

*Dedicated to the memory of
Professor Maria Brezeanu (1924–2005)*

USE OF β -RAYS BACKSCATTERING TO STUDY THE CRYSTALLIZATION PROCESS OF SIMPLE SALTS FROM SOLUTIONS

Alexandru CECAL,^{*a} Anca Irena BALAN,^a Nicoleta MELNICIUC-PUICA^b and Karin POPA^a

^a“Al. I. Cuza” University, Faculty of Chemistry, 11 Carol I Bd., 700506 Iași, Roumania

^b“Al. I. Cuza” University, Faculty of Theology, 11 Cloșca Street, 700065 Iași, Roumania

Received September 12, 2005

This paper deals with a radiokinetic study on the appearance of crystals from aqueous solutions, using a method based on β -ray backscattering. The study points out a correlation between the intensity of the β -rays backscattered and the solution concentration where simple salts crystals appeared, by means of slow evaporation of the solvent. The experimental data obtained, plotted as the intensity of β -ray backscattering vs. time, resulted in curves of a sinusoidal shape. The maximum point of each studied system corresponds to the beginning of the nucleation process, while the minimum one can be assimilated with the image of the solid crystal at a maximum concentration of the crystallization germs. From a kinetic point of view, the values of the parameters: global rate constant and beginning time for the nucleation process were estimated. Actually, these parameters represent a real measure of the growing rate of crystals in time, in different experimental conditions.

INTRODUCTION

The process of crystallization from solutions or molten salts was studied in detail by several authors.¹⁻⁵ According to these studies, the crystals turn up from the solutions by slow evaporation of solvent, the change of solution composition by adding an extra solvent, or varying the given medium as result of slow chemical processes, etc. The crystal growth from molten salts can be achieved by slow decreasing of the foundry temperature, the spontaneous nucleation or the inducted one from the outside, crystallization at a constant temperature as well as by the extraction of the crystal from that system, slow solidification with a constant gradient of the temperature of the molten salt, etc.

The radioactive tracers were used in the investigation of the crystal growth kinetics from aqueous concentrated solutions, in different experimental conditions, offering improved accuracy of the studies.⁶

This paper is a continuation of some previous studies regarding the radiokinetic investigation of crystal growth in gels.⁷⁻⁸ It proposes a new radiometric method based on β -ray backscattering in the investigation of the germinating process and growing of simple crystals (*e.g.*, sulfocyanides, halides, sulfates, etc.) of some cations from aqueous solutions.

EXPERIMENTAL

The salts used in experiments were:

- Fe(SCN)₂·3H₂O, Co(SCN)₂·3H₂O, Ni(SCN)₂, Mn(SCN)₂·H₂O;
- (NH₄)₂SO₄, MgSO₄·7H₂O, K₂SO₄, CoSO₄·7H₂O, NiSO₄·6H₂O;
- Cd(CH₃COO)₂·2H₂O, Cd(NO₃)₂, CdCl₂·2H₂O, CdI₂.

Then, from these salts the same volumes of saturated aqueous solutions⁹ were prepared and poured each into cylindrical glass flasks of 50 mL.

* Corresponding author. Fax: + 40-232-201313; E-mail: cecal@uaic.ro

The samples with saturated solutions were thermostatted at 21.5°C starting the slow evaporation of water. At given time intervals the intensity of the β -rays backscattered was measured for every solution.

The used experimental device for the activity measurements of β -rays backscattered by solution surface is shown in Fig. 1.

