MASS-TRANSFER AND SUPERSATURATION IN CRYSTAL GROWTH IN GELS
Application to $CaSO_4 \cdot 2H_2O$

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Supersaturation evaluation is an essential requirement to describe, confront and explain crystal growth experiences. However, in the particular case of crystal growth in gels, experiences are often described by attending to the initial concentration of reagents. This fact is connected with deficiencies in the theoretical quantification of mass-transfer, and therefore in both time and location prediction for the first precipitate. In this paper laboratory experiences have been specifically designed to test supersaturation evolution through an actual (finite) diffusion system. The problem is carried out by keeping into account several complexity factors: free ions as well as complexes and silica gel Na^+ and Cl^- "unloading" are considered to evaluate the supersaturation.

1. Introduction

Supersaturation evaluation is an essential requirement to describe, compare and interpret crystal growth experiences. In the case of crystal growth from solution, the relative supersaturation may considerably depend on the applied concentration definition [1]. The use of concepts such as "thermodynamic supersaturation" [2] and "growth affinity" [1,3] is an attempt to get rigorous and comparable expressions for the driving force.

Despite all the afore-mentioned facts, in crystal growth in gels the experiments are often described by attending to the initial concentrations of the diffusing reagents and to the geometric configuration of the experimental system. Any quantitative mention of supersaturation is absent. This fact is related to theoretical deficiencies about two aspects of the technique: the mass-transfer quantification and the establishement of rigorous crystallization criteria to predict time and location for the first precipitate.

In crystal growth in gels, volume mass-transfer occurs by diffusion. Consequently, theoretical treatments have usually been based on Fick's diffusion law analytic solutions. However, in such analytic approach to the mass-transfer problem, diffusion systems and source reservoirs are respectively considered semi-infinite and inexhaustible, whereas actual systems are finite.

Recently, Henisch and García-Ruiz [4] have described a microcomputer implementation which allows one to solve Fick's diffusion equation, as a time function, by numerical methods. This treatment is a suitable procedure for finite systems with differents configurations.

Regarding the second theoretical problem, the crystallization criteria, Henisch and García-Ruiz [5] consider the case of a system where two counter-diffusing reagents meet to generate a sparingly soluble reaction product. Following these authors, for a precipitate to form, it is not enough that the local concentration product exceeds a critical value K_s^*. A new concept, "equality range" of reagent concentrations, stated in equivalents, needs to be introduced in order to explain experimental results. By using both conditions, Henisch [6] carries out a microcomputer analysis to predict the first and subsequent precipitates position, in the case of Liesegang ring formation.

Unfortunately, up to now, such microcomputer implementations are based on a one-dimensional algorithm and do not distinguish between micro- and macrocrystalline precipitates. Moreover, the systems they have worked with are hypothetical and several assumptions have been made for the sake of simplicity (complete ionization, the diffusion constant is independent of concentration levels, etc.). So, this approach is a good instrument in an interpretative way, but not in a quantitative one.

This paper deals with laboratory experiments which have been specifically designed to test supersaturation evolution (space and time). This allows one to overcome the problem by attending to actual complexity factors, and to check the effective weight of the commonly made assumptions in the theoretical approach. So, the influence of concentration levels in the diffusion constant, and the presence of both, free ions and complexes, in solution are considered.

2. Experimental

Mass-transfer testing was carried out in a double diffusion-reaction system (fig. 1). In such a system, two reagents, $CaCl_2$ and Na_2SO_4, diffuse through a silica gel column (9 mm diameter and 280 mm long) to meet and generate $CaSO_4 \cdot 2H_2O$ as a reaction product. Silica gel was prepared by the acidification of a Na_2SiO_3 solution (Merck, sp.gr.: 1.059 g/cm^3; pH 11.2) with HCl (1N) solution until the desired pH level (5.5 in all the experiences) was obtained. The source reservoirs were filled with 8 cm^3 of $CaCl_2$ and Na_2SO_4 solutions (initially 1 M, 0.5 M and 0.3 M). The temperature of the experiments was 25 ° C.

Mass-transfer testing was carried out by reactant diffusion during previously stated periods of time (3, 8, 16, 24, 32, 40, 48, 56, 64, 72 and 80 days). After the diffusion period, the gel columns were sliced, and the gel slices (10 mm long) were chemically analyzed.

