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Solubility of the Three Calcium Oxalate Hydrates in Sodium Chloride Solutions and Urine-Like Liquors

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Summary. Calcium oxalate forms three hydrates (stable monoclinic mono-hydrate (*COM*), metastable tetragonal dihydrate (*COD*) and triclinic trihydrate (*COT*)), which are of medical importance in urinary calculi formation. In this work, the solubility of these calcium oxalate hydrates was determined at 20, 25, 30, 37, and 40°C in aqueous NaCl (0.02–0.20 mol · dm^{-3}) and in urine-like liquors. Also, for the first time, the solubility of *COM* was systematically studied as a function of *pH* in artificial urine solutions which contain organic compounds. The concentrations of calcium ions were measured continuously using a calcium ion selective electrode and also determined by AAS. The thermodynamic solubility products were obtained from computer simulations in which all possible complexes formed in aqueous solution were taken into account. These values were compared to those available in the literature; it was found that the present results, especially for *COD* and *COT*, constitute a major improvement on the previously reported values. The constants determined in this work were used to predict the solubility of calcium oxalate hydrates at different *pH* in urine-like liquors. It was found that in artificial urine solutions, citrate and magnesium ions promote the solubility of *COM*, whereas urea and creatinine have no significant effect.

Keywords. *COM*; *COD*; *COT*; Computer simulations; Renal calculi.

Löslichkeit der drei Calciumoxalathydrate in Natriumchloridlösungen und urinähnlichen Flüssigkeiten

Zusammenfassung. Calciumoxalat bildet das stabile monokline Monohydrat (*COM*) sowie zwei metastabile Phasen, das tetragonale Dihydrat (*COD*) und das trikline Trihydrat (*COT*). Da die drei Calciumoxalathydrate bei der Entstehung von Nierensteinen eine wichtige Rolle spielen, wurde ihre Löslichkeit bei 20, 25, 30, 37, und 40°C in NaCl-Lösungen (0.02–0.20 mol · dm^{-3}) sowie in künstlichen Urinlösungen, die zum Teil auch organische Substanzen enthielten, gemessen. In letzteren wurde die Löslichkeit von *COM* als Funktion des *pH*-Werts erstmalig systematisch untersucht. Die Ca^{2+}-Konzentrationen wurden mit Hilfe einer ionenselektiven Elektrode sowie durch AAS bestimmt. Die thermodynamischen Löslichkeitsprodukte wurden aus Computersimulationen erhalten, in denen die in der wäßrigen Lösung vorkommenden Komplexe weitestgehend

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berücksichtigt wurden. Beim Vergleich dieser Größen mit Literaturwerten stellte sich heraus, daß insbesondere die Werte für *COD* und *COT* eine wesentliche Verbesserung gegenüber den bisherigen Daten darstellen. Die in dieser Arbeit ermittelten Löslichkeitsprodukte wurden zur Berechnung der Löslichkeit der Calciumoxalathydrate in künstlichem Urin verwendet. Es zeigte sich, daß Mg^{2+} und Citrat die Löslichkeit erhöhen, wogegen Harnstoff und Creatinin keine signifikante Auswirkung haben.

Introduction

It is generally accepted that human urine is commonly supersaturated with respect to the three hydrates of calcium oxalate, *i.e.* the stable monoclinic monohydrate (*COM*) as well as the metastable tetragonal dihydrate (*COD*) and triclinic trihydrate (*COT*). Calcium oxalate monohydrate (whewellite) and dihydrate (weddellite) together with calcium phosphate (hydroxyapatite) are the major components of most of the urinary calculi [1, 2]. Calcium oxalate trihydrate has been rarely found in kidney stones [3], but it might be important as a possible precursor in their formation [4, 5].

Although the thermodynamic solubility products of *COM*, *COD*, and *COT* have been reported in literature at some temperatures, more refined values are required for the proper prediction of the solubility of calcium oxalate hydrates in, for example, urine. In this work, the solubility of all three hydrates was measured at various temperatures, ionic strengths (with NaCl as background electrolyte), and in urine-like liquors. The thermodynamic solubility products determined were incorporated into the JESS (Joint Expert Speciation System [6–8]) database which was then employed in computer simulations to predict the solubility of *COM*, *COD*, and *COT* in various solutions. Moreover, for the first time the solubility of *COM* was studied as a function of *pH* in artificial urine solutions which contain organic compounds such as citrate, urea, and creatinine.

