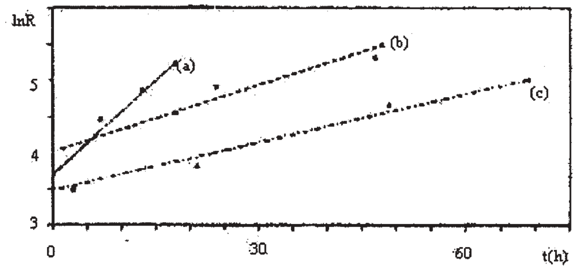

Fig. 4B. The diagrams for the crystalization studies:
(a) tg(α) =0.0861; (b) tg(α) =0.0303; (c) tg(α) = 0.0217

Table 1

VALUES OF NUCLEATION RATE CONSTANT, DIFFUSION COEFFICIENT AND BEGINNING TIMES OF NUCLEATION, AS WELL AS THE SOLUBILITY AND CRYSTALLOGRAPHIC RADIUS OF THE CATIONS FOR THE STUDIED SYSTEMS

Crystals (double salts and precursors)	Solubility* [12] g/100 ml H_2O	Rate constant of nucleation k (h^{-1})	Diffusion coefficient $D \cdot 10^5 (cm^2 \cdot s^{-1})$	Ionic radius [12] (Å)	t (h)
$CdCl_2 \cdot KCl \cdot H_2O$	168^{20}	0.0192	0.493	-	95
KCl	34^{20}	0.0166	0.933	1.33 (K^+)	100
$CdCl_2 \cdot 2H_2O$	134.5^{20}	0.0174	2.050	0.97 (Cd^{2+})	70
$2NH_4Cl \cdot CuCl_2 \cdot 2H_2O$	33.8^{0}	0.0302	0.980	-	37
$CuCl_2 \cdot 2H_2O$	110.4^{0}	0.0167	1.130	0.69 (Cu^{2+})	68
NH_4Cl	37.2^{20}	0.0292	0.868	1.48 (NH_4^+)	48
$(NH_4)_2SO_4 \cdot CoSO_4 \cdot 6H_2O$	20.5^{20}	0.0310	1.210	-	46
$(NH_4)_2SO_4$	70.6^{0}	0.0303	1.200	1.48 (NH_4^+)	48
$CoSO_4 \cdot 7H_2O$	60.4^{3}	0.0297	2.200	0.72 (Co^{2+})	40
$K_2SO_4 \cdot NiSO_4 \cdot 6H_2O$	7^{0}	0.0861	0.990	-	18
K_2SO_4	9.22^{10}	0.0303	1.210	1.33 (K^+)	48
$NiSO_4 \cdot 6H_2O$	32^{20}	0.0217	1.100	0.69 (Ni^{2+})	69

* the exponent means the temperature (°C)

established from the first maximum of the each curve drawn in figs. 1-4), the values of the diffusion coefficient can be calculated. The calculated D data correspond to those found by other authors [4], using other methods.

The established values of *"k"*, *"D" and "t"*, from experimental data, are given in table 1.

Conclusions

Taking into considerations the presented data, the following conclusions can pointed out:

The experimental data suggest that the values of global constant rate of nucleation process and the solubility of the crystalline substance is a reverse proportional dependence; this observation should be verified on a higher number of systems regarding the nucleation process of crystals;

The cations with smaller radius (at the same electrical charge and for the same anion) have smaller values of the nucleation rate constants comparing to those with higher ones;

In the case of double salts, the values of the nucleation rate constants are higher than those corresponding to the simple salts.

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