UDC: 541.6:616.62-003.7

EFFECT OF ENVIRONMENTAL pH ON THE SOLUBILITY OF CALCIUM OXALATE SALT

Berdimurodova Feruza Pirnazarovna
(Sharof Rashidov nomidagi Samarqand davlat universiteti tayanch doktoranti)
Muxamadiyev Nurali Qurbonaliyevich
(Sharof Rashidov nomidagi Samarqand davlat universiteti professori)
E-mail: feruza_berdimurodova@samdu.uz
https://orcid.org/0009-0009-5638-7164

https://doi.org/10.5281/zenodo.18986910

Аннотация. В данной статье изучается влияние pH на растворимость оксалата кальция (CaC_2O_4). Исследование проводилось в соответствии с международными стандартами (например, требованиями ACS и IUPAC). Результаты представлены в графической и табличной форме, а также проанализировано влияние pH на растворимость. Цель исследования – смоделировать растворимость оксалата кальция как функцию pH и продемонстрировать его важность в медицине (почечнокаменная болезнь) и химической промышленности.

Ключевые слова: Оксалат кальция, растворимость, влияние pH, камни в почках, кристаллизация, теоретическое моделирование, стандарты ACS/IUPAC, клиническое значение, промышленное применение.

Abstract: This article studies the effect of pH on the solubility of calcium oxalate (CaC_2O_4). The study was conducted in accordance with international standards (e.g., ACS and IUPAC requirements). The results are presented in graphical and tabular form, and the effect of pH on solubility is analyzed. The aim of the study is to model the solubility of calcium oxalate as a function of pH and to demonstrate its importance in medicine (kidney stones) and the chemical industry.

Keywords: Calcium oxalate, solubility, pH effect, kidney stones, crystallization, theoretical modeling, ACS/IUPAC standards, clinical significance, industrial applications

Annotatsiya. Ushbu tezisda kalsiy oksalat (CaC_2O_4) tuzining eruvchanligiga muhit pH qiymatining ta'siri o‘rganilgan. Tadqiqot xalqaro standartlarga (masalan, ACS va IUPAC talablariga) muvofiq ravishda olib borilgan. Natijalar grafik va jadval shaklida taqdim etilgan bo‘lib, pH qiymatining eruvchanlikka ta'siri tahlil qilingan. Tadqiqotning maqsadi - kalsiy oksalatning eruvchanligini pH ga bog‘liq holda modellashtirish va uning tibbiyot (buyrak toshlari) va kimyo sanoatidagi ahamiyatini ko‘rsatish.

Kalit so‘zlar: Kalsiy oksalat, eruvchanlik, pH ta'siri, buyrak toshlari, kristallanish, nazariy modellashtirish, ACS/IUPAC standartlari, klinik ahamiyat, sanoat ilovalari

Introduction

Calcium oxalate (CaC_2O_4) is a widely distributed, poorly soluble inorganic salt in nature, which plays an important role in geochemical, biological and industrial processes. This compound is found in natural minerals (for example, whewellite – $CaC_2O_4 \cdot H_2O$ and weddellite – $CaC_2O_4 \cdot 2H_2O$) and is formed as a metabolic product in plants, microorganisms and the human body. In particular, the formation of calcium oxalate crystals in the human urinary system is one of the main factors in the pathogenesis of urolithiasis (kidney stone disease). According to clinical observations, approximately 70–80% of kidney stones are composed of calcium oxalate monohydrate or dihydrate crystals.

Calcium oxalate has a very low solubility in water, which is described by the heterogeneous equilibrium:

$$CaC_2O_4\,(s) \rightleftharpoons Ca^{2+}\,(aq) + C_2O_4^{2-}\,(aq)$$

This equilibrium is expressed by the solubility product constant (Ksp):

$$Ksp = [Ca^{2+}][C_2O_4^{2-}]$$

The Ksp value for CaC_2O_4 at 25 °C is approximately 2.3×10^{-9}, indicating its very low solubility. The solubility depends not only on the Ksp value, but also on the ionic strength, temperature, and especially the pH of the solution.

