Influence of pH, Temperature and Common Ion on Magnesium Hydrogenurate Octahydrate Solubility

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A B S T R A C T

Physico-chemical investigation of urolithiasis today is mostly focused on applying physico-chemical description of precipitation processes to the stone formation with the aim to distinguish between stone formers and nonstone formers. This is done by calculating supersaturation for different solid phases which can be formed in urine using data obtained by urine analysis and existing solubility product, dissociation and complexation constants. In order for this approach to succeed it is of utmost importance that system is described as detailed as possible, i.e. that all species that can be formed are taken into account. Magnesium hydrogenurate octahydrate, $Mg(C_5H_3N_4O_3)_2 \cdot 8H_2O$ ($Mg(HU)_2 \cdot 8H_2O$), is among species which can precipitate in the urine and for which solubility data doesn't exist. In order to fill this void crystals of $Mg(C_5H_3N_4O_3)_2 \cdot 8H_2O$ phase I and phase II have been prepared and characterized. Solubility product constant of $Mg(C_5H_3N_4O_3)_2 \cdot 8H_2O$ phase I in water at 37 °C and phase II at different temperatures, pH and in different solvents have been determined by measuring total concentration of uric acid and magnesium ions in solutions at different time periods. Results show that in water at 37 °C thermodynamically less stable phase I is more soluble (K_{sp}=(5.64±0.20)·10^{-9} mol^3 dm^{-9}) than phase II (K_{sp}=(1.66±0.13)·10^{-9} mol^3dm^{-9}). Solubility of $Mg(HU)_2 \cdot 8H_2O$ phase II increases with temperature. At equilibrium the solubility of phase II is the lowest in the presence of excess of magnesium ions, while solubility in the presence of uric acid is comparable with the one obtained in water.

Key words*: magnesium hydrogenurate octahydrate, solubility, preparation, characterisation*

Introduction

Urolithiasis, formation of stones in urine, is an important medical and social problem. The formation of urinary stones is a complex physico-chemical process, influenced by many factors, the most significant being urine composition. Urine is frequently oversaturated with respect to different inorganic salts (calcium oxalate, calcium phosphate, sodium and ammonium hydrogenurate) as well as some organic compounds. Will the stone be formed in such oversaturated solution depends also on presence of promoters and inhibitors[1].

Parameter which is used for prediction of precipitate formation in certain system is supersaturation. This approach has been validated in treatment of urinary stones formation and reoccurrence, since it enables to determine if a patient is susceptible to stone formation based solely on urine composition. Different computer programs, e.g. EQUIL2[2] and SEQUIL[3], have been used to facilitate supersaturation calculations in such a complex solution as urine. However, the success of this calculation depends on the inclusion of formation and dissociation constants of all species (precipitates, complexes) which can be formed. Although much work has been done in determining these parameters for main urinary stone components calcium oxalate[4,5], calcium phosphate[6,7] and uric acid[8,9], data for some urates are scarce[10].

Uric acid and its potassium, sodium and calcium salts urate occur in the acid urine, while ammonium urate can be found in basic urine. Stones formed at lower pH (<5.5)

are usually composed of uric acid dyhidrate and anhydrous uric acid. Frequency of occurrence of these stones is around 5%. Uric acid and urates are also found in mixture with calcium oxalates[11]. Although, chemical composition and properties of the urates are known, there is not enough data about their structure and interaction of the uric acid with some biologically important metals, such as Mg, Ca, Fe, Co, Cu and Zn.

Magnesium can act as an inhibitor of calcium (calcium phosphate and oxalate) stone formation[12]. It can also be part of the stones in the form of magnesium hydrogenphosphate trihydrate ($MgHPO_4 \cdot 3H_2O$), magnesium ammoniumphosphate hexahydrate, struvite ($MgNH_4PO_4 \cdot 6H_2O$), and magnesium phosphate octahydrate $Mg_3(PO_4)_2 \cdot 8H_2O$[13,14] usually in the mixture with calcium oxalates and phosphates, urates, cystin and xanthin.

However, although magnesium urate or hydrogenurate can be formed in the urine, they were not detected as urinary stone constituents[15]. Some authors detected magnesium – calcium urates in mixture with uric acid as possible stone constituents[10,16].

As early as 1845 Bensch[17] has synthesized uric acid salt of unknown formula, which could be identical to $Mg(C_5H_3N_4O_3)_2 \cdot 6H_2O$, prepared also by Behrend and Roosen[18]. In 1938 Hannawelt and collaborators[19] have published *d*-lines values for magnesium urate $MgC_5H_2N_4O_3$. Kopajtić and collaborators[12,15] have described growth of the monocrystals of new compound $Mg(C_5H_3N_4O_3)_2 \cdot 8H_2O$ two phases. Structures of both phases contain isolated $[Mg(H_2O)_6]^{2+}$ cations, hydrogenurate anions and two molecules of crystal water per unit cell. Anions are hydrogen bonded between themselves and with water molecules, forming chains. Both phases crystallize in monoclinic system, phase I in the form of needles and phase II in the form of plates. Phase II is thermodinamically more stable[12,15]. Transformation between two phases occurs in the solution, but it is long process (2–3 month)[20]. Data for magnesium urates physico-chemical characteristics are scarce or old. For example solubility of $Mg(C_5H_3N_4O_3)_2 \cdot 6H_2O$ is 0.043 mmol dm^{-3} at 22.7 °C as was determined in 1848[17].

