Differences in Adsorption of Anionic, Cationic and Nonionic Surfactants on Calcium Oxalate Crystals: Effect of Crystal Size

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Abstract. The adsorption differences of surfactants with different types of charges onto nano/micron calcium oxalate monohydrate (COM) and calcium oxalate dihydrate (COD) crystals were investigated to explore the effects of urinary molecules with different types of charges on formation of urinary stones. These surfactants include anionic surfactant sodium dodecyl sulfate (SDS), cationic surfactant cetyltrimethyl ammonium bromide (CTAB), and nonionic surfactant nonylphenol ethoxylate (NP-40). The sizes of COM and COD crystals are 100 nm and 10 μm, respectively. The adsorption capacity of different surfactants on nano/micron COM and COD crystals and the Zeta potential on crystal surface after adsorption were measured. The settling velocity of the crystal suspensions after adding different surfactants was compared. The adsorption quantity of three surfactants on COM and COD was ranked in the following order: SDS > CTAB > NP-40. The adsorption quantity of COM was greater than that of COD with the same size. It indicated that the adsorption capacity is related to the crystal structure of the crystal surface. The absolute value of Zeta potential on surface of COM and COD increased after adsorption of surfactants. The crystal settling velocity was negatively correlated with the amount of surfactants adsorbed and the Zeta potential of the crystals. Surfactants can interact with the calcium sites or oxalate sites on the crystal surface. There are different interactions between different surfactants and nano/micron crystals. We proposed a molecular model of crystal adsorption with different surfactants. Larger adsorption quantity of surfactants can slow the sedimentation rate of crystals and thus stabilizes crystal suspension, finally inhibits the formation of calcium oxalate stones.

Introduction

Numerous organic substances exist in human urine, such as amino acid, citric acid, albumin and acid mucopolysaccharide [1-3]. These substances can significantly affect the nucleation, growth, aggregation, and crystalline phase transformation of calcium oxalate in urine. The cell membrane is composed of a phospholipid bilayer, which have a hydrophilic head and two hydrophobic tails each. The hydrophilic phosphate heads point “out” into the water on either side of the bilayer, and the hydrophobic tails point “in” to the core of the bilayer. Therefore, the phospholipid bilayer in the cell membrane performs an obvious character of surfactant, and the cell membrane usually shows a certain negative charges.

Since urine system is very complex and there are many kinds of the surface active substances in urine, we often use a representative substance to study the effect of certain kind of substance
on the formation of calcium oxalate crystal. The anionic surfactant commonly used in biomineralization simulation are mainly sodium diisoctyl sulfosuccinate (AOT) and sodium dodecyl sulfate (SDS).

The innovation of this article is to study the adsorption differences of SDS, CTAB and NP-40 onto calcium oxalate monohydrate (COM) and calcium oxalate dihydrate (COD) crystals with the size of 100 nm and 10 μm, based on the presence in urine of urinary crystals with different sizes and surfactants with different types of charges [4], respectively. We hope to explore the effect of urinary crystallite size and the charges of urinary molecules on calcium oxalate stone formation.

Experiments

Materials and Methods

Reagents and Instruments

All of the chemicals used in this study were of analytical grade and purchased from Guangzhou Chemical Reagent Factory of China. The water used in all of the experiments was double distilled water.

The instruments used include D/max2400 X-ray powder diffractometer (XRD, Rigaku, Japan), UV-visible spectrophotometer (Cary 500, Varian, and USA), Zetasizer Nano-ZS nano particle sizer (Malvem, UK), KQ3200 DE ultrasonic instrument (Kunshan, China), and Centrifugal sedimentation machine (TGL-16C, Shanghai, China).

Preparation of COM and COD with Different Sizes

SFP was degraded by hydrogen peroxide (H₂O₂). In brief, SFP (1.2 g) was dissolved in 40 mL distilled water at 70 °C. After heating to 90 °C, H₂O₂ (27 ml) with the concentration of 1%, 4%, 8%, and 12% were introduced directly into the solution. The degradation reaction was allowed to proceed for 2 h, at that point the pH of solution was adjusted to 7.0 by adding 2 mol/L sodium hydroxide solution. Then, the resultant was precipitated by addition of anhydrous ethanol to the actual volume. The solution was stored at 4 °C overnight and then filtered. The filtrated was washed with anhydrous ethanol twice and dried in a vacuum.