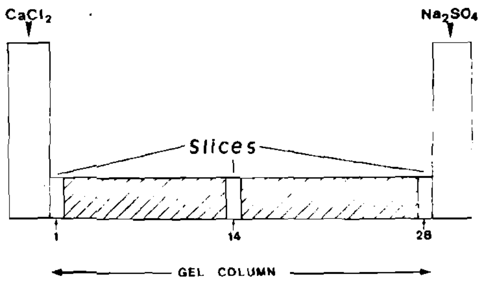

Fig. 1. Gel growth system schematic representation.

Chemical analysis of calcium and sodium was done by atomic absorption spectrophotometry (an UNICAM SP90 atomic absorption spectrophotometer with acetylene burner was used). The detection limit was 0.0001 mmol/l for calcium and 0.0004 mmol/l for sodium. The SO_4^{2-} concentration was analyzed by precipitating the sulphate with a barium chloride standard solution in acid medium. Then the barium excess was measured by atomic absorption spectrophotometry. So, precision for sulphate analysis was 1.04 mmol/l. However, the accuracy limit is only determined by the analytical method for low concentration values. Effective control of chemical determinations is done by the slicing process precision: a gel column is easily deformable and consequently an error up to 1% for gel slice weight may be expected. So, the error margin for concentration values is 1% concentration dependent.

Chemical constituent concentrations, measured in that particular way, are related to the whole volume of the gel slice (0.65 cm^3 = polymers + interstitial solution). Consequently, these values may be corrected to obtain the actual concentration of interstitial solutions. In order to establish the actual concentration values, the "effective water" per unit of gel volume had to be determined. With this aim, 100 cm^3 of 1M solution and 100 cm^3 of inert gel were put in contact with each other in a crystallizer. The interface between gel and solution was a circle of 10 cm of diameter. After 90 days, the concentration of the solution was measured, and out of this datum the weight percent of "effective water" was found; in this case 95.6%. This value is near the weight percent of total water in the gel, which reflects the weak polymer–water interaction in these kinds of gels.

The so-corrected concentration values are the total values for each entire slice, by removing the concentration gradient inside each slice. So, the concentration graphics throughout the gel column are stepped, on the understanding that the actual concentration gradient would be done by the step enveloping.

3. Mass-transfer in finite diffusion systems

In finite systems, mass-transfer follows a different outline from the theoretical forecast for semi-infinite systems. Total concentration values of calcium (mmol/l) through the diffusion column are represented in fig. 2a and pointed out in table 1. The slices are numbered from 1 to 28, the first being the nearest one to the $CaCl_2$ mother solution. Different curves correspond to different diffusion times.

Curve morphologies continuously change in time. The curve corresponding to a short diffusion period (8 days) is the only one that shows an aspect similar to that expected, from a theoretical point of view, for a semi-infinite system with infinite solution reservoirs. This curve also agrees with the one obtained by Henisch and García-Ruiz [4] for brief computation times. For longer diffusion times, the curves are not comparable with those obtained by these authors, since, in the experimental system, the boundary conditions are different (for instance the end of the gel column (slice 28) is not a sink of concentration 0).

The concentration decreases in the initial extreme, whereas it increases in the final extreme as diffusion time passes by. This fact means a continuous change in the edge conditions that precludes the analytic treatment of the mass-transfer. If the formation of a precipitate would not interrupt the process, concentration curves would logically tend to be straight horizontal lines that would represent the final concentration, homogeneous for the entire gel column. In fig. 2b evolution in time of the concentration is drawn for several gel slices. In all cases, after an initial upward flight, the concentration decreases. The slice 1 is not an exception but its upward flight occurs during the first days of diffusion and therefore the increase is not shown in the graphic.

Only the furthermost slices show a continuous concentration increase during the diffusion periods concerned. This is why all curves converge towards closer and closer values as diffusion time increases.

As complementary information, the total concentration values of sulphate throughout the gel column are pointed out in table 2. The pH profiles are also given in table 3. (Complete mass-transfer data used for this work are available to readers upon request.)