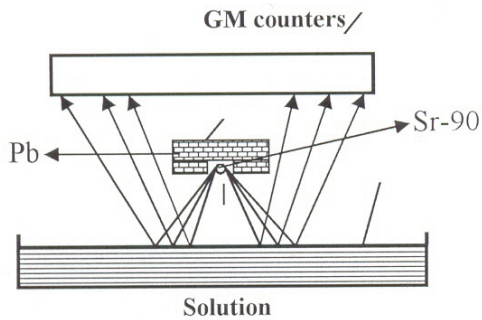
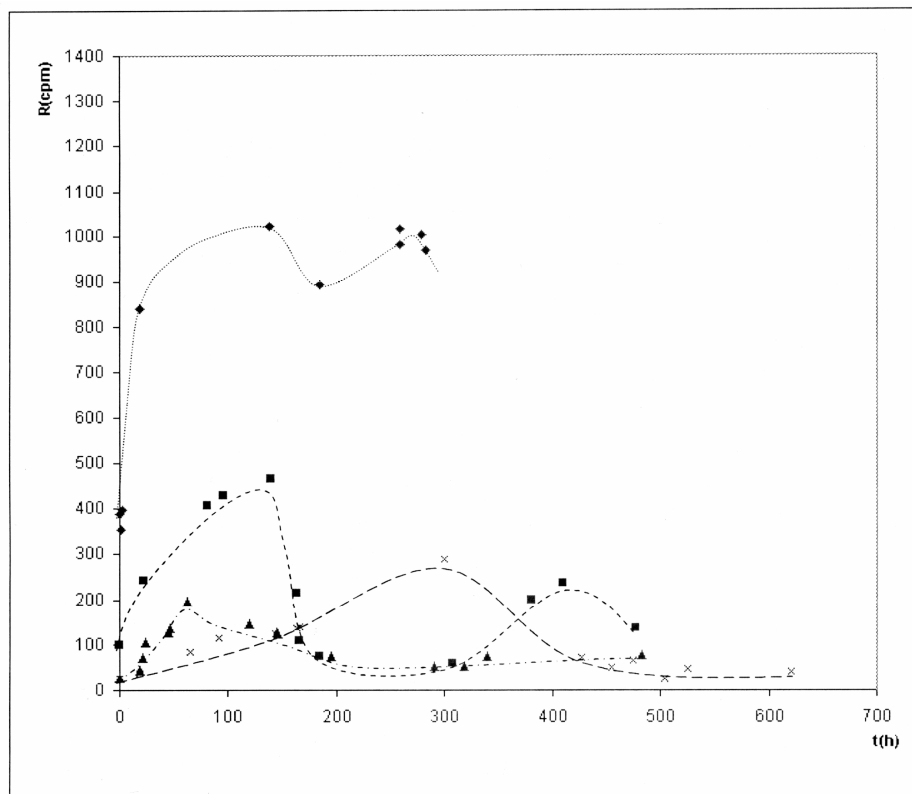


Fig. 1 – Experimental device for the β -rays backscattering measurements by GM-CTC counters.

As a β^- irradiation source ^{90}Sr radionuclide was used, having a total activity $\Lambda = 5.6 \cdot 10^7$ Bq, well screened upsides by a lead shield. The used 5 GM-CMC beta-counters, set in parallel-horizontal position, were connected to Decimal Scalar VA-M-14.

RESULTS AND DISCUSSION

The obtained experimental results were plotted as the measured intensity of backscattered β - rays vs. time (Figs. 2–4).