In this paper synthesis and characterization of $Mg(C_5H_3N_4O_3)_2 \cdot 8H_2O$ phase I and phase II is described. Influence of temperature, pH and common ion concentration on solubility of thermodynamically more stable phase II was also determined.

Materials and Methods

Analytical grade chemicals uric acid ($C_5H_4N_4O_3$, Sigma), potassium hydroxide (KOH, Merck), hydrochloric acid (HCl, Merck), magnesium chloride ($MgCl_2$, Merck), Tris – hydroxymethyl aminomethan ($C_4H_{11}NO_3$, Merck), magnesium sulphate heptahydrate ($MgSO_4 \cdot 7H_2O$, Kemika) and bidestiled water were used. Uric acid stock solution was prepared by dissolving required amount of chemical dried overnight in a desiccator over silica gel. Concentration of KOH solution was determined by titration with HCl and concentration of magnesium chloride

by conductometric titration with silver nitrate. pH of the solutions were adjusted to desired value by addition of NaOH and/or HCl.

Preparation of magnesium urate octahydrate

Magnesium urate octahydrate was prepared by dissolving 400 mg of uric acid in 500 mL (2×10^{-2} moldm^{-3}) of Tris buffer (pH=8) with magnetic stirring. After dissolution solution was filtered through Millipore filter 0.22 μm, 3.5 g of $MgSO_4 \cdot 7H_2O$ was added to filtered solution and pH was adjusted with KOH to 8. Solution was left undisturbed at room temperature until crystals were formed. After 3 hours needle-like crystals of phase I were detected. After longer aging time, mixture of needle-like and plate-like crystals was observed, and after 3 month plate-like crystals of phase II were only crystals observed. Crystals were filtered through Millipore filter and dried before solubility experiments and characterization.

Solubility experiments

Solubility of $Mg(HU)_2 \cdot 8H_2O$ was determined in bidestiled water, uric acid($1 \cdot 10^{-4}$ moldm^{-3}) and magnesium chloride solutions (1×10^{-3} moldm^{-3}). Known amount of $Mg(HU)_2 \cdot 8H_2O$ (about 200 mg) was weighted into Erlenmeyer flask and 100 mL of solvent was added. Suspensions were equilibrated in water bath at 310 K with constant shaking. At predetermined time intervals aliquots of suspension were taken and filtered through Millipore filter 0.22 μm. In thus obtained filtrates concentrations of uric acid and magnesium were determined. Precipitates were filtered, dried and analyzed.

Please note that kinetics of dissolution were followed in order to determine time needed for reaching equilibrium and to calculate solubility product. They were not used in order to determine rate of dissolution constant.

Characterization of the solutions

pH of the solutions was measured by pH meter Mo. 26 (Radiometer, Copenhagen). Total concentration of uric acid was determined by measuring absorption at 285 nm[21] using UV spectrometers Beckman Model 34 and Model Varian Cary 3. Total magnesium concentration was determined by atomic absorption spectroscopy using Perkin Elmer 3030B Atomic – Absorption Spectrophotometer.

Characterization of the precipitates

$Mg(HU)_2 \cdot 8H_2O$ crystals were characterized by:

i) optical microscopy – samples of the suspensions were taken at predetermined time intervals, observed and photographed by light and polarized microscopy using Orthoplan photomicroscop (Ernst Leitz, Wetzlar),

ii) thermogravimetric analysis (TG) – water and purin content in dry precipitates was determined by thermal analysis system Mettler TG 50. Rate of heating was 20 °C/min,

iii) powder X-ray diffraction patterns (RTG) – powder X-ray diffraction patterns were obtained by »Philips« PW diffractometer with graphite filtered CuKα radiation,

iv) elemental analysis – carbon, hydrogen and nitrogen content was determined using microchemical analytical method.

Solubility product calculations

Concentration solubility product, K_{sp} can be determined from equilibrium solubility data:

$$Mg(HU)_2 \cdot 8H_2O(s) \leftrightarrow Mg^{2+}(aq) + 2HU^-(aq) + 8H_2O(l) \quad (1)$$
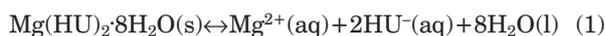
$$K_{sp} = [Mg^{2+}][HU^-]^2 \quad (2)$$

If composition of solution in equilibrium with solid phase is known, it is possible to calculate standard solubility product:

$$K_s^\theta = [\ Mg^{2+}][\ HU^-]^2 (\Sigma y_\pm)^3 / (c^\theta)^3 \quad (3)$$

where $y_\pm$ is average activity coefficient, c is concentration. In cases of sparingly soluble salts, when ionic strength is not too high, average activity coefficient can be estimated using Debye-Hückel limiting law:

$$\log y_\pm = -A_d |z_+ z_-| (I_c / c^\theta)^{1/2} \quad (4)$$

where z is charge number, A_c constant with values 0.5002, 0.5115, 0.5242 and 0.5296 at 288 K, 298 K, 310 K and 318 K respectively[22,23].