4. Gel Na^+ and Cl^- unloading

During the preparation of the described silica gel, NaCl is formed as soluble byproduct that is incorporated to the interstitial solution. So the

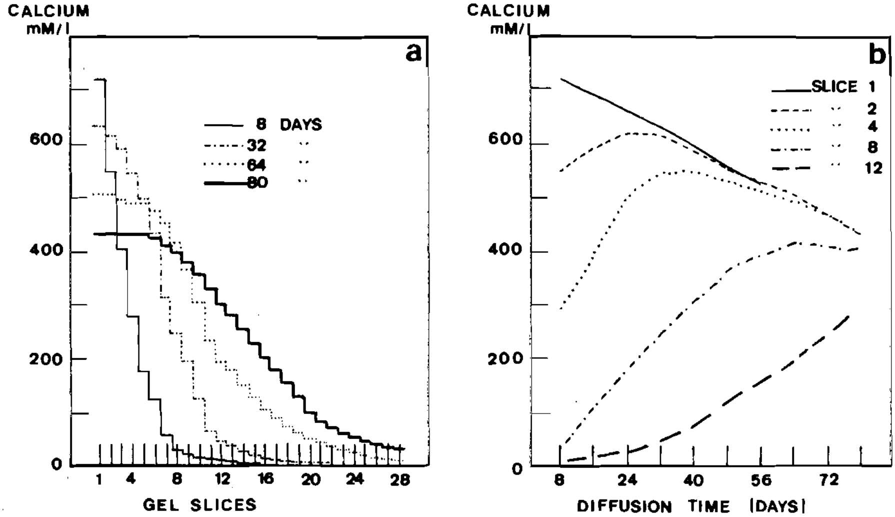

Fig. 2. Transport of calcium. Mother solution: 1M $CaCl_2$. (a) Total calcium concentration throughout the gel column for different diffusion times. (b) Calcium concentration evolution in time for different gel slices.

Table 1
Total calcium concentration (mmol/l) throughout the gel column for different diffusion times; mother solution 1M Ca_2Cl

Slice number	Diffusion time (days)				
	8	16	32	64	80
1	722	691	633	508	433
2	550	591	613	505	434
3	405	518	590	498	435
4	281	388	545	493	434
5	175	326	497	490	431
6	123	278	434	478	426
7	59	198	314	455	412
8	30	109	246	418	399
9	21	68	195	369	380
10	15	46	126	307	375
11	12	25	67	233	331
12	9	19	47	195	300
13	7	15	40	181	279
14	5	11	31	153	254
15	3	9	22	128	229
16	2	6	16	108	205
17	1	4	12	91	180
18	1	3	10	76	156
19	–	2	7	64	129
20	–	2	6	54	98
21	–	1	5	45	84
22	–	1	2	38	72
23	–	1	2	32	62
24	–	–	2	27	54
25	–	–	1	22	47
26	–	–	1	19	42
27	–	–	1	16	37
28	–	–	1	13	33

expression "inert gel technique", when it is applied to experimental devices as those used here, it is only a conventional term but not an actual one.

In fact, the presence of Cl^- and Na^+ in the interstitial solution means, in the first place, an alteration of the reagent's diffusion coefficients, and second, that the interaction of these ions with the reagents in solution may produce complex formation. For instance, the formation of the $NaSO_4^-$ ionic pair is very important in the growth of gypsum crystals, because it involves an important concentration decrease of SO_4^{2-} free ions, so that the actual supersaturation of the system is smaller than in a Na^+ free gel.

The interference of interstitial Na^+ and Cl^- in mass-transfer and supersaturation may not be removed in a rigorous treatment of the problem. On the other hand, the initial homogeneous concentration for both elements changes with diffusion time: the two solution reservoirs are, at the same time, reception chambers for Cl^- and Na^+ ions coming from the gel which is "unloaded" this way.

In fig. 3a, gel Na^+ unloading is shown. The reservoirs are initially filled with 8 cm^3 of bidistilled water. Once again, both edge conditions and curve morphologies change continuously with diffusion time. The curves would tend towards the horizontal at the limit.

Fig. 3b shows the interaction influence between different species in solution in the diffusivity of each one. In this case the solution reservoir No. 1 was filled with 1M $CaCl_2$ and No. 2 with bidistilled water. Consequently the gel unloading becomes asymmetric, decreasing the sodium diffusivity towards the reservoir that was filled with the reagent.

5. Free ions and ionic associations throughout the gel column

For gypsum growth [7], the supersaturation can be given as follows:

$$\beta = a(\mathrm{Ca}^{2+})\,a(\mathrm{SO}_4^{2-})/K_{\mathrm{sp}}, \qquad (1)$$

where $a(\mathrm{Ca}^{2+})$ and $a(\mathrm{SO}_4^{2-})$ are the activities of the free ions in solution and K_{sp} is the thermodynamic solubility product ($K_{\mathrm{sp}} = 10^{-4.62}$ at 25 °C).

