

## CRYSTAL GROWTH

# The Particle-Size Distribution Method for Studying the Crystallization of Calcium Oxalate in the Presence of Impurities

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**Abstract**—The crystallization of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  from model solutions of a crystal-forming medium (human urine) has been studied by the dispersion method. It is shown that addition of amino acids to a model solution slows down the growth of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystals and affects the specific surface area and dispersivity of solid samples. The decelerating effect of amino acids increases with an increase in their concentration and depends on the amino acid structure.

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## INTRODUCTION

Recently, the elaboration and development of theoretical and physicochemical bases of biomineral formation have become of key importance in view of the rapid increase in the sickness rate and, correspondingly, necessity of searching for new methods of treatment and diagnostics [1–8].

It is well known that pathogenic biominerals can be formed in many human tissues and organs [9–14]. The most widespread pathogenic mineral formations are kidney stones (uroliths), which affect no less than 1–3% population, most often people in the able-bodied age: from 20 to 50 years old [2, 9–13].

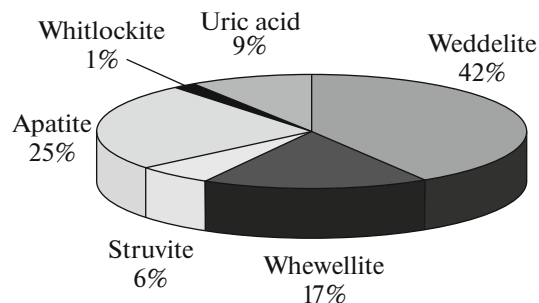
The factors causing the formation of kidney stones have not been completely cleared up and call for further study. Nowadays, when the chemical composition and morphology of uric stones has been investigated fairly completely [1–13], the new stage of research in this field should involve the models that most completely describe the natural crystal-forming medium. Based on these models, one can analyze the relationships in the crystal–organism system. This system is interesting not only from the medical point of view but also for studying the processes occurring in supersaturated biological solutions.

One of the approaches to the study of the crystallization of the phases entering the kidney stone composition is experimental modeling, based on which one can determine the formation mechanism, reveal the factors affecting the character of this process, and predict specific features of the behavior of the system with a change in particular parameters.

The composition of the kidney stones in people living in different regions of Russia and other countries

has been analyzed in detail in previous complex studies [1, 2, 8, 13, etc.]. This analysis showed that uric stones contain both mineral and organic components. Different minerals are involved in the formation of kidney stones, and study of the crystallization of each mineral is a time-consuming and laborious task. However, the regularities obtained when modeling one mineral phase can be extended to others. Therefore, it was decided to model the most widespread mineral phase in the uric stone composition, specifically, calcium oxalate. This compound was found in uric system stones, salivary stones, stones existing in the eye crystalline lens, and other pathogenic mineral formations [1, 14–18]. Calcium oxalates are present in a human organism in the form of two minerals: whewellite  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and weddellite  $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , with dominance of whewellite (Fig. 1).

Currently, many researchers acknowledge the important role of organic materials (in particular,



**Fig. 1.** Occurrence rate of mineral phases in kidney stones for the Omsk oblast population.

**Table 1.** Amino acids used in model solutions

AA	Structure
DL-Glutamic acid	
Glycine	
L-Alanine	
L-Proline	

some proteins and amino acids (AAs) in the formation of biominerals [3, 9, 19–24]. However, the mechanism of their action has not been investigated in detail. Therefore, our purpose was to analyze the influence of AAs on model media under close to in vivo conditions. AAs were chosen as an object of study because, according to the data of amino acid analysis of biominerals, they enter the composition of mineral groups of pathogenic minerals [9, 19, 20] and are present in physiological fluids [1, 5].

One of promising methods for studying the mass crystallization processes in biological solutions is the dispersion method. It provides a particle-size distribution [22], which is directly related to the parameters determining the mechanisms of crystal nucleation and growth. Despite the convenience of this tool, it has not been widely used in experimental studies of crystallization.

Thus, the purpose of this work was to investigate the crystallization of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  in the presence of AAs using dispersion analysis.