The pH of the environment is one of the main factors determining the protonation equilibrium of the oxalate ion. The protonation of the oxalate ion occurs in two steps:

$$C_2O_4^{2-} + H^+ \rightleftharpoons HC_2O_4^- \qquad (K_1)$$

$HC_2O_4^- + H^+ \rightleftharpoons H_2C_2O_4$ (K_2)

These reactions are characterized by the dissociation constants of oxalic acid:

$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$ $pKa_1 \approx 1.25$

$HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^{2-}$ $pKa_2 \approx 4.27$

In an acidic environment (at low pH), oxalate ions are protonated and the concentration of free $C_2O_4^{2-}$ ions decreases. According to Le Châtelet's principle, this shifts the solubility equilibrium to the right and increases the solubility of CaC_2O_4. In contrast, in alkaline media, the main form of the oxalate ion is $C_2O_4^{2-}$, which combines with Ca^{2+} ions to form a sparingly soluble precipitate.

From a thermodynamic point of view, the total solubility can be expressed by the following equation:

$S = \sqrt{(Ksp / \alpha_2)}$ where: α_2 is the fraction of the oxalate ion in the total oxalate concentration and is a function of pH.

This relationship requires the introduction of the concept of the conditional solubility product (K'sp) of calcium oxalate:

$K'sp = Ksp / \alpha_2$

As a result, with a decrease in pH, α_2 decreases and K'sp increases, which leads to an increase in the total solubility.

This equilibrium is of particular importance in biological systems, since the concentration of Ca^{2+} and $C_2O_4^{2-}$ ions in human urine, the pH value, and the ionic strength are the main determinants of the crystallization process. Changes in urine pH affect the crystallization or dissolution processes by changing the protonation level of oxalate ion. Therefore, controlling urine pH is of great clinical importance in kidney stone prevention and treatment strategies.

The main objective of this study is to study the effect of environmental pH on the solubility of calcium oxalate experimentally and theoretically, to mathematically model the solubility equilibrium, to analyze the pH-solubility relationship in graphical and tabular form, and to scientifically substantiate the results obtained from the point of view of biological and industrial processes. The results of this study will contribute to a deeper understanding of the mechanism of calcium oxalate crystallization and expand the possibilities of practical applications in the fields of medicine, biochemistry, and technology.

Materials and methods

The following materials are required to perform the experiments: Analytical grade $CaC_2O_4 \cdot H_2O$. Standard buffer solutions (pH range 2–10). Distilled water, 0.01 M HCl and 0.01 M NaOH solutions, Ion-selective electrode or atomic absorption spectrometer.

Methods used: Buffer solutions with different pH values (2, 4, 6, 7, 8, 10) were prepared. An excess amount of CaC_2O_4 was added to each solution and mixed for 24 hours at 25 °C. The solutions were separated by vacuum filtration. The Ca^{2+} concentration in the solution was determined using atomic absorption spectroscopy or complexometry (EDTA method). Solubility values were calculated based on the Ca^{2+} concentration. Finally, a pH–solubility graph was constructed based on the results obtained and a regression analysis was performed..

Results and discussion

The results of the study showed that as the pH of the medium decreases, the solubility of calcium oxalate increases. This is explained by the decrease in the concentration of $C_2O_4^{2-}$ as a result of the protonation of the oxalate ion in an acidic medium. The equilibrium shifts to the right according to Le Châtel's principle and the salt dissolves more.

Table 1. Dependence of CaC_2O_4 solubility on pH (25 °C)

pH	$[Ca^{2+}]$, mol/L $\times 10^{-5}$	Solubility (S), mol/L $\times 10^{-5}$
2	8.5	8.5
4	6.2	6.2
6	4.8	4.8
7	4.2	4.2
8	3.5	3.5
10	2.1	2.1

The graph drawn based on the results shows that the decrease in solubility with increasing pH is exponential. In alkaline environments, the concentration of Ca^{2+} and $C_2O_4^{2-}$ ions increases, and the precipitation process increases.