Eq. (1) shows that the estimation of supersaturation requires knowledge of the free ion activities. Van Leeuwen and Blomen [3] express the driving force in terms of mole fractions and activity coefficients from the Debye–Hückel theory for moderately concentrated solutions. These authors have shown that this method gives accurate results up to very high supersaturations, even for the fairly soluble gypsum.

The application of the Debye–Hückel formula for an estimation of the activity coefficients requires a calculation of the ionic strength of the solution, and this involves the consideration of the ionic associations as well as of the existing free ions in solution [8]. This is especially important in

Table 2
Total sulphate concentration (mM/l) throughout the gel column for different diffusion times; mother solution 1M Na_2SO_4

Slice number	Diffusion time (days)				
	8	16	32	64	80
1	677	649	594	476	406
2	516	555	575	473	407
3	380	486	554	467	405
4	262	364	511	462	406
5	161	305	466	459	404
6	113	260	406	449	400
7	54	184	294	427	386
8	26	101	230	392	374
9	19	62	181	346	356
10	13	41	117	287	334
11	11	23	61	217	310
12	9	17	42	181	281
13	7	13	36	169	262
14	4	10	28	143	238
15	3	8	20	119	213
16	2	6	15	100	192
17	1	3	11	84	168
18	1	2	9	70	145
19	–	2	6	58	120
20	–	2	5	49	91
21	–	1	3	42	78
22	–	1	2	33	67
23	–	1	2	28	57
24	–	–	1	23	50
25	–	–	1	20	43
26	–	–	1	17	39
27	–	–	1	14	34
28	–	–	1	11	29

the case of gypsum, since the $CaSO_4$ soluble complex is almost as abundant in solution as the free ions [7].

In this particular way, based on the analytic values of total concentrations of chemical constituents in solution, free ion and complex concentrations must be calculated. This involves the resolution of a equation system that is formed by mass-balance equations and by ionic association equilibria. In the present case, the total concentrations in calcium, sulphate, sodium and chlorine are known from the chemical analysis of gel slices, the pH being a complementary piece of information. From these data, the concentration of both, free ions ($[Ca^{2+}]$, $[SO_4^{2-}]$, $[Cl^-]$, $[Na^-]$, $[H^+]$) and soluble complexes ($[CaSO_4]$, $[HSO_4^-]$, $[CaOH^+]$, $[NaSO_4^-]$, $[NaOH]$), must be figured out. With this aim, a microcomputer programme was used. The programme is similar to the one described by Lundager Madsen [8] for calcium oxalate. The equilibrium constants of ionic associations were obtained from Martell and Smith [9].

Fig. 4a shows the total concentration in calcium and sulphate ($[Ca^{2+}]_T$; $[SO_4^{2-}]_T$) of the gel slices.

Table 3
Profiles of pH for different diffusion times; mother solutions: 1M $CaCl_2$ and 1M NA_2SO_4; initial gel pH: 5.5

Slice number	Diffusion time (days)				
	8	16	32	64	80
1	6.2	6.2	6.1	6.0	6.0
4	5.9	6.0	6.0	6.0	6.0
8	5.7	5.8	5.9	6.0	6.0
12	5.5	5.7	5.9	5.9	6.0
16	5.6	5.8	5.9	6.0	6.0
20	5.9	6.0	6.0	6.2	6.1
24	6.0	6.2	6.2	6.2	6.2
28	6.4	6.4	6.3	6.2	6.2

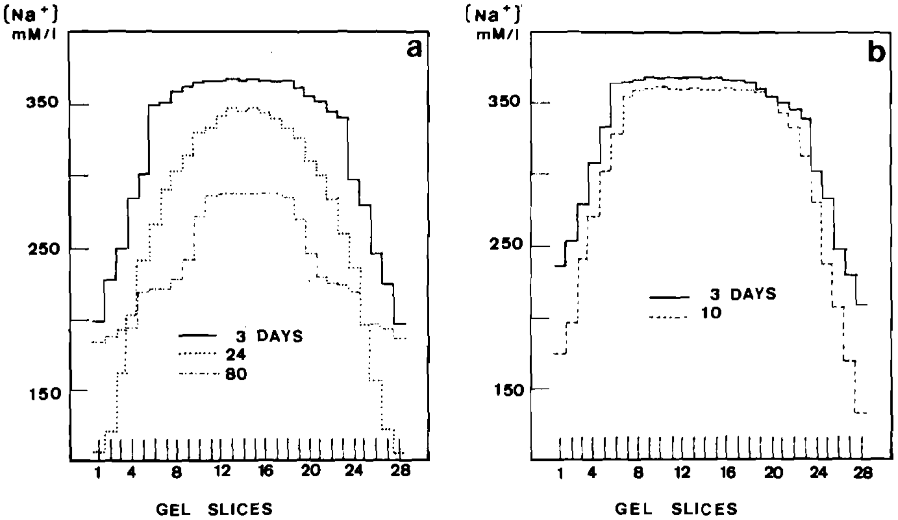

Fig. 3. Gel Na^+ unloading. (a) Both solution reservoirs filled with bidistilled H_2O. (b) Solution reservoir No. 1 filled with 1 M $CaCl_2$.