## EXPERIMENTAL

The dispersion analysis of synthesized calcium oxalate phases included the following main stages:

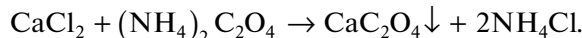
(i) synthesis of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  samples by precipitation at a temperature  $t = 37 \pm 0.2^\circ\text{C}$ ;

(ii) dispersion analysis of newly formed crystallites and solid phase on a Shimadzu SALD-2101 analyzer.

The crystallization was studied in a glass crystallizer. To exclude spontaneous formation of crystallization centers, the crystallizer was rinsed with concentrated sulfuric acid and then in double-distilled water.

Supersaturation ( $\gamma$ ) was formed due to the chemical reaction under conditions of interdiffusion of

reagents, because the solubility of the reaction product ( $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ) is lower than that of the starting materials,  $\text{CaCl}_2$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ :



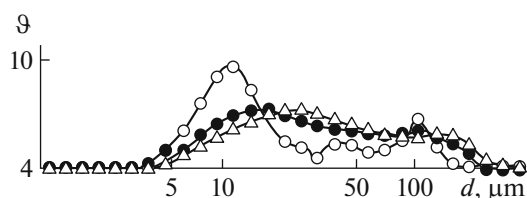
The initial reagents were salts of analytical or reagent grades and double-distilled water. Solutions containing cations and anions (their joint presence excluded the formation of poorly soluble compounds under the aforementioned conditions) were prepared for each series of experiments. Then the solutions mixed in equivalent volumes.

The conditions for the experiments with the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystallization, specifically, the supersaturation under study ( $\gamma = 7$ ) and pH ( $6.00 \pm 0.05$ ) of the solutions, were chosen proceeding from the properties of natural crystal-forming medium (human urine) [5]. In the second series of experiments, crystallization was performed at a constant ionic strength  $I = 0.3$  [5]. When carrying out experiments in an AA medium, a solution of ammonium oxalate was prepared in an AA solution (Table 1) with a specified concentration in the range from  $10^{-2}$  to  $10^{-5}$ , which corresponds to their presence in the physiological solution (human urine) and in the composition of oxalate kidney stones [9, 19, 20, 23]. The instant of merging was considered to be the reaction onset. Bidistillate played the role of background.

After the precipitate ripening under the mother liquor (7 days), the solid phase was separated from the solution by filtration, dried at a temperature of  $\sim 80^\circ\text{C}$  to a constant mass and complete removal of chemically unbound water, weighted, and investigated using a set of physicochemical methods.

To measure the powder dispersivity, 0.2% aqueous solution of  $\text{Na}_6\text{P}_6\text{O}_{18}$  was used as a fluid for the measuring medium when preparing a suspension. The latter was formed as follows: a small amount of the sample under study was placed in a weighing bottle containing a fluid  $15 \text{ cm}^3$  in volume, after which the mixture was dispersed using an UZG 13-0.1/22 ultrasonic disperser. To prevent particles from aggregation, we chose the optimal dispersion time: 10 s. The sample suspension (from 0.1 to 0.5 mL in volume, depending on the degree of light scattering) was transferred by a graduated pipette to the fluid-containing cell. Five measurements were performed on the suspension prepared for each sample.

According to the dispersion analysis technique, curves of two types can be plotted: volume and numerical size distributions. An analysis of these dependences shows that average linear size differs from the average volume size. Particles with  $d = 1\text{--}2 \mu\text{m}$  make the main contribution to the average linear size; therefore, the particle growth cannot be estimated from the results of numerical distribution. In regards to the volume distribution, the main contribution is from the particles of largest volume; hence, the growth of parti-



**Fig. 2.** Size distributions of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystals in bidistillate at supersaturation  $\gamma = 7$  after (empty circles) 20, (triangles) 30, and (filled circles) 40 min;  $\vartheta$  (%) is the normalized number of particles.

cles can be estimated from their average size in this case. Therefore, we will use below only the volume (mass) particle-size distribution, and the average size of crystals will be defined as the average-volume size.