Results and Discussion

Determination of Ca^{2+} concentrations

X-ray diffraction, thermogravimetric analyses, and SEM photos of the samples after the solubility measurements confirmed that both *COD* and *COT* were not transformed to *COM* under the present experimental conditions. Results of the dissolution experiments in NaCl solutions, measured at least in duplicate, are summarized in Table 1.

The discrepancies between the AAS and ISE results in Table 1 deserve to be discussed in detail. Due to the formation of CaC_2O_4 (*aq*) complexes, the AAS results for Ca^{2+} concentrations were expected to be higher than the potentiometric ISE data. Generally, this was the case, but the difference was often significantly larger than the calculated concentrations of $CaC_2O_4(aq)$ complexes (1–4% of the total Ca^{2+} concentrations, depending on the solid phase and the NaCl concentrations). Moreover, some of the AAS results were lower than the ISE data. Thus, the formation of $CaC_2O_4(aq)$ complexes cannot be solely responsible for the discrepancies in Table 1. Given that the experimental reproducibility of the ISE and AAS measurements is about $\pm 4\%$ and $\pm 2.5\%$, respectively, these two

Table 1. Solubility of calcium oxalate hydrates in NaCl solutions

t (°C)	[NaCl]	$10^4 \cdot [Ca^{2+}](mol \cdot dm^{-3})$					
		COM		*COD*		*COT*	
	$(mol \cdot dm^{-3})$	ISE	AAS	ISE	AAS	ISE	AAS
20	0.02	0.64	0.73	1.07[1]	1.26[1]	1.21	1.30
	0.05	0.83	0.94	1.32[1]	1.50[1]	1.58	1.65
	0.10	0.99	1.11	1.66[1]	1.83[1]	1.91	2.01
	0.20	1.28	1.43	2.19[1]	2.30[1]	2.44	2.61
25	0.02	0.70	0.78	1.21[2]	1.35[2]	1.33	1.49
				1.16[1]	1.27[1]		
	0.05	0.94	0.98	1.52[2]	1.70[2]	1.74	1.86
				1.55[1]	1.63[1]		
	0.10	1.15	1.23	1.88[2]	2.12[2]	2.17	2.32
				1.93[1]	2.00[1]		
	0.20	1.45	1.61	2.48[2]	2.58[2]	2.84	2.85
				2.58[1]	2.45[1]		
30	0.02	0.83	0.83	1.37[1]	1.52[1]	1.62	1.68
	0.05	1.01	1.10	1.82[1]	1.94[1]	2.07	2.09
	0.10	1.27	1.35	2.09[1]	2.19[1]	2.58	2.74
	0.20	1.64	1.66	2.72[1]	2.71[1]	3.39	3.32
37	0.02	0.88	0.93	1.50[2]	1.70[2]	1.81	1.97
				1.47[1]	1.62[1]		
	0.05	1.17	1.15	1.96[2]	2.02[2]	2.45	2.35
				1.99[1]	2.08[1]		
	0.10	1.38	1.43	2.58[2]	2.83[2]	2.98	3.02
				2.43[1]	2.59[1]		
	0.20	1.94	1.98	3.33[2]	3.24[2]	4.04	4.18
				3.22[1]	3.08[1]		
40	0.02	0.91	0.94	1.61[2]	1.67[2]	1.93	2.03
				1.54[1]	1.76[1]		
	0.05	1.19	1.18	2.01[2]	2.18[2]	2.57	2.52
				2.07[1]	2.12[1]		
	0.10	1.52	1.48	2.81[2]	2.97[2]	3.24	3.20
				2.57[1]	2.74[1]		
	0.20	2.03	1.98	3.46[2]	3.24[2]	4.31	4.35
				3.36[1]	3.24[1]		

[1] *COD* Sample 2; [2] *COD* Sample 1

techniques were not sensitive enough for a quantitative evaluation of the concentration of the $CaC_2O_4(aq)$ complexes. Although the results qualitatively indicated the existence of $CaC_2O_4(aq)$ species, the average of ISE and AAS results was taken as the total Ca^{2+} concentrations in all subsequent calculations with an estimated experimental uncertainty below 5%.