Ionic strength, I, is given by:

$$I_c = (1/2) \Sigma c_i z_i^2 \quad (5)$$

where i represents ionic species.

Uric acid is weak acid which dissociate in two steps. Hydrogenurate ions equilibrium concentration is determined by pH and total urate concentration. Therefore uric acid dissociation constant should be taken into calculations. Values of uric acid[24–26] and water dissociation constants[22,27] at different temperatures are given in Table 1.

For calculation of the solubility product computer program »Magurat« was used[28].

Results

Characterization of the precipitates

Formation and transformation of $Mg(HU)_2 \cdot 8H_2O$ during synthesis was followed with optical microscopy (Figure 1). Small needle-like crystals appeared after 1 hour (Figure 1a). After 3 hours aging time a mixture of needle-like (phase I) and plate-like crystals (phase II) was observed (Figure 1b). Transformation of phase I into phase II was completed after 3 month (Figure 1c).

Elemental analysis of the $Mg(HU)_2 \cdot 8H_2O$ crystals is given in Table 2.

RTG powder patterns of phase I, mixture of the phases and of phase II contain reflections with d-lines values in good agreement with existing data[12,15]. TG curves of both phases point to their structural differences. Release of water is a two step process. First to be released are two molecules of crystal water followed by six water molecules from magnesium hexahydrate cation, as determined from mass loss given in Table 3. Thermal decomposition of phase I starts at higher temperature (97 °C), than decomposition of phase II (70 °C). Second mass loss occurs at 140 °C for phase I and at 155 °C for phase II. Mass loss at around 300 °C corresponds to decomposition of purin.

Phase I and phase II dissolution kinetics at 310 K

Dissolution kinetics of both phases is shown at Figure 2. Dissolution of phase I reaches equilibrium earlier than the one of phase II, as seen from the plateau in absorbance curves. Dissolution of phase I reaches equilibrium after 30 min, while for phase II equilibrium is reached after 90 min. Similar results were obtained by measuring Mg^{2+} concentration. Average K_{sp} values given in Table 4 were obtained as average values of K_{sp} determined in different time intervals after equilibrium was reached, i.e. in time interval 60–180 min for phase I and 120–300 min for phase II.

TABLE 1
URIC ACID AND WATER DISSOCIATION CONSTANTS AT DIFFERENT TEMPERATURES

	pK				Ref.
	15 °C	25 °C	37 °C	45 °C	
$H_2U \leftrightarrow H^+ + HU^-$	5.65	5.61	5.44	5.34	24, 25
$HU^- \leftrightarrow H^+ + U^{2-}$	9.15	9.15	10.51	10.51	26
$H_2O \leftrightarrow H^+ + OH^-$	14.35	13.99	13.61	13.39	22, 27

TABLE 2
ELEMENTAL ANALYSIS OF THE $Mg(HU)_2 \cdot 8H_2O$

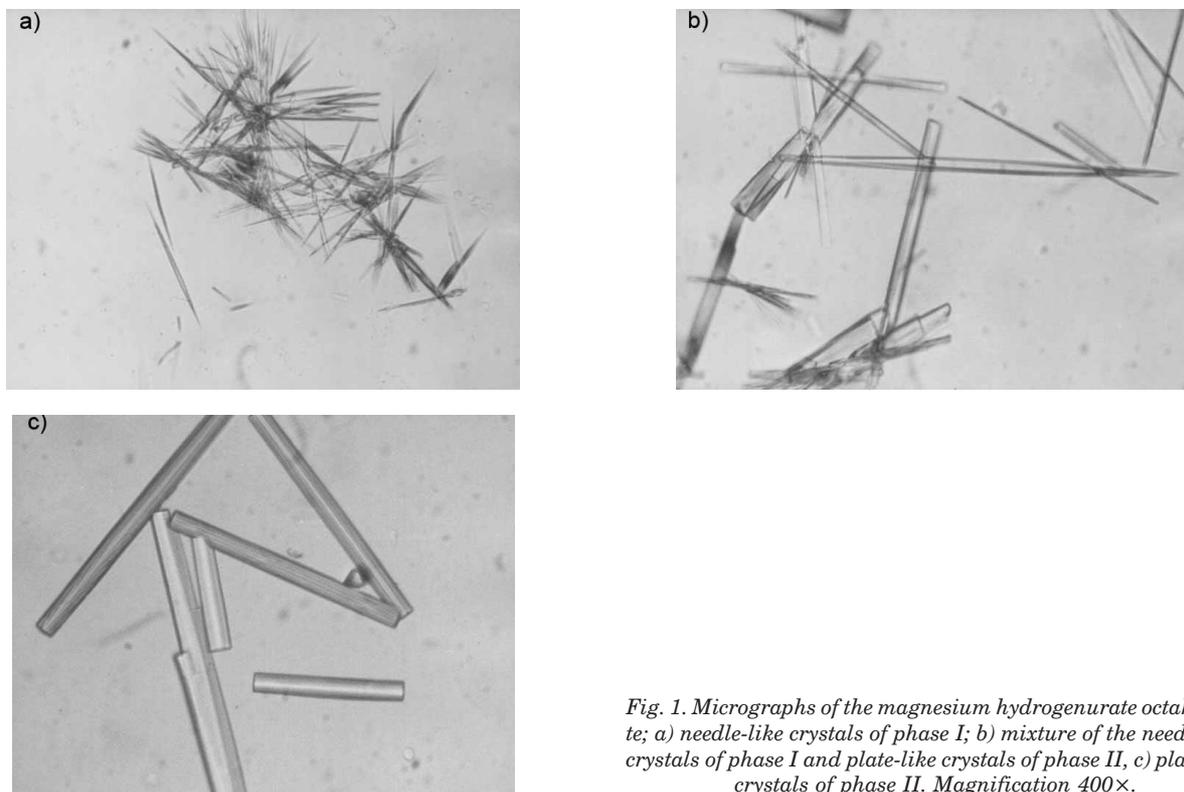|	%Mg	%C	%H	%N	%H_2O
Calculated	4.84	23.90	4.41	22.29	28.70
Obtained	5.58	24.10	4.16	22.12	29.50