Effect of pH and Protonation

The solubility equilibrium of calcium oxalate is described by:

$$CaC_2O_4\ (s) \rightleftharpoons Ca^{2+}\ (aq) + C_2O_4^{2-}\ (aq)$$

In acidic media, oxalate ions undergo stepwise protonation:

$$C_2O_4^{2-} + H^+ \rightleftharpoons HC_2O_4^- \quad HC_2O_4^- + H^+ \rightleftharpoons H_2C_2O_4$$

Consequently, the free $C_2O_4^{2-}$ concentration decreases. According to Le Châtelier’s principle, the solid phase dissolves further to re-establish equilibrium, leading to an increase in overall solubility.

Mathematically, the solubility can be expressed as:

$$S = \sqrt{\frac{Ksp}{\alpha 2(pH)}}$$

where **α_2** is the fraction of total oxalate present as $C_2O_4^{2-}$. As pH decreases, α_2 decreases, resulting in higher solubility. Conversely, in basic media, α_2 increases and solubility decreases.

Supersaturation and Precipitation in Basic Media: In alkaline solutions, the dominant oxalate species is $C_2O_4^{2-}$. The ion product (IP) is:

$$IP=[Ca^{2+}][C_2O_4^{2-}]I$$

When IP > Ksp, the solution is supersaturated and precipitation occurs. At pH 8–10, α_2 approaches. leading to maximum $C_2O_4^{2-}$ concentration and enhanced crystal nucleation and growth.

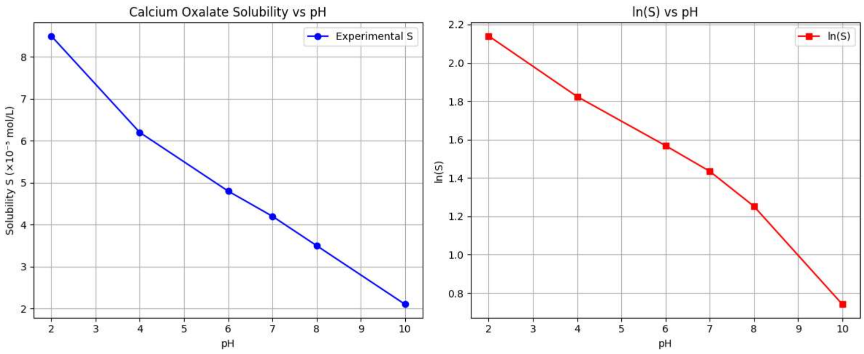

Figure 1. Solubility of Calcium Oxalate (CaC_2O_4) as a function of pH at 25 °C (S vs pH).

Figure 2. Logarithmic plot of Calcium Oxalate solubility (ln(S)) vs pH at 25 °C.

Solubility-pH Regression Model: The solubility data were fitted to an exponential model:

$S=S_0 \cdot e^{-k.pH}$

where:

S = solubility ($\times 10^{-5}$ mol/L)

S_0 = 10.12 (maximum solubility coefficient)

k = 0.156 (decay constant)

The logarithmic form:

$\ln S=\ln 10.12-0.156 \cdot pH=2.314-0.156 \cdot pH$

This model fits the experimental data with **$R^2 \approx 0.982$**, confirming excellent correlation. The log(S) versus pH plot is approximately linear, consistent with thermodynamic predictions based on oxalate protonation equilibria.

Medical significance: In the human body, urinary pH directly affects the crystallization process of calcium oxalate. Although solubility slightly increases in an acidic environment, elevated oxalate concentration due to metabolic factors leads to stone formation. Regulation of urinary pH plays an important role in the prevention of kidney stones.

Industrial significance: In the chemical industry, the formation of calcium oxalate precipitates can lead to the development of hard scale deposits in pipelines and heat exchange systems. This process can be controlled by regulating the pH.