It has to be noted that the results obtained from *COD* Sample 2 are very similar to those from *COD* Sample 1 (see Experimental). Therefore, the method to prepare *COD* given in Ref. [13] is recommended being simpler than that of Ref. [12].

Solubility of calcium oxalate hydrates in NaCl solutions

The thermodynamic solubility products of *COM*, *COD*, and *COT* were derived using the JESS package of computer programs [6–8]. The experimental total concentrations of Ca^{2+}, which should be equal to those of oxalate, were employed to calculate the Ca^{2+} and oxalate speciation in the saturated solutions of the calcium oxalate hydrates in NaCl media. The extrapolation of the products of the free concentrations to $I = 0$ was performed with some of the built-in activity coefficient models of JESS. These were the extended *Debye-Hückel* equation when the semi-empirical species-specific parameters were known, and the *Davies* equation in all other cases. The thermodynamic solubility products calculated in this way are given in Table 2 and shown in Fig. 1 together with the literature values.

Our K_{s0} values for COM agree with most of the previously reported values and are, moreover, perfectly consistent with recent calorimetric data [20]. The solid line in Fig. 1 was constructed using the enthalpies of crystallization of *COM* measured at 25 and 37°C (-19.83 ± 1.24 and $-16.69 \pm 0.58\,\mathrm{kJ \cdot mol^{-1}}$,

Table 2: Calculated thermodynamic solubility products of calcium oxalate hydrates

	$-\log K_{s0}$ ($\mathrm{mol^2 \cdot dm^{-6}}$)		
t (°C)	*COM*	*COD*	*COT*
20	8.84±0.02	8.42±0.02	8.33±0.01
25	8.77±0.01	8.34±0.02	8.24±0.01
30	8.71±0.01	8.26±0.03	8.12±0.02
37	8.65±0.03	8.17±0.03	8.02±0.02
40	8.62±0.02	8.13±0.04	7.97±0.02

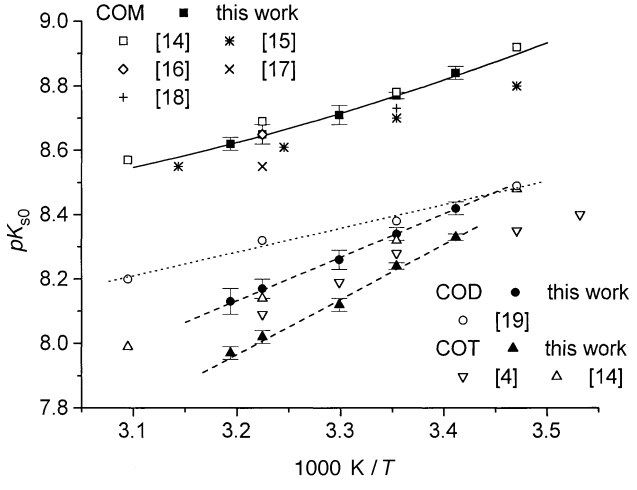

Fig. 1. Temperature dependence of *COM*, *COD*, and *COT* solubility products; the solid line is consistent with calorimetric data for *COM* [20], the dashed and dotted lines were obtained by linear regression analysis applied to the data of this work and of Ref. [19], respectively

respectively) [20]. In the case of *COD* and *COT*, however, there are marked differences between the values obtained in this work and those reported previously which, for most temperatures, are higher than the present constants [4, 14, 19]. Another discrepancy concerns the enthalpies of dissolution derived from the temperature dependence of the solubility constants in terms of the *van't Hoff* equation. Since the enthalpies of dehydration, corresponding to *e.g.* $COT \rightarrow COD + H_2O(aq)$ or $COD \rightarrow COM + H_2O(aq)$, are always positive [21] (a rule which has already been discovered 120 years ago [22]), the enthalpies of dissolution should become progressively more endothermic with increasing extent of hydration. Whereas this is true for the present results (ΔH^o of 16.7 to 19.8 [20], 25.6 and 32.1 $kJ \cdot mol^{-1}$ for *COM*, *COD*, and *COT*, respectively), this is not the case for ΔH^o derived from literature solubility constants [14, 19] (17.3, 14.1 and 25.1 $kJ \cdot mol^{-1}$ for *COM*, *COD*, and *COT*, respectively).