- (♦) Fe (SCN)₂ · 3H₂O
- (■) Co (SCN)₂ · 3H₂O
- (▲) Ni (SCN)₂
- (x) Mn (SCN)₂ · H₂O

Fig. 2

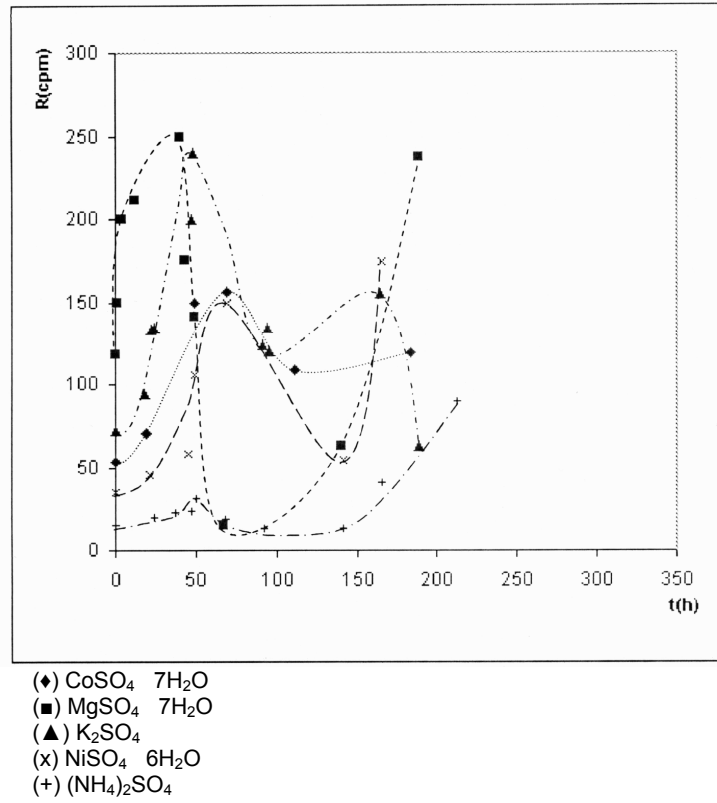


Fig. 3

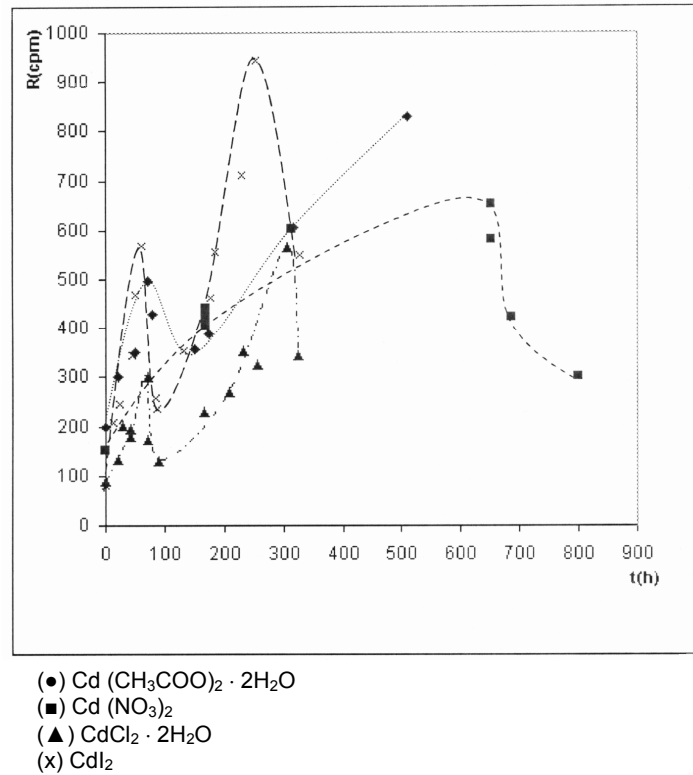


Fig. 4

Fig. 2-4 – The diagrams from the studied crystallization systems.

The curve model of these figures can be explained as follows:

Within the framework of the appearance and growth process of crystals from aqueous solutions, the chemical species of the systems create crowds of individual growing particles, due to the evaporation of the solvent, covering the following sequences: hydrolysis/polymerization/ germination/crystal geometry well defined.

However, the inner process of crystallization is simultaneous, due the permanent increase of the temporary concentration of the solved substance by evaporation of the solvent. After a given time, the first crystal germs in the colloidal viscous mass appear, being distributed in all the saturated solution. Therefore, this moment was assimilated with the maximum of every curve shown in Figs. 2-4, where the intensity of the backscattered β -rays reached the highest values; here crystallization germ concentration is the lowest. From this "peak" position, the beginning time of the crystal appearance could be determined for each investigated system.

By going on with the solvent evaporation, from this maximum point, concentration of crystallization germs increases by crowding, until they turn into the final solid crystal. As a result, the measured activity begins to decrease up to a minimum value. At this new point, the crystal is considered as being formed, by means of condensation of the proper germs. Here the β -rays lost a part of their initial energy, after touching and (partially) penetrating the solid surface; these rays will no more be totally backscattered.

If the resulted crystal is hygroscopic, the intensity of the backscattered β -rays increases again, resulting in a second germination, in the contact with the water vapours from the atmosphere.

The shapes of the curves shown in Figs. 2-4 resemble those reported by others authors,¹⁰⁻¹¹ when the evolution in time of concentration or of the number of crystallization germs, for some other systems were plotted graphically. That justifies the credibility of the suggested new method, based on the backscattered β -rays to be used in the study of the crystallization process.

Furthermore, from a kinetic point of view,¹²⁻¹³ since the solvent evaporates, the variation in time of the concentration of the solved substance can be expressed as follows:

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

when " 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 germination process.

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

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

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

Plotting (2) as: $\ln \frac{R_s}{R_s - R} = f(t)$ with the experimental values corresponding to the first part of each

crystallization curve (until maximum is reached), straight lines are obtained. From the slopes of these lines, the values of " k " can be evaluated.

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

$$\frac{dC}{dt} = A \cdot D \cdot \left(\frac{\Delta C}{\Delta x} \right)_t \quad (3)$$

where " D " and " A " means the diffusion value coefficient and the liquid/solid interface area, respectively.

When considering:

$$\left(\frac{\Delta C}{\Delta x} \right)_t = \frac{C_s - C}{\delta} \quad (4)$$

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

$$\frac{dC}{dt} = \frac{A \cdot D}{\delta} (C_s - C) \tag{5}$$

is obtained. From relation (1) and (5), it results:

$$k = \frac{A \cdot D}{\delta}$$

then follows:

$$\ln \frac{R}{R_s - R} = D \cdot t \tag{6}$$

for “A” and “δ” considered as constant in a given experiment.

Taking into account the initial “R” and final (maximum) “R_s” values of intensity of the backscattered β rays, as well as the starting moment of the germination process (which can be established from the first maximum of each curve drawn out in Figs. 2-4), the values of the diffusion coefficient can be determined.

Meanwhile, considering the Einstein–Stokes relation:

$$D = \frac{RT}{6\pi N \eta} \cdot \frac{1}{r} \tag{7}$$

the radius (r) of the colloidal particle can be calculated.