Fig. 1. Micrographs of the magnesium hydrogenurate octahydrate; a) needle-like crystals of phase I; b) mixture of the needle-like crystals of phase I and plate-like crystals of phase II, c) plate-like crystals of phase II. Magnification 400×.

TABLE 3
MASS LOSS OF $Mg(HU)_2 \cdot 8H_2O$ PHASE I AND PHASE II CRYSTALS UPON HEATING TO 800 °C. RATE OF HEATING 20 °C/ MIN

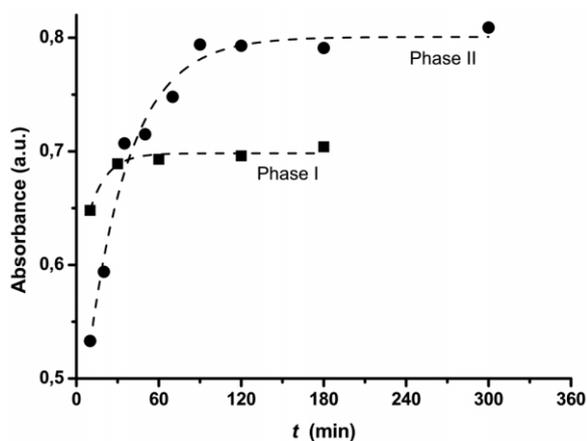|	Mass loss / %		
	2 water molecules	6 water molecules	purin
Phase I	6.68	23.15	65.47
Phase II	7.56	21.06	66.16
Calculated	7.17	21.51	66.53

Fig. 2. Change of uric acid absorbance with aging time for the phase I and phase II in water solutions at 37 °C.

Temperature influence on solubility of $Mg(HU)_2 \cdot 8H_2O$ phase II at equilibrium

Crystals of $Mg(HU)_2 \cdot 8H_2O$ phase II were dissolved in water at pH=7.09±0.08 and temperatures 15 °C, 25 °C, 37 °C and 45 °C (Figure 3). As can be seen from Figure 3 solubility increases with temperature, with abrupt increase above 37 °C[32].

pH influence on solubility of $Mg(HU)_2 \cdot 8H_2O$ phase II in water at equilibrium and different temperatures

Since uric acid is a dibasic acid, distribution of ionic species, namely H_2U, HU^- and U^{2-}, depends on the solution pH. In this part of the study a pH range 6.5–9.0 in which HU^- is dominant ionic species was chosen. Solubility of $Mg(HU)_2 \cdot 8H_2O$ depends on initial pH, this effect being smallest at 15 °C and 25 °C. At 25 °C and 37 °C solubility is higher at higher pH, and reversely at 45 °C (Figure 4)[32].

Influence of common ion on solubility of $Mg(HU)_2 \cdot 8H_2O$ phase II at equilibrium

In order to determine the influence of common ion on solubility of $Mg(HU)_2 \cdot 8H_2O$ at equilibria crystals were dissolved in uric acid (1×10^{-4} mol dm^{-3}) and magnesium chloride solutions (1×10^{-3} mol dm^{-3}) at different temperatures and pH=8. In all cases solubility increases with temperature (Figure 5). At 15 °C and 25 °C lowest $Mg(HU)_2 \cdot 8H_2O$ solubility has been in $MgCl_2$ solutions,