In Figs. 2–4, the present solubilities in NaCl solutions are compared to previously reported data. It should be emphasized again that the excellent agreement between the present experimental results and the calculated curves was achieved by adjusting the solubility products only. The aqueous model employed was generated by JESS using the literature formation constants stored in the JESS thermodynamic database.

COM

The literature solubility data are generally higher than the present ones as can be seen from Fig. 2. *Hammarsten*'s results [23] at 37°C are smooth; however, this author reported that her data were not consistent with the *Debye-Hückel* law even at very low ionic strength. *Knappwost* and *Matouschek*'s data [24] show a large scatter, some of them are lower and some are higher than the data from all other sources. The data of Ref. [25] are actually total oxalate concentrations which should be equal to total Ca^{2+} concentrations. Although *Tomazic* and *Nancollas*' results [14] are also higher than ours, their calculated thermodynamic solubility

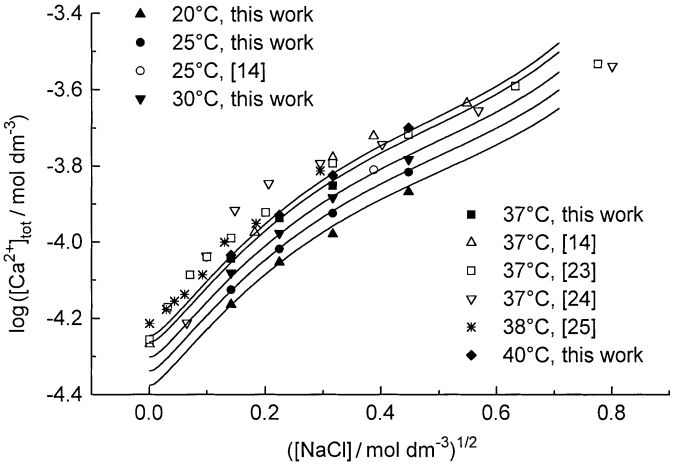

Fig. 2. Solubility of *COM* in NaCl solutions; the calculated curves correspond to 20, 25, 30, 37, and 40°C, respectively

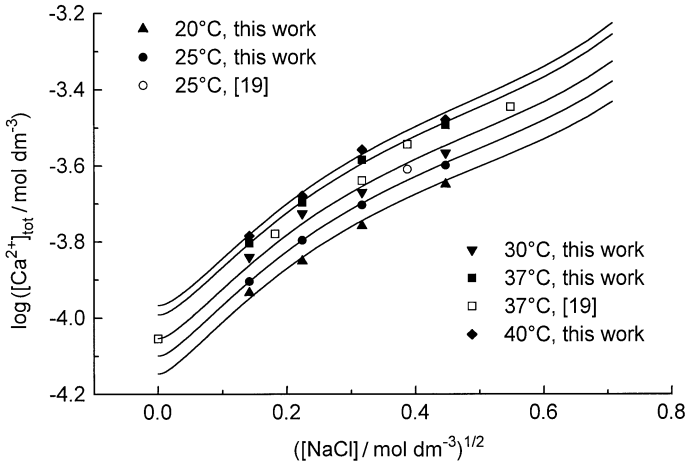

Fig. 3. Solubility of *COD* in NaCl solutions; the calculated curves correspond to 20, 25, 30, 37, and 40°C, respectively

products are lower (Fig. 1). The reason most likely stems from the different speciation models for the aqueous phase used by the two groups. Moreover, it is not quite clear how these authors [14] calculated the ionic strengths of their equilibrated solutions.

COD

Figure 3 shows that *Tomazic* and *Nancollas*' results [19] for 25 and 37°C are slightly higher and lower than the current ones.