In this relation R is the universal constant of perfect gases; T means the temperature in °K; N represents the Avogadro number and η is the dynamic viscosity of the disperse medium.

The obtained results are given in Table 1.

Table 1

The kinetic and diffusion parameters, as well the solubility and crystallographic radius, for the studied systems

Crystals	Solubility ⁹ g/100ml H ₂ O	Global rate constant of nucleation k (s ⁻¹)	Diffusion coefficient D.10 ⁵ (cm ² .s ⁻¹)	Radius of the colloidal particle r(Å)	Crystallographic radius ⁹ (Å)	Time of nucleation appearance t(h)
Fe(SCN) ₂ ·3H ₂ O	-	0.0119	2.10	1.02	0.75 (Fe ²⁺)	135
Co(SCN) ₂ ·3H ₂ O	-	0.0110	1.03	2.08	0.72 (Co ²⁺)	139
Ni(SCN) ₂	-	0.0141	4.77	1.20	0.69 (Ni ²⁺)	119
Mn(SCN) ₂ ·H ₂ O	-	0.0129	1.79	1.20	0.80 (Mn ²⁺)	300
(NH ₄) ₂ SO ₄	70.6 ⁰	0.0145	0.156	3.78	1.48(NH ₄ ⁺)	50
MgSO ₄ ·7H ₂ O	71 ²⁰	0.0297	2.200	0.97	0.65(Mg ²⁺)	40
K ₂ SO ₄	9.22 ¹⁰	0.0303	1.210	1.77	1.33(K ⁺)	48
CoSO ₄ ·7H ₂ O	60.4 ³	0.0178	1.970	1.09	0.72(Co ²⁺)	69
NiSO ₄ ·6H ₂ O	32 ²⁰	0.0217	1.100	1.95	0.69 (Ni ²⁺)	69
Cd(CH ₃ COO) ₂ ·2H ₂ O	v.solub.	0.0126	2.100	1.02	0.97 (Cd ²⁺)	72
Cd(NO ₃) ₂	109 ⁰	0.0022	1.186	1.81	0.97(Cd ²⁺)	653
CdCl ₂ ·2H ₂ O	168 ²⁰	0.0174	2.050	1.04	0.97(Cd ²⁺)	70
CdI ₂	86.2 ¹⁵	0.0321	1.200	1.79	0.97(Cd ²⁺)	61

CONCLUSIONS

Taking into account these data, the following can be concluded :

The complex process of crystal appearance and growth in different experimental conditions can be followed by the proposed method based on the backscattered β-rays.

From a kinetic point of view, this process could be described by means of 2 parameters: the global rate constant and the beginning time of the germs appearance.

Crystallization germs appear more rapidly for cations with a smaller electrical charge compared to those with a higher charge, depending on the anions nature, too.

For all systems, the radius of the colloidal particle in the germination stage, calculated from experimental data is higher than the crystallographic radius of a given cation.

REFERENCES

1. W. L. McCabe, *Ind. Eng. Chem.*, **1929**, *21*, 30.
2. H. Remy, "Grundriss der Anorganischen Chemie", Akademische Verlagsgesellschaft mbH, Leipzig, 1937.
3. W. Trzebiatowski, "Lehrbuch der Anorganischen Chemie", VEB- Deutscher Verlag der Wissenschaft, Berlin, 1963.
4. K. Th. Wilke and J. Bohm, "Krystallzuchtung", VEB Deutscher Verlag der Wissenschaft, Berlin, 1988.
5. D. T. J. Hurle, "Handbook of Crystal Growth", Elsevier, Amsterdam, 1994.
6. J. Töglyessy, V. Jesenak and T. Braun, "Radiochemical Methods of Analysis", vol. I-II, IAEA Viena, 1965.
7. A. Cecal, M. Palamaru, A.I. Juverdeanu and S. Chisca, *J. Cryst. Growth*, **1996**, *158*, 181.
8. A. Cecal, K. Popa, S Chisca, A I. Balan and S. Patachia, *Rev. Chim. (Bucharest)*, **2003**, *54*, 731.
9. K.V. La Mer, *Ind. Eng. Chem.*, **1952**, *44*, 1270.
10. K.S. Mazdiyasi, *Ceramic Intern.*, **1982**, *8*, 42.
11. W. Jost, "Diffusion in Solids, Liquids and Gases", John Wiley and Sons, New York, 1960.
12. S.W. Benson, "The Fundamentals of the Chemical Kinetics", McGraw-Hill Book Co, New York, 1960.
13. "Handbook of Chemistry and Physics", 55th Edition, CRC Press Cleveland, Ohio, 1974-1975.