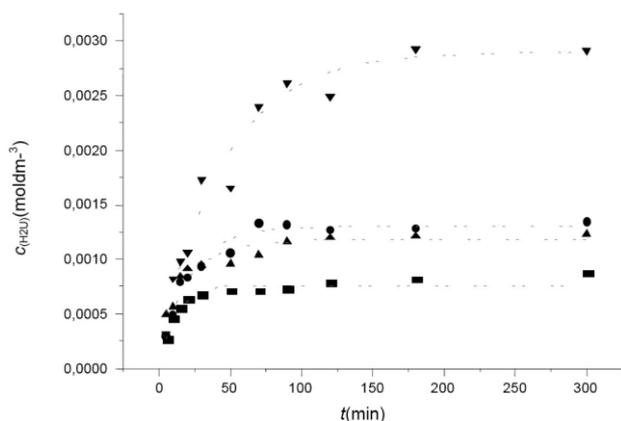| Compound	Medium	$K_{sp} \times 10^9$ (equilibrium)	$K_{sp} \times 10^{10}$ (24 hours)	Reference
$H_2U \cdot 2H_2O$	water	(2.25 ± 0.05), 1 hour	(0.18 ± 0.003)	25, 29
H_2U	water	0.824	—	30
H_2U	water	0.987	—	24
$Ca(HU)_2 \cdot 6H_2O$	water	(0.53 ± 0.004), 3 hours		29, 31
$Mg(HU)_2 \cdot 8H_2O$, phase I	water	(5.64 ± 0.020), 1–3 hours	—	20, this paper
$Mg(HU)_2 \cdot 8H_2O$, phase II	water	(1.66 ± 0.13), 2–5 hours	(6.37 ± 2.71)	20, this paper

Fig. 3. Dissolution kinetics of $Mg(HU)_2 \cdot 8H_2O$ in water at different temperatures. ■ T=15 °C; ● T=25 °C; ▲ T=37 °C; ▼ T=45 °C. pH=7.09±0.08.

while solubilities in water and H_2U solutions don't differ much (Figures 5a and b). The difference in solubility is decreasing with temperature (Figures 5c and d)[32].

Solubility of phase II at 37 °C in different solvents, t=24 hours

Solubilities of $Mg(HU)_2 \cdot 8H_2O$ thermodynamically more stable phase II determined after 24 hours in water, magnesium chloride and uric acid solutions are given in Table 5. Solubility of $Mg(HU)_2 \cdot 8H_2O$ in magnesium chloride is higher than in water and uric acid. Measured pH values indicate that in all suspensions uric acid crystals can coexist with $Mg(HU)_2 \cdot 8H_2O$ crystals. This is confirmed by H_2U/Mg molar ratio 1:1 and RTG powder pattern

TABLE 5
SOLUBILITY OF $Mg(HU)_2 \cdot 8H_2O$ PHASE II IN WATER, MAGNESIUM CHLORIDE AND URIC ACID SOLUTIONS AND CORRESPONDING pH RANGE DURING AGING TIME AT 37 °C AFTER 24 HOURS

Solvent	Solubility, K_{sp}/mol^3 dm^{-9}	pH range
Water	$(6.366\pm2.709)\times10^{-10}$	6.74–7.10
Magnesium chloride	$(5.038\pm1.726)\times10^{-10}$	6.28–7.21
Uric acid	$(6.638\pm2.123)\times10^{-10}$	6.61–6.88

which contain characteristic peaks of both $Mg(HU)_2 \cdot 8H_2O$ and uric acid[20].

Discussion and Conclusions

Magnesium hydrogenurate octahydrate precipitates in the form of two phases, thermodynamically less stable phase I and more stable phase II[12,15,20]. The transformation of phase I to phase II is long process lasting up to 3 month[20]. As expected the solubility of phase I is higher than that of phase II (Figure 2). Literature K_{sp} values of anhydrous uric acid, uric acid dihydrate and calcium hydrogenurate hexahydrate, as well as K_{sp} values of magnesium hydrogenurate octahydrate phase I and II determined and described in this paper at 37 °C are listed in Table 4. It can be seen that at equilibrium the most soluble is $Mg(HU)_2 \cdot 8H_2O$ phase I, while calcium hydrogenurate hexahydrate is the least soluble compound. The higer solubility of $Mg(HU)_2 \cdot 8H_2O$ phase I than uric acid dihydrate can be the reason that $Mg(HU)_2 \cdot 8H_2O$ crystals were not detected as urinary stone constituents in contrast to $H_2U \cdot 2H_2O$ crystals which are frequent constituents[11]. Values obtained after longer aging time (24h) can't be used as reliable due to the partial transformation of calcium hydrogenurate hexahydrate and magnesium hydrogenurate octahydrate into uric acid.

Solubility of $Mg(HU)_2 \cdot 8H_2O$ phase II increases with temperature (Figure 3). K_{sp} values determined at different temperatures ($K_{sp}(15$ °C$)=(2.18\pm0.46)\cdot10^{-10}$ mol^3 dm^{-9}; $K_{sp}(25$ °C$)=(7.36\pm0.43)\cdot10^{-10}$ mol^3 dm^{-9}; $K_{sp}(37$ °C$)= (6.15\pm0.30)\cdot10^{-10}$ mol^3 dm^{-9} and $K_{sp}(45$ °C$)=(6.71\pm 1.28)\cdot 10^{-9}$ mol^3 dm^{-9})[32] were used to calculate dissolution enthalpy and log K_{sp} *vs.* 1/T plots. As it can be seen from Figure 6 the plot has discontinuity at 25 °C. This could be explained by the existence of two kinds of water molecules in the crystal structure, i.e. crystal and coordination water. Due to this difference it is probable that several different reactions take place at the same time during dissolution of $Mg(HU)_2 \cdot 8H_2O$. Phase II enthalpy of dissolution determined from linear dependence of log K_{sp} *vs.* 1/T at 15 °C, 37 °C and 45 °C is $\Delta_{sol}H=86$ kJmol^{-1}.