COT

On the other hand, despite being the least stable hydrate, *Tomazic* and *Nancollas*' solubilities for *COT* [14] are in excellent agreement with ours (Fig. 4). However,

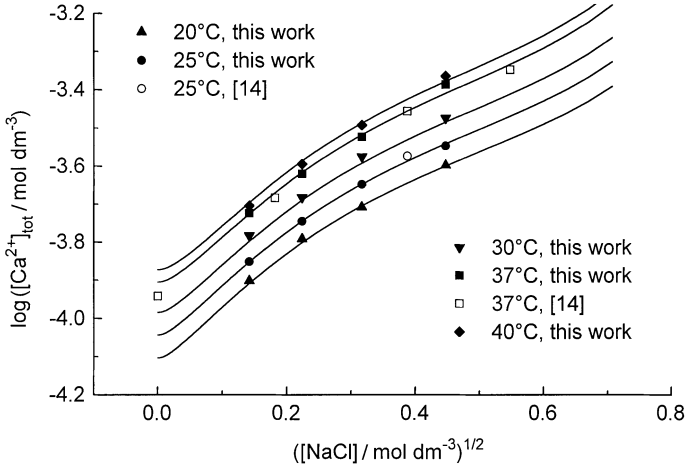

Fig. 4. Solubility of *COT* in NaCl solutions; the calculated curves correspond to 20, 25, 30, 37, and 40°C, respectively

again their solubility products derived from these data are lower than the present ones (Fig. 1).

Solubility of calcium oxalate hydrates in urine-like liquors

For the calculation of the total Ca^{2+} concentration in artificial urine, it is necessary to take into account the formation of all possible complexes in the solution. The values of their thermodynamic formation constants were taken from the JESS database, and the simulation was performed using the JESS computer programs [6–8] with a urine model like that employed previously [26]. In this way, a good agreement between the experimental and calculated values for the solubility of the three calcium oxalate hydrates in urine-like liquors (see Experimental) was obtained as shown in Table 3 and Fig. 5.

Table 3. Solubility of calcium oxalate hydrates in urine-like liquors

	$10^4 \cdot [Ca^{2+}](mol \cdot dm^{-3})$								
t (°C)	*COM*			*COD*			*COT*		
	ISE	AAS	calc.	ISE	AAS	calc.	ISE	AAS	calc.
25	2.29[1]	2.48[1]	2.26	3.77[1]	3.89[1]	3.78	4.38[1]	4.46[1]	4.54
	2.51[2]	2.58[2]	2.57	4.08[2]	4.25[2]	4.20	4.80[2]	4.77[2]	4.72
37	2.98[1]	3.11[1]	2.85	4.96[1]	4.79[1]	5.00	6.09[1]	6.22[1]	5.79
	3.12[2]	3.22[2]	3.32	5.16[2]	5.24[2]	5.66	6.50[2]	6.52[2]	6.46
40	3.13[1]	2.98[1]	3.05	5.14[1]	5.09[1]	5.43	6.34[1]	6.36[1]	6.16

[1] Urine 1, COD Sample 1; [2] Urine 2, COD Sample 2

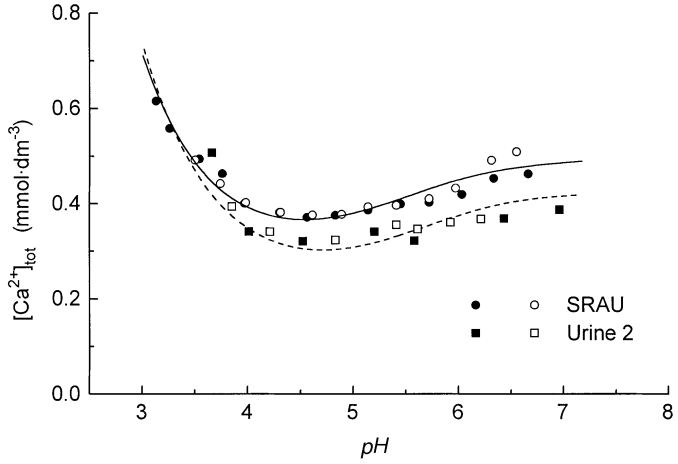

Fig. 5. Solubility of *COM* in *SRAU* (circles) and Urine 2 (squares) at 37°C; two series of measurements are shown (solid and open symbols); solid and dashed lines were calculated using JESS