XRD Characterization of Crystals after Adsorption

The crystal and surfactants were mixed and stanced for 24 h, then centrifuged to remove the supernatants. The crystals were collected and dried in 55 °C, and measured using XRD.

Adsorption Experiments of Surfactants

The amount of adsorbed surfactant (SDS, CTAB, or NP-40) was determined using the depletion method; 50 mg of COM or COD crystals were added into 12 mL of surfactant solution at different concentrations (C₀). The suspension was dispersed by ultrasonic processing for 10 min and then placed into a thermostat water bath at 37 °C. The suspension was centrifuged after adsorption for 24 h, and the residual concentration of surfactant was measured (Cₑq). The adsorbed amount (Q_ads) of surfactant on COM or COD was calculated using the formula $Q_{ads} = \frac{V(C_0 - C_{eq})}{m}$, where $V$ is the volume of the solution, and $m$ is the weight of the crystals.
Results and Discussion

XRD spectra of COM and COD Crystals after Adsorption

Fig. 1 shows the molecular structure of the three surfactants. Fig. 2 showed the X-ray powder diffractometer (XRD) patterns of different sizes of COM and COD after adsorption by different surfactants for 24 h. All the COM crystals (Fig. 2A) after adsorption showed diffraction peaks at \( d = 0.593, 0.365, 0.296, \) and \( 0.235 \) nm, which were assigned to \((\hat{1}01), (020), (\hat{2}02)\) and \((130)\) planes of COM crystals (PDF card number: 20-231), respectively [5]. The COD crystals (Fig. 2B) after adding SDS and CTAB showed diffraction peaks at \( d = 0.618, 0.442, 0.277, \) and \( 0.224 \) nm, which were assigned to \((200), (211), (411)\) and \((213)\) planes of COD crystals (PDF card number: 17-541), respectively [5]. However, the diffraction peaks of COM crystals were also detected for COD crystals after adding NP-40, indicating part of COD crystal were converted into COM crystals. COD crystal is metastable and is not as stable as COM crystal [6]. After adding SDS and CTAB, the stability of COD is enhanced, and thus the crystalline phase transformation of COD crystal was inhibited.

Cody et al. [7] showed that the adsorption sites in COD per unit area were the least and the adsorption capacity was the weakest compared with those of COM and COT crystals. So the inhibitor had to increase its concentration in order to find enough adsorption sites. Since NP-40 binds with the adsorption site of COD through hydrogen bonds and coordination bonds, and both the bonding ability are not strong enough [2], so the inhibition ability of NP-40 to crystal phase transformation is not as strong as the anionic and cationic surfactants (SDS and CTAB), thus, part of the COD was converted into COM after NP-40 was added into COD crystals.

The Adsorption Curves of Micron and Nanometer Calcium Oxalate

Fig. 3 showed the adsorption curves of micron/nano COM and COD. It can be seen that:
1) The adsorption quantities of different surfactants onto COM and COD always were in the order: SDS > CTAB > NP-40.
2) The adsorption quantity of COM is greater than that of COD with the same crystal size.
3) The adsorption quantities of nano crystals to surfactants are much larger than those of the micron crystals.
4) The adsorption curves of nano COM and COD were linear (Fig. 3A), whereas the curves of micron COM and COD were S-type (Fig. 3B).

Figure 2. XRD patterns of COM (A) and COD (B) with different sizes after adsorbing different surfactants. Adsorption time: 24 h.

Figure 3. Adsorption curves of micron and nano calcium oxalate crystals to different surfactants (A) nano COM and COD; (B) micron COM and COD.

Comparison of Maximum Adsorption Quantities of COM and COD with Different Surfactants

The adsorption quantities of different surfactants on nano/micron COM and COD were showed in Fig. 4. The maximum adsorption quantity and adsorption density of SDS is always greater than CTAB with the same crystal size. It is attributed to that the crystal surface has positive charge for the COM crystal, the adsorption capacity of anionic surfactant SDS is generally stronger than that of cationic surfactant CTAB. While for COD crystals, Sikiric et al. [8] measured the mobility of COD crystals in solution and found that the surface of COD crystals had a positive charge, so the adsorption of COD on SDS is higher than that of CTAB.
Figure 4. The maximum adsorption quantity of different surfactants onto micron and nano calcium oxalate crystals. Surfactant concentration was 450 mg/L.