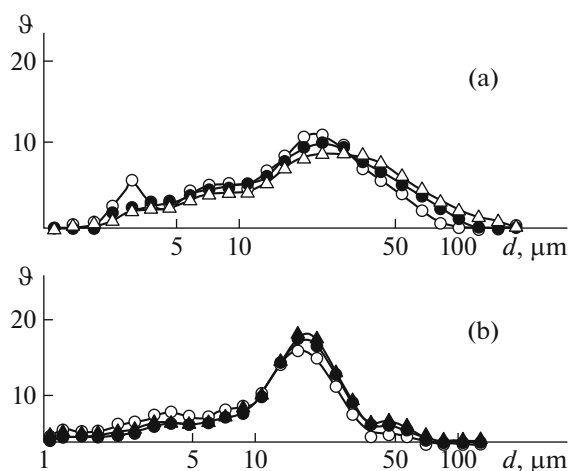
The AA concentration was determined by the analysis based on the transformation of AAs into soluble copper salts using the biuret test and subsequent photometric determination. Measurements were performed on a KFK-2 photocolormeter. The optical density of standard solutions was determined in the wavelength range including 670 nm. Cells with a 1-cm-thick light-absorbing-layer were used for measurements.

The specific surface of solid samples was investigated using the technique of single-point nitrogen adsorption at 77.4 K, implemented on a Sorptometer instrument (OOO Katakona, Russia). The  $S_{\text{BET}}$  values ( $\text{m}^2/\text{g}$ ) were calculated according to the Brunauer–Emmett–Teller (BET) method (a technique for mathematical description of physical adsorption, based on the theory of polymolecular (multilayer) adsorption, proposed by Brunauer, Emmett, and Teller).

The sign of the charge of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  sol particles was found by capillary analysis [25]: sols were poured into vessels, filter paper strips were immersed in them, the liquid rise level through the paper was measured 1 h after, and the particle charge sign was determined.

## RESULTS AND DISCUSSION

As the dispersion analysis showed, the formation of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystals in a system without AA additives is observed immediately after merging solutions. The minimum crystal size is  $0.05 \mu\text{m}$ . The size distribution of calcium oxalate crystals has a bimodal character (Fig. 2), which is smoothed out with time, because the crystal growth begins to dominate. The average crystal size increases with time from 10 to  $30 \mu\text{m}$ , and, 40 min after the crystallization onset, the growth processes are accompanied by aggregation of crystallites and occurrence of polymodality in the distribution curves. One can see that, during crystallization, the size distribution curves for the produced



**Fig. 3.** Size distributions of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystals in bidistillate at supersaturation  $\gamma = 7$  and GA concentrations in solution  $C_{\text{GA}} =$  (a)  $10^{-4}$  and (b)  $10^{-3}$  mol/L, after (empty circles) 20, (triangles) 30, and (filled circles) 40 min.

crystallites are diffused (the dispersion increases), and the curve peak shifts to the right along the size axis; the distribution becomes polymodal in many cases. This behavior is explained well by the mechanism of capture of small particles by large ones [25] against the background of nonuniform particle density distribution in the crystallization space. The data obtained are in agreement with the results of [21, 22, 24, 26, 27].

The crystallization of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  under a constant ionic strength characteristic of natural crystallizing medium (urine),  $I = 0.3$ , showed the absence of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystals 2 h after the reaction onset. This result, along with others, confirms the stability of supersaturated biological solutions (human urine,  $\gamma = 7$ ), where conditions for forming kidney stones are absent.

Concerning the solutions containing AA impurities, the situation is as follows. When adding proline, glycine, and alanine (in a concentration of  $10^{-5} \text{ M}$ ), first  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystals are observed 1 min after the crystallization onset, whereas in a solution with glutamic acid (GA) in the same concentration first crystals were observed 5 min after the instant of merging initial solutions. Thus, the induction period of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  formation in the presence of this AA is longer than in the case of pure systems and other AAs.

Figure 3 shows the size distribution curves for  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystals in the case of crystallization in model solutions in the presence of GA in different concentrations. We chose GA as an impurity, because its fraction in the total AA content in biominerals is maximum [20].

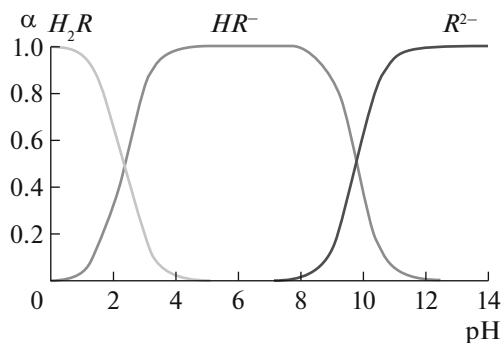
One can see that the growth of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystals is stabilized in the GA solution (Table 2); the corresponding curve demonstrates unimodal distribution