According to the Le Chatelier principle, addition of common ion shifts dissolution equilibrium towards solid phase formation. That means that solubility of the salt is lower in the presence of common ion. In the case of
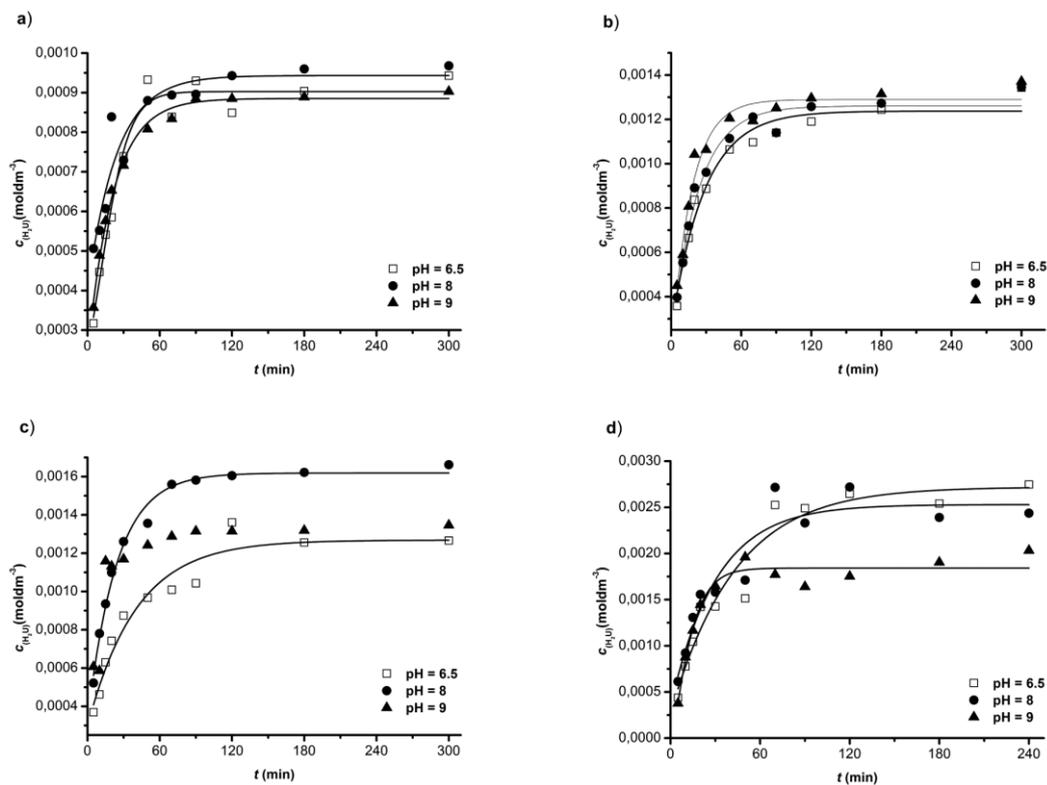
Fig. 4. Dissolution kinetics of $Mg(HU)_2 \cdot 8H_2O$ at a) 15 °C, b) 25 °C, c) 37 °C, d) 45 °C and at different pH.
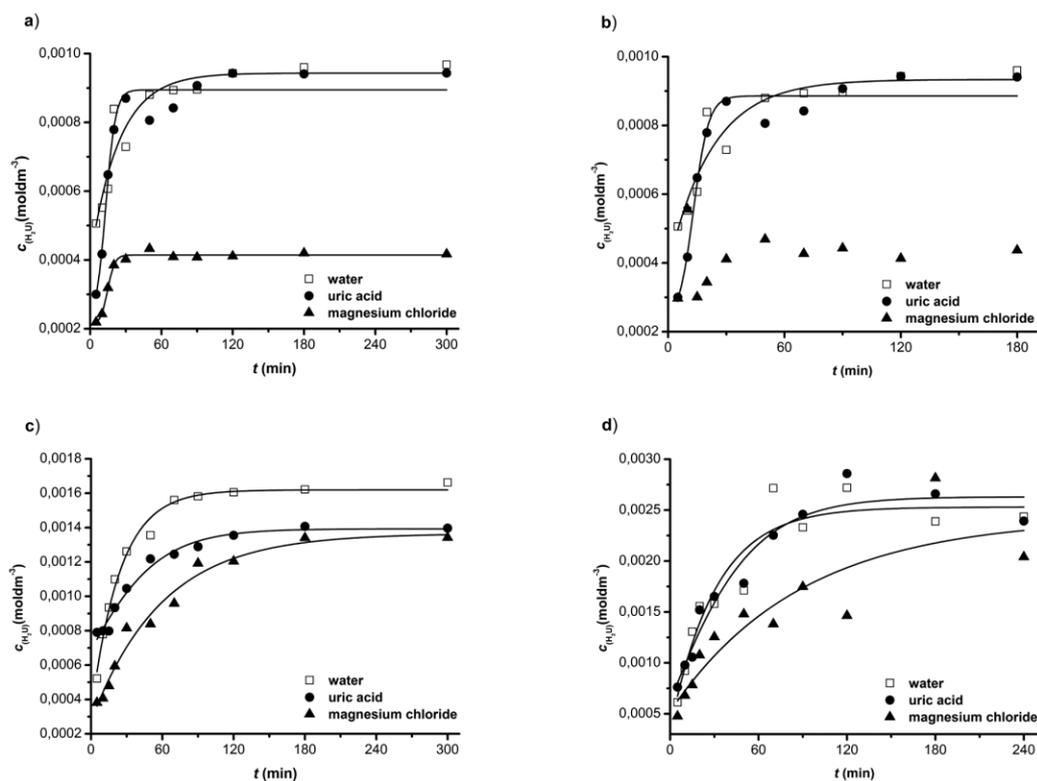Lines are only guidance for the eye.