Tab. 1 Size and adsorption density of micron/nano COM and COD crystals

<table>
<thead>
<tr>
<th>Crystal name</th>
<th>Crystal size</th>
<th>Adsorption density $\Gamma^\ast$ / N/nm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>COM-100nm</td>
<td>100±30 nm</td>
<td>8.23</td>
</tr>
<tr>
<td>COD-100nm</td>
<td>100±20 nm</td>
<td>5.24</td>
</tr>
<tr>
<td>COM-10μm</td>
<td>10±3 μm</td>
<td>31.9</td>
</tr>
<tr>
<td>COD-10μm</td>
<td>10±3 μm</td>
<td>27.2</td>
</tr>
</tbody>
</table>

Adsorption Density Difference of SDS, CTAB and NP-40

The adsorption density ($\Gamma$) of COM-100μm and COD-100μm was 8.23 and 5.24 molecule/nm² at $c$(SDS) = 450 mg/L (Table 1), that is, 8.23 or 5.24 SDS molecules was absorbed on one nanometer square of COM-100nm or COD-100μm surface. This adsorption did not reach equilibrium. The value (8.23 and 5.24) is much smaller than the saturated adsorption density of COM-10 μm and COD-10μm (31.9 and 27.2 molecule/nm² respectively). It indirectly showed that nano COM and nano COD did not reach saturated at $c$(SDS) = 450 mg/L. Since the system had been cloudy, so the concentration of SDS could not be further increased. Namely, the $c$(SDS) was much higher than 450 mg/L when nano COM and COD crystals reached adsorption equilibrium.

Sedimentation of COM and COD Crystals after Adsorption of Different Surfactants

The sedimentation speed of COD-100 nm was faster than that of COM-100 nm, while COM-10 μm was faster than COD-10 μm at the same conditions (Fig. 5). This result mainly is due to the difference of Zeta potential on various crystals. The Zeta potential of COM-100 nm (2.20 mV) is slightly higher than that of COD-100 nm (-1.5 mV). The absolute value of Zeta potential of COD-10 μm (-15.5 mV) is higher than that of COM-10 μm (-6.95 mV). The hydrated diameters of COM-100 nm and COD-100 nm were 1071 nm and 1240 nm, respectively, and that of COM-10μm and COD-10μm were 4252 nm and 3443 nm, respectively. It indicated that the larger the absolute value of Zeta potential was the less agglomeration and the smaller the particle size was in the aqueous solution [9, 10].

Fig. 6 showed the molecular models of adsorption of SDS and CTAB molecules on calcium oxalate crystals. It can be seen that the charge property of COD and COM was changed after
adsorption of specific surfactant, thereby the agglomeration of crystals was inhibited, and ultimately the formation of calcium oxalate kidney stones may be inhibited.

Figure 5. Sedimentation of COM-10 μm(a) and COD-10 μm(b) crystals after adding different surfactants for 5min. From left to right distilled H2O, SDS, CTAB and NP-40.

Figure 6. Molecular models of adsorption SDS and CTAB molecules on calcium oxalate crystals. (COM crystals are similar to COD). (COM and COD crystal; : the molecular of CTAB; : the molecular of SDS.)

Conclusions

The adsorption quantities of various surfactants onto micron/nano COM and COD were ranked in the following order: anionic SDS > cationic CTAB > nonionic NP-40. Different surfactants have different interaction with nano/micron COM and COD crystal, resulting in different adsorption capacity. After adsorption of the surfactant, the absolute value of Zeta potential of the crystals increases, which is helpful to inhibit crystal agglomeration. After adsorbed surfactants, the settling velocity of crystals was slowed down. The sedimentation rate is negative correlation with the adsorption capacity of surfactants and the Zeta potential of the crystals. Anionic surfactant has a greater potential to inhibit the formation of calcium oxalate kidney stones.

Acknowledgements

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References