**Table 2.** Average size of calcium oxalate crystals for different AA concentrations (supersaturation  $\gamma = 7$ )

Additive	$C_{AA}$ , mol/L	Average diameter, $\mu\text{m}$
Without additives	—	30
Glutamic acid	$10^{-5}$	29
	$10^{-4}$	24
	$10^{-3}$	18
	$10^{-2}$	3.2
	$10^{-1}$	3.2
Glycine	$10^{-5}$	29
	$10^{-2}$	25
Alanine	$10^{-5}$	29
	$10^{-2}$	22
Proline	$10^{-5}$	29
	$10^{-2}$	20

(Fig. 3). Thus, GA slows down the growth of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystals, whereas an increase in the AA concentration enhances the decelerating effect, because the average size of calcium oxalate crystals decreases several times. This effect of AA can be explained by its possible adsorption on the active centers of newly formed crystals; in this case, the fraction of blocked crystallization centers increases with an increase in the acid concentration.

An analysis of the surface charge of the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  solid phase (Table 3) showed the surface of calcium oxalate monohydrate to be charged positively. It follows from Table 3 that an addition of GA in a small amount (2 mmol/L) leads to charge exchange on the surface. This occurs both due to the AA adsorption on the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  surface [27] and due to the formation of polydentate chelating complexes of AA with calcium ions ( $pK_{st} = 1.4$ ). The interaction between GA and  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystal surface becomes stronger with an increase in the negative charge of the GA form

**Fig. 4.** Ion diagram of GA.**Table 3.** Sign of the surface charge of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  in the presence of AAs in different concentrations

AA	$C_{AA} \times 10^3$ , mol/L	Sign of whewellite surface charge
Glutamic acid	0	+
	2	—
	4	—
	8	—
	10	—
	14	—
	20	—

dominant in the solution, which is in agreement with the ion diagram of existence of different forms for the given AA (Fig. 4). Similar data were obtained for other AAs (Table 2).

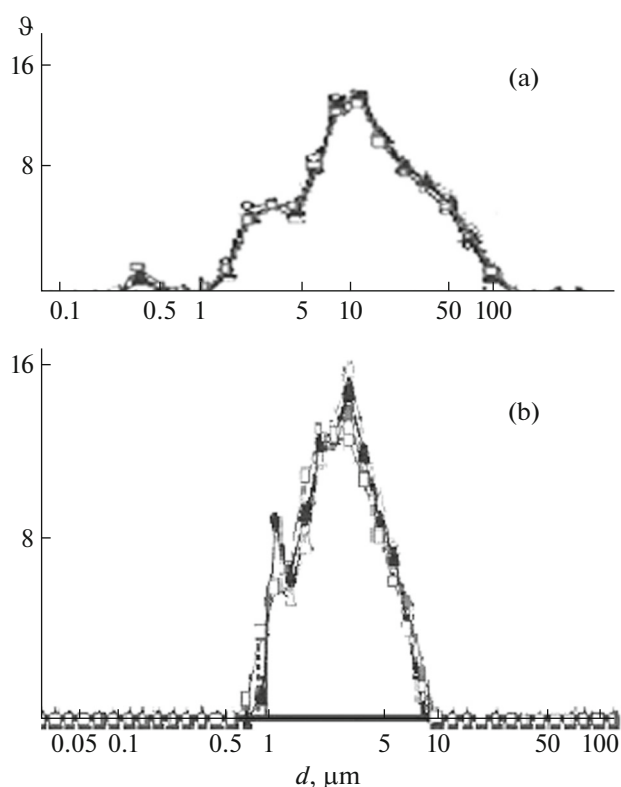
We can state that the average size of the newly formed particles is affected by both the nature of introduced additive and its concentration. It can be seen in Table 2 that, when an AA has a concentration of  $10^{-5}$  mmol/L, its influence is almost nullified, while an increase in the AA concentration reduces the average size of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystals. AA additives slow down the crystal growth, compress the size distributions, and shift the peaks of dispersion curves to the left (towards smaller particle sizes). Thus, the average sizes of the crystals formed in the reaction decrease.