It should be noted that from the computer simulations for Urine 1 (without any other organic substances besides oxalate), the free Ca^{2+} concentrations were calculated to be 25 to 40% lower than the concentrations shown in Table 3. This supports the conclusion that the ISE data represent total Ca^{2+} concentrations, provided that the calibrating solutions have the same background electrolytes as the solutions used in the solubility experiments. The predominant Ca^{2+} complexes involve phosphate, chloride, and sulfate. Regarding the distribution of oxalate, only up to *ca*. 50% are free, whereas the major complexes are formed with Mg^{2+} and Na^{+}. It is noteworthy that $CaC_2O_4(aq)$ contributes only to *ca*. 2% of the total Ca^{2+} or oxalate concentrations.

pH Dependence of the solubility of COM in urine-like liquors

The solubility of *COM* was studied as a function of *pH* at 37°C in artificial urine solutions containing organic compounds such as citrate, urea, and creatinine (Urine 2 and *SRAU* in Table 5). Figure 5 shows the solubility of *COM* measured in *SRAU* (circle symbols) and in Urine 2 (square symbols); the curves were calculated using JESS. The models of *SRAU* and Urine 2 have the same composition as the artificial urine solutions shown in Table 5, but without urea and creatinine. The reason is that only very few of the required formation constants of metal ions with urea and creatinine have been reported in the literature. Nevertheless, the good agreement between the calculated curves and the experimental data shown in Fig. 5 reveals the obviously weak interaction between these compounds and Ca^{2+}. It should be noted that due to the high concentration of urea in Urine 2, this artificial urine becomes mouldy after a few days; thus, the solution should be kept in a refrigerator to prolong its life, and acidification is necessary to preserve the sample at the end of each solubility measurement. However, in order to avoid any influence on the solubility, no substances known to prevent the growth of bacteria (*e.g*. H_2O_2) were added to the test solutions. Therefore, probably because of the decomposition of urea, the results obtained from Urine 2 are not as good as from *SRAU* (Fig. 5).

Although the *pH* range of urine is quite wide (*ca*. 4.5 to 8.5), no experimental data for $pH > 7.5$ were collected because the precipitation of calcium phosphates was predicted by computer simulations. This work covers the *pH* from 3.5 to 7.5, and the solubility of *COM* was found to be higher in *SRAU* than in Urine 2; this is because there are more Ca^{2+} complexing agents (such as citrate, sulfate, and phosphate) present in *SRAU* (Table 5). It was also found that the solubility of *COM* reaches its minimum at a *pH* around 4.5 and 4.7 in *SRAU* and *Urine* 2, respectively. In both solutions, the solubility of *COM* increases at higher *pH*, but even more rapidly at the acidic end due to the formation of hydrogenoxalate. As expected, at $pH < 3$ aqueous Ca^{2+} exists as the predominant species. At higher *pH*, citrate plays an important role in the solubility of *COM*, and to a lesser extent phosphate also takes part. Table 4 shows the distribution of Ca^{2+} and oxalate at some *pH* values of interest. It is noteworthy that citrate forms stronger complexes with Mg^{2+} than with Ca^{2+}; thus, there are less Ca-citrate species formed in *SRAU* than in Urine 2 (although citrate concentration in *SRAU* is higher than in Urine 2, the concentration of Mg^{2+} is also higher). As an example, at $pH = 7.2$ the computer simulations show