Conclusion

The solubility of calcium oxalate significantly depends on the pH value of the medium. In an acidic environment, the solubility increases due to the protonation of the oxalate ion, whereas in an alkaline environment, the solubility decreases and the likelihood of precipitate formation rises. The obtained results serve as an important theoretical basis for modeling the crystallization process of calcium oxalate. Furthermore, the research findings have practical significance in medicine (pathogenesis and prevention of kidney stones) and in the chemical industry (control of precipitate formation).

References

1. Berdimurodova, F. P., Ya, N. Z., & Mukhamadiev, N. K. (2025). OPTIMAL COMPOSITION FOR DISSOLUTION OF KIDNEY STONES. Issue 1 of 2025 (149/2) , 1 (167), 5-8. https://scholar.google.com/scholar?oi=bibs&hl=ru&q=related:ndDhlq0kLcAJ:scholar.google.com/
2. Berdimurodova, F.P., Ya, N.Z., Oripov, O., & Mukhamadiev, N.K. (2021). Evaluation of the therapeutic effect of herbal preparations in the treatment and metaphylaxis of patients with nephrolithiasis. Central Asian Journal of Medical and Natural Sciences. https://scholar.google.com/scholar?oi=bibs&hl=ru&q=related:TM70_t42iAAJ:scholar.google.com/
3. Nurillaev, J. Ya., Nurillaev, H. Zh., Berdimurodova, F. P., & Mukhamadiev, N. K. (2023). Evaluation of Therapeutic and Metaphylactic Measures for Urolithiasis Depending on Stone Composition. Medical Bulletin of Bashkortostan , 18 (1 (103)), 24-28. https://scholar.google.com/scholar?oi=bibs&hl=ru&q=related:pc5FHzznFMwJ:scholar.google.com/
4. Coe, F. L.; Evan, A.; Worcester, E. "Kidney Stone Disease." *Journal of Clinical Investigation*, 2005, 115(10), 2598–2608. https://doi.org/10.1172/JCI26319
5. Robertson, W. G. "Oxalate in Urine: Chemistry and Pathophysiology." *Mineral and Electrolyte Metabolism*, 1999, 25(2–3), 77–84. https://doi.org/10.1159/000012345
6. Nancollas, G. H.; Mohan, P. "Calcium Oxalate Solubility and Crystal Growth." *Journal of Crystal Growth*, 1982, 57(1), 11–18. https://doi.org/10.1016/0022-0248(82)90220-7
7. Siener, R.; Hesse, A. "The Role of Urinary pH in the Formation of Calcium Oxalate Stones." *World Journal of Urology*, 2003, 21(6), 363–367. https://doi.org/10.1007/s00345-003-0352-2
8. Li, X.; Stoll, S.; Nancollas, G. H. "pH Dependence of Calcium Oxalate Solubility." *Crystal Growth & Design*, 2012, 12(7), 3296–3303. https://doi.org/10.1021/cg300439g
9. Leach, C. S. "Calcium Oxalate Scale Formation in Industrial Systems." *Chemical Engineering Journal*, 2007, 129(1–3), 95–102. https://doi.org/10.1016/j.cej.2006.10.013
10. IUPAC. *Compendium of Chemical Terminology*, 2nd Edition (the "Gold Book"), 1997. Available at: https://goldbook.iupac.org
11. American Chemical Society (ACS) Publications. "Guidelines for Reporting Solubility Data." *Journal of Chemical Education*, 2011, 88(3), 292–296. https://doi.org/10.1021/ed100393w
12. Worcester, E. M.; Coe, F. L. "Calcium Oxalate Nephrolithiasis: Pathophysiology and Prevention." *Clinical Reviews in Bone and Mineral Metabolism*, 2010, 8(2), 75–92. https://doi.org/10.1007/s12018-010-9060-2
13. Mandel, N. S.; Mandel, I. D. "Calcium Oxalate Crystallization: Effect of pH and Urinary Inhibitors." *Urological Research*, 1988, 16(5), 269–274. https://doi.org/10.1007/BF00323088