These data are compared with the values of their respective free ions. The curves have been obtained from 1M mother solutions after 50 days diffusion time. Total concentration values are much higher. This is due to the existence of calcium and sulphate forming complexes in solution.

Fig. 4b shows the concentrations of the most important complexes with SO_4^{2-} as a constituent. The concentration of the soluble complex $CaSO_4$, the major calcium "consumer", is maximum in slices 14 and 15. That is the point where the product of calcium and sulphate total concentrations is higher.On the contrary, $[NaSO_4^-]$ is higher where $[SO_4^{2-}]$ is also higher, that is to say, near the solution reservoir of this reagent. So, whereas the greatest difference between $[Ca]_T$ and $[Ca^{2+}]$ is

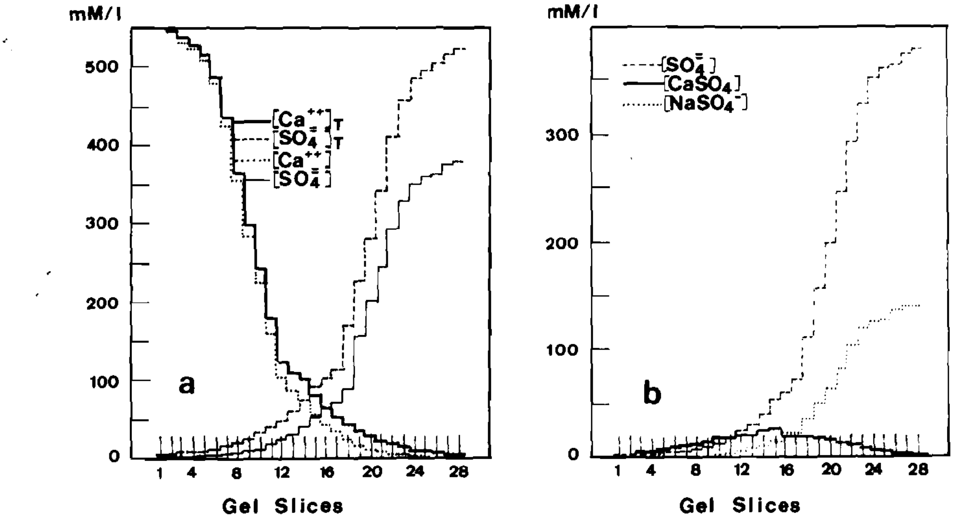

Fig. 4. Free ions and complexes throughout the gel column. Mother solutions: 1M $CaCl_2$ and 1M Na_2SO_4. Diffusion time: 50 days. (a) Total concentrations in relation to the respective free ion concentrations. (b) Concentration of sulphate main species throughout the gel column.

found in slices 14 and 15, in the case of sulphate this difference is maximum for slices 24–28.

The consideration of ionic associations is very important to calculate the actual supersaturation, considerably lower than the values that would be expected from the total concentrations. Furthermore, the unequal distribution of the different ionic associations throughout the gel column disturbs the spatial distribution of supersaturations, which has undoubted implications in the first precipitate location.

The knowledge of the concentration of free ions and complexes throughout the diffusion column allows us to work out the ionic strength and the activity coefficients Γ of the free ions. Finally, the knowledge of $[Ca^{2+}]$, $[SO_4^{2-}]$, $\Gamma(Ca^{2+})$ and $\Gamma(SO_4^{2-})$ allows us to calculate $a(Ca^{2+})$ and $a(SO_4^{2-})$ and hence the actual supersaturation β.