Table 4. Distribution of Ca^{2+} and oxalate in *SRAU* and Urine 2 solutions

SRAU				Urine 2			
Species	% total Ca^{2+}	Species	% total oxalate	Species	% total Ca^{2+}	Species	% total oxalate
$pH = 3.04$				$pH = 3.01$			
Ca^{2+}	79	$HOxalate^-$	67	Ca^{2+}	80	$HOxalate^-$	83
$CaSO_4$	11	MgOxalate	16	$CaSO_4$	13	MgOxalate	6
$CaCl^+$	5	$Oxalate^{2-}$	9	$CaCl^+$	4	$Oxalate^{2-}$	5
$CaH_2PO_4^+$	2	$NaOxalate^-$	5	$CaH_2PO_4^+$	1	$NaOxalate^-$	2
$pH = 4.48$ (minimum solubility)				$pH = 4.68$ (minimum solubility)			
Ca^{2+}	70	MgOxalate	44	Ca^{2+}	69	MgOxalate	35
$CaSO_4$	10	$Oxalate^{2-}$	26	$CaSO_4$	12	$Oxalate^{2-}$	34
$CaCitrate^-$	8	$NaOxalate^-$	14	$CaCitrate^-$	9	$NaOxalate^-$	15
$CaCl^+$	5	$HOxalate^-$	11	CaHCitrate	3	$HOxalate^-$	12
$pH = 5.26$				$pH = 5.43$			
Ca^{2+}	50	MgOxalate	44	Ca^{2+}	49	$Oxalate^{2-}$	40
$CaCitrate^-$	32	$Oxalate^{2-}$	32	$CaCitrate^-$	35	MgOxalate	35
$CaSO_4$	7	$NaOxalate^-$	17	$CaSO_4$	8	$NaOxalate^-$	18
$pH = 7.17$				$pH = 7.21$			
$CaCitrate^-$	37	MgOxalate	40	$CaCitrate^-$	50	$Oxalate^{2-}$	44
Ca^{2+}	34	$Oxalate^{2-}$	33	Ca^{2+}	30	MgOxalate	30
$CaHPO_4$	13	$NaOxalate^-$	21	$CaHPO_4$	9	$NaOxalate^-$	21
$Ca_2H_2(PO_4)_2$	8	$KOxalate^-$	4	$CaSO_4$	4	$KOxalate^-$	4

that in *SRAU* 36% of the total citrate complexes with Mg^{2+} and only 6% with Ca^{2+}; in Urine 2, Mg^{2+} takes 33% of total citrate and Ca^{2+} takes 10%.

Solubility of calcium oxalate hydrates in other solutions

Besides for the items discussed above, the thermodynamic solubility constants determined here were also used to predict the solubility of *COM* at 37°C and different *pH* values in solutions containing $CaCl_2$, $MgCl_2$, citrate, and NaCl in various combinations [27]. The good agreement obtained between the experimental data taken from the literature and the predicted values using the constants derived in this work strongly supports their reliability.

Conclusions

- The solubilities of *COM*, *COD*, and *COT* were measured in NaCl solutions. The results were consistently described by computer simulations using (*i*) the solubility products derived in this work, (*ii*) the literature formation constants for Ca^{2+} and oxalate complexes, and (*iii*) the extended *Debye-Hückel* and the *Davies* equations as models for the activity coefficients.

- For the first time, the solubility of *COM* was studied systematically as a function of *pH* in urine-like liquors containing organic compounds. It was found that whereas citrate and Mg^{2+} enhance the solubility of *COM*, urea and creatinine have very little influence. Sulfate and phosphate also promote the solubility of *COM*. In the three artificial urine solutions studied, the predominant oxalate complexes involve Mg^{2+} and Na^{+}; Ca^{2+} takes only a minute amount of total oxalate concentration.
- A calcium ion selective electrode can be used to measure the total Ca^{2+} concentration in NaCl and in artificial urine solutions. It was found that the ISE results were comparable to those obtained by AAS determination, provided that the calibrating solutions have the same background electrolytes as the solutions used in the solubility experiments.
- The reliability of the thermodynamic solubility constants obtained in this work is confirmed by their consistency with calorimetric data and their capacity to accurately predict the solubilities of the three calcium oxalate hydrates in NaCl solutions, in other aqueous solutions, and in urine-like liquors.

Experimental

In all experiments, analytical reagent grade chemicals (minimum 99% purity) were used without further purification. Bidistilled water, high purity nitrogen (99.999%), and A-grade glassware were employed throughout. The Ca^{2+} standard solutions were prepared from solid $CaCl_2 \cdot 2H_2O$ (Merck, 99.5%). Their concentrations were determined by complexometric titration with *EDTA* solutions, which were prepared from Riedel-de Haën concentrated volumetric standard ampoules. To minimize matrix effects, standard solutions always contained the same background electrolytes as the solutions used in the solubility experiments.