Having analyzed the structure of AAs and their state in the solution (Table 1), one can conclude that the deceleration of whewellite crystal growth is enhanced with an increase in the length of hydrocarbon radical, rise in the number of carboxyl groups in AAs, and their existence in the form of charged ions in a solution at physiological pH values. An increase in the hydrocarbon radical length by one  $-\text{CH}_2-$  group leads to an increase in the surface activity [22].

The inhibiting effect of AAs is explained by their adsorption on growing  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystals. Based on the data of [27], according to which AAs exist in the form of zwitter ions in aqueous solutions, one can suggest that the adsorption mechanism is based on electrostatic interaction of AAs with growing faces of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystal.

In addition, AAs exist in four forms in aqueous solutions: conjugate acid, conjugate base, neutral molecule, and bipolar form. At a certain pH value, which is characteristic of each AA, the latter exists completely in the form of zwitter ion (particle with positive and negative charges); i.e., chemisorption may occur. These pH values (isoelectric points pI) for the AAs under consideration are listed in Table 1 [23]. Under experimental conditions, glycine, proline, and alanine may be in the form of zwitter ion or neutral





**Fig. 5.** Size distributions of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  solid phase crystals synthesized for (empty squares) 1, (triangles) 2, and (filled squares) 3 weeks: (a) without impurity and (b) in the presence of glycine.

molecule; GA can also exist as a conjugate base. Taking into account that the inhibiting effect of GA is the strongest, one can suggest interaction between the negatively charged acid and positively charged  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystal.

When studying the effect of glycine on the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystallization, it was found that the influence of this AA is weaker than that of all other amino acids. This behavior of glycine in the experiment is likely related to the possibility of being incorporated into channels of calcium oxalate lattice, because the sizes of oxalate ion and glycine are comparable (3.82 and 3.77 Å, respectively [28]).

The above results demonstrate that the AAs form the following a series in descending order with respect to their decelerating effect on the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crys-

tallization: glycine < alanine < proline < glutamic acid.

When studying the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystallization in the presence of AA by carrying out a model experiment in vitro, it was found that the AA concentration in the mother liquor above the precipitate increases with an increase in the synthesis time. This may be related to the competition between several processes: formation of the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  solid phase, AA adsorption on the surface, and AA complexing with calcium ions. In particular, the crystallization equilibrium shifts in the course of time towards the process that is more favorable thermodynamically: formation of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . The latter is accompanied by the destruction of previously formed AA complexes with calcium ions and their release into the solution.

An X-ray diffraction analysis of the solid phases formed during crystallization from a model solution was performed in [29]. It was established that the presence of AAs does not affect the phase composition of the precipitate, because the latter is  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  in all cases. IR spectroscopy showed that these AAs are indeed adsorbed on  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  powders.

The differential particle-size distributions for the solid samples synthesized for 1 week indicate that the presence of AAs also affects the solid phase dispersivity (Fig. 5). In the case of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystallization in the presence of glycine, the crystallite size in the powders is smaller than that of crystals of this compound synthesized in pure solutions. This fact correlates well with the experimental data (Table 4), which demonstrate that the samples grown from a model glycine-containing medium have a larger specific surface area than the samples synthesized in the absence of AA. However, the numerical values of the specific surface area for the solid samples synthesized in the presence of GA are smaller than the corresponding data on the samples crystallized in pure solutions. These results for the specific surface area of solid phases are explained by the strong decelerating effect of GA on the growth of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystals, which leads to a decrease in their sizes and number.

## CONCLUSIONS

The main regularities of changes in the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  dispersivity during mass crystallization without additives and in the presence of AAs were established.

It was shown that addition of AAs reduces the dispersivity of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystals. The decelerating effect of AAs increases with an increase in their concentration and depends on the acid structure.

The following AA series in ascending order with respect to the decelerating effect on the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  dispersivity was proposed: glycine < alanine < proline < glutamic acid.

**Table 4.** Values of specific surface area of solid phase

Solid phase	$S_{\text{spec}}$ , $\text{m}^2/\text{g}$
Whewellite	15
With glycine, 0.04 mol/L	17
With glutamic acid, 0.04 mol/L	13

It was revealed that the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  crystals grown in a glycine-containing medium have smaller sizes and the solid phase possess a larger specific surface area. The samples obtained with a GA additive are characterized by a smaller specific surface area due to the strong decelerating effect of this impurity.

#### ACKNOWLEDGMENTS

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