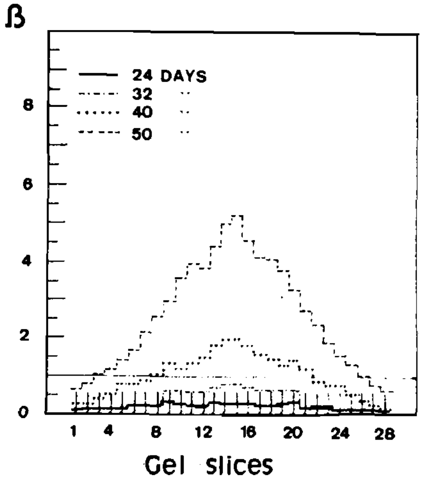

Fig. 5. Supersaturation throughout the gel column for different diffusion times. Mother solutions: 1M $CaCl_2$ and 1M Na_2SO_4. The base line for $\beta = 1$ detaches the unsaturated and the supersaturated regions.

6. Supersaturation evolution throughout the gel column

It has usually been considered that the first precipitate may develop at the point where the concentration product is maximum. Therefore, if the reagents' diffusion coefficients are equal (complete ionizations and independence of the diffusion coefficient related to the concentration level are assumed in this asserveration), the first precipitate must always form in the middle of the diffusion column, even for different initial concentrations of mother solutions. However, this prediction stands in contradiction to the experimental facts [10], meaning that either the simplifications introduced are not possible or a complementary hypothesis is necessary. The experimental testing of supersaturation may allow us to check whether the commonly made simplifications are excessive.

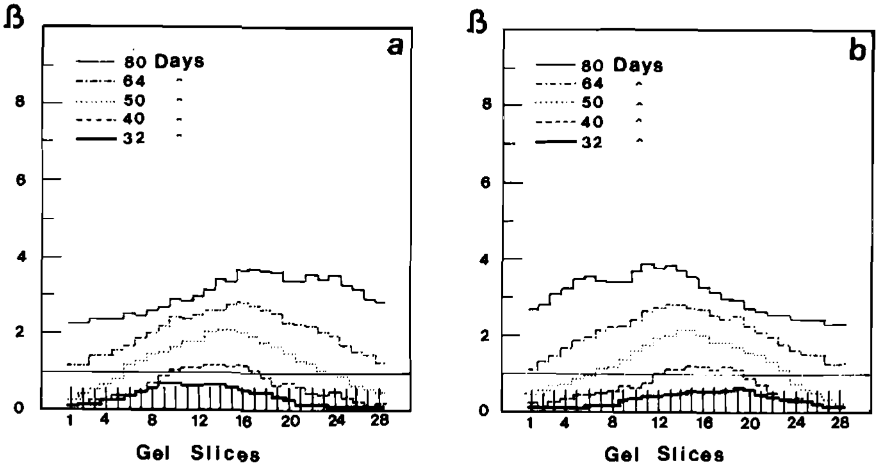

Fig. 6. Supersaturation throughout the gel column for different diffusion times. The base lines for $\beta = 1$ detach the unsaturated and supersaturated regions. (a) Mother solutions: 1M $CaCl_2$ and 0.3M Na_2SO_4; (b) Mother solutions: 0.3M $CaCl_2$ and 1M Na_2SO_4.

The supersaturation has been calculated from analytical data by means of the procedure described in section 5. Figs. 5 and 6 show the supersaturation values throughout the gel column for different initial concentrations of mother solutions.

The results are not adaptable to simple curves. When the initial concentration for both mother solutions is the same (fig. 5), the highest supersaturation is reached in slice 15 for all diffusion times. The slight shifting of this maximum from the middle of the column is easily understandable by the lower diffusion coefficient of SO_4^{2-}, this being the reagent towards which this maximum is displaced.

However, when the concentrations for both mother solutions are different, the maximum supersaturation is not in the middle and its location changes notable in time. Figs. 6a and 6b show this evolution. Both figures look symmetrical to each other. The 32-day curve maximum is shifted towards the highest concentration reagent, but as time goes by it is progressively displaced towards the reagent of lower concentration.

The preceding phenomena may only be explained under the concentration influence in the reagent's diffusion coefficient. This is especially evident in the case of the two mother solutions with very different initial concentrations. Moreover, the interaction between the two reagents, diffusing from both ends, produces cross-interference in their respective diffusivities, and this is another factor to take into account. Finally, free ion and complex distribution throughout the gel column may also influence the supersaturation maximum location. At any rate, experimental facts show that the commonly made simplifications to model the mass-transfer may lead to remarkable deviations from reality. Any interpretation of the first precipitate location must be found in the actual distribution of the supersaturation and other experimental data. For instance, the knowledge of actual concentration distributions is important to check in which region of the gel column the "equality range" condition [5] is fulfilled.

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