Fig. 5. Dissolution kinetics of $Mg(HU)_2 \cdot 8H_2O$ at a) 15 °C, b) 25 °C, c) 37 °C, d) 45 °C and pH=8 in different solvents.
Lines are only guidance for the eye.

$Mg(HU)_2·8H_2O$ phase II at equilibrium the solubility is the lowest in the presence of excess of magnesium ions, while solubility in the presence of uric acid, although somewhat higher, is comparable with the one in water. This trend is observed at all other investigated temperatures. The difference in solubility in different solvents is decreasing with increasing temperature (Figure 5). It is assumed that $Mg(HU)_2·8H_2O$ solubility is decreased by magnesium chloride addition due to the formation of soluble complexes which are in equilibrium with solid phase.[32] Phase II K_{sp} values after 24 hours in water, magnesium chloride and uric acid solutions at 37 °C (Table 5) are lower than the value obtained in water in equilibrium conditions (Table 4). After 24 hours the solubility is the highest in magnesium chloride solutions, contrary to the equilibrium solubility and the Le Chatelier principle. Also, standard deviation of measurements is higher in these cases[20]. The reason again could be partial transformation of $Mg(HU)_2·8H_2O$ into uric acid.

These results indicate that in order to fully understand what is happening in urate solutions more work

Fig. 6. log K_{sp} of $Mg(HU)_2·8H_2O$ phase II vs. 1/T plot, water, pH≅7.0.

needs to be done in determining the course and the extent of urates transformation to uric acid.