COM, *COD*, and *COT* solubilities were studied at 20, 25, 30, 37, and 40°C, at $I_c = 0.02$, 0.05, 0.10, and 0.20 $mol \cdot dm^{-3}$ NaCl, and in urine-like liquors. Three different artificial urine solutions were used. They are called (*i*) Urine 1 [9], (*ii*) Urine 2, and (*iii*) Standard Reference Artificial Urine (abbreviated as *SRAU*, [10]); their respective compositions are shown in Table 5. All potentiometric measurements were carried out in a thermostatted (to ± 0.03 K) solubility vessel in which the solution was percolating through the calcium oxalate hydrate sample [11]. The galvanic cells employed in this work can be represented as:

$$\mathrm{Ag|AgCl|1\ mol \cdot dm^{-3}NaCl|NaCl}(I_c)\mathrm{|test\ solution}\ (I_c)\mathrm{|Ca^{2+}\ ISE} \qquad \text{(A)}$$

or

$$\mathrm{Ag|AgCl|5\ mol \cdot dm^{-3}\ NaCl|5\ mol \cdot dm^{-3}\ NaCl|artificial\ urine|glass\ electrode} \qquad \text{(B)}$$

The concentration of Ca^{2+} in cell (A) was continuously measured by a calcium ion selective electrode (ISE, Orion 93–20) connected to an ionanalyzer (Orion EA 940). The reference half-cell consisted of a homemade silver–silver chloride electrode of thermal-electrolytic type and a *Wilhelm* salt bridge. The pair of electrodes was calibrated with a Ca^{2+} standard solution (see above). After 2–3 h of intimate contact between the solid phase and the solutions, constant potentials of the Ca^{2+} ISE were obtained indicating equilibration. The Ca^{2+} concentrations were also measured by AAS (Hitachi 8001). In cell (B), the glass electrode (SCHOTT H2680)/silver–silver chloride electrode pair was calibrated in 0.01 $mol \cdot dm^{-3}$ HCl and 0.29 $mol \cdot dm^{-3}$ KCl. This solution is believed to have about the same ionic strength and hence the same activity coefficient of H^{+} as the artificial urine solutions used. Thus, with cell (B), $pH = -\log [H^{+}]$ is measured. After a few hours at a constant *pH*, samples were taken to determine the Ca^{2+} concentrations by AAS. The *pH* of the artificial urine solutions was then varied by dropwise addition of either concentrated HCl or concentrated NaOH solutions.

Table 5. Composition of urine-like liquors used

	Urine 1 [9]	Urine 2	*SRAU*[1] [10]
Composition	$mol \cdot dm^{-3}$	$mol \cdot dm^{-3}$	$mol \cdot dm^{-3}$
NaCl	0.1115	0.090	0.1055
$Na_3Citrate$		0.002	0.00321
Na_2SO_4	0.00965	0.013	0.01695
NaH_2PO_4	0.0077	0.016	0.0323
Na_2HPO_4	0.0078		
$MgSO_4$	0.00296	0.002	0.00385
KCl	0.0815	0.042	0.0637
NH_4Cl	0.04335	0.020	0.0276
Creatinine		0.007	
Urea		0.300	
measured *pH*	5.88	5.58	5.14

[1] 0.00575 $mol \cdot dm^{-3}$ $CaCl_2$ and 0.000318 $mol \cdot dm^{-3}$ $Na_2C_2O_4$ (sodium oxalate) are not included since the presence of Ca^{2+} and $C_2O_4^{2-}$ is undesirable in the measurements of the solubility of calcium oxalate hydrates

The calcium oxalate hydrates used in this work were prepared by precipitation from aqueous solutions as reported in Ref. [12] for *COM* and *COD* (Sample 1), Ref. [13] for *COD* (Sample 2), and Ref. [14] for *COT*. All calcium oxalate hydrates were characterized by a combination of X-ray diffraction, scanning electron microscopy (SEM), and thermogravimetric analysis. After the solubility measurements, the *COD* and *COT* crystals were analyzed again to determine whether a transformation to the thermodynamically stable *COM* had occurred.

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