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1. CHUNG HJ, ABRAHAMS HA, MENG MV, STOLLER ML, Theories of stone formation. In: STOLLER ML, MENG MV (Eds) Urinary stone disease (Humana Press, New Jersy, 2007). — 2. WERNESS PG, BROWN CM, SMITH LH, FINLAYSON B, J Urol, 134 (1985) 1242. — 3. ASHBY RA, SLEET RJ, Clin Chim Acta, 210 (1992) 157. — 4. MILLER NL, EVAN AP, LINGEMAN JE, Urol Clin N Am, 34 (2007) 295. — 5. PARK S, PEARLE MS, Urol Clin N Am, 34 (2007) 323. — 6. WORCESTER EM, Pathophysiology and management of calcium stones. In: PEARLE MS, NAKADA SY (Eds) Urolithiasis Medical and Surgical Management (Informa, UK, 2009). — 7. PARKS JH, WORCESTER EM, COE FL, EVAN AP, APLINGEMAN JE, Kidney Int, 66 (2004) 777. — 8. CAMERON AM, SAKHAEE K, Urol Clin N Am, 34 (2007) 335. — 9. SAKHAEE K, Uric acid nephrolithiasis: Pathogenesis, diagnosis, and treatment. In: PEARLE MS, NAKADA SY (Eds) Urolithiasis Medical and Surgical Management (Informa, UK, 2009). — 10. HERRING LC, J Urol, 88 (1962) 545. — 11. LONSDALE K, MASON P, Science, 152 (1966) 1511. — 12. DUBLER E, JAMES GB, KOPAJTIĆ Z, J Inorg Biochem, 26 (1986) 1. — 13. LONSDALE K, SUTOR DJ, Sov Physic – Crystalogr, 16 (1972) 1060. — 14. WILLIAMS & WILKINS Co, J Urol, 88 (1962) 557. — 15. KOPAJTIĆ Z, Kristalline Metall-Harnsäureverbindungen: Synthese, Struktur und thermisches Verhalten. PhD Thesis. In Germ (Universität of Zürich, Zürich, 1985). — 16. BELLANATO J, CIFUENTES J, Calcium in urate calculi. In: GASSER G, VAHLENSIECK (Eds) Fortschr Urol Nephrol 23 Pathog Klin Harsteine XI (S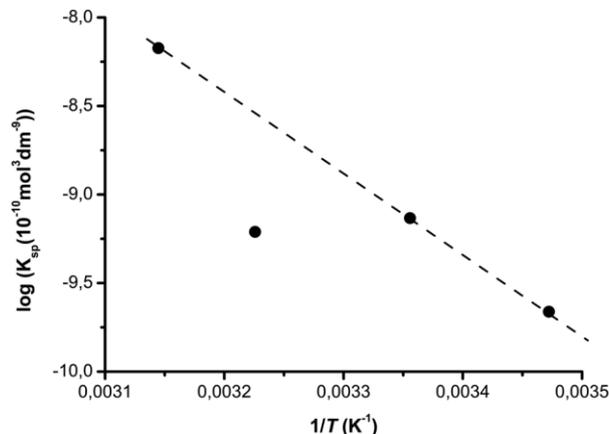teinkopff, Darmstadt, 1985). — 17. BENSCH A, ALLEN J, Liebig's Annalen, 65 (1848) 186. — 18. BEHREND R, ROOSEN O, Liebig's Annalen, 251 (1889) 235. — 19. HANAWALT JD, RINN HW, FREVEL LK, Ind Eng Chem, 10 (1938) 475. — 20. JENDRIC M, Characterisation and determination solubility of magnesium hydrogenurate octahydrate, B.Sc. Thesis. In Croat (University of Zagreb, Zagreb, 1996). — 21. MENTASTI E, RINAUDO C, BOISTELLE R, J Chem Eng Dana, 28 (1983) 247. — 22. HARNED HS, OWEN BB, The Physical Chemistry of Electrolytic Solutions, 3rd ed (Reinhold Publ Corp, New York, 1958). — 23. STOKES RH, ROBINSON RA, Electrolyte Solutions (Butterwooth and Co., London, 1959). — 24. LAM CY, NANCOLLAS GH, KO SJ, Invest Urol, 15 (1978) 473. — 25. BABIĆ-IVANČIĆ V, FÜREDI-MILHOFER H, BROWN WE, GREGORY TM, J Cryst Growth, 83 (1987) 581. — 26. LAM-ERWIN CY, NANCOLLAS GH, J Crystal Growth, 53 (1981) 215. — 27. HARNED HS, ROBINSON RA, Trans Faraday Soc, 36 (1940) 973. — 28. BABIĆ D, Computer program (Magurat, Zagreb, 1995). — 29. BABIĆ-IVANČIĆ V, Precipitation and solubility uric acid, natrium and calcium urates. PhD Thesis. In Croat (University of Zagreb, Zagreb, 1987). — 30. WOHLER F, LIEBIG J, Ann Pharmacie, XXVI (1838) 241. — 31. BABIĆ-IVANČIĆ V, FÜREDI-MILHO- FER H, BRNIČEVIĆ N, MARKOVIĆ M, J Res Natl Inst Stand Technol, 97 (1992) 365. — 32. ŠOŠTARIĆ N, The influence of pH and temperature on the solubility of crystals of magnesium hydrogenurate octahydrate. B. Sc. Thesis. In Croat (University of Zagreb, Zagreb, 1997).

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UTJECAJ PH, TEMPERATURE I ZAJEDNIČKOG IONA NA TOPLJIVOST MAGNEZIJEVOG HIDROGENURATA OKTAHIDRATA

S A Ž E T A K

Fizičko-kemijska istraživanja urolitijaze, danas su uglavnom usmjerena na primjenu fizičko-kemijskog opisa procesa taloženja na stvaranje mokraćnih kamenaca s ciljem određivanja potencijalnih stvaralaca kamenaca. Taj pristup uključuje izračun prezasićenosti za različite čvrste faze koje mogu nastati u mokraći. Pri tome se koriste rezultati analize mokraće i postojeće konstante produkta topljivosti, disocijacije i kompleksiranja. Da bi izračun bio valjan potrebno je uzeti u obzir sve vrste koje mogu nastati u sistemu. Magnezijev hidrogenurat oktahidrat, $Mg(C_5H_3N_4O_3)_2 \cdot 8H_2O$ $(Mg(HU)_2 \cdot 8H_2O)$, je jedna od vrsta koja može istaložiti u mokraći, a za koju ne postoje podaci o topljivosti. Pripremljeni su i karakterizirani kristali $Mg(C_5H_3N_4O_3)_2 \cdot 8H_2O$ faze I i faze II. Konstante produkta topljivosti faze I u vodi na 37 °C, te faze II pri različitim temperaturama, pH i otapalima određene su mjerenjem ukupnih koncentracija mokraćne kiseline i magnezijevih iona u suspenzijama u različitim vremenskim intervalima. Rezultati pokazuju da je u vodi na 37 °C termodinamički nestabilnija faza I ($K_{sp}=(5,64\pm0,20)\times10^{-9} \text{mol}^3\text{dm}^{-9}$) topljivija od termodinamički stabilnije faze II ($K_{sp}=(1,66\pm0,13)\times10^{-9} \text{mol}^3 \text{dm}^{-9}$). Topljivost $(Mg(HU)_2 \cdot 8H_2O$ faze II se povećava s temperaturom. U ravnotežnim uvjetima topljivost faze II je najmanja u suvišku magnezijevih iona, dok je topljivost u suvišku uratnih iona slična topljivosti u vodi.