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Thermodynamic calculation of the formation of ceramic coatings based on dicalcium phosphate dihydrate and octacalcium phosphate

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This research is focused on preliminary calculations of the thermodynamic model and total Gibbs energy for ceramic coatings based on dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$) and octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$) obtained by chemical modification of ceramics based on α-tricalcium phosphate ($Ca_3(PO_4)_2$). The formation of thermodynamically favorable calcium phosphate (CP) phases during the formation of coatings is shown. The calculations were carried out using the Medusa software. Solutions of sodium acetate (CH_3COONa) and phosphoric acid (H_3PO_4) were used as initial components of the system. According to the calculations, at a pH value of 5.1 and a concentration of $pH = 5.1$ ions $= 10^{-2}$ M and $PO_4^- = 0.45$ M, a coating based on DCPD is formed, and at a pH value of 9 and a concentration of $pH = 9$ ions $= 10^{-3}$ M — phase OCP
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The production of materials for reconstructive surgery is an important and highly relevant objective. The surface state affects the biological properties of implants [1]. Ceramic materials based on thermodynamically favorable calcium phosphate (CP) phases. which are chemically similar to biological human bone tissue, are used widely in medical practice. CPs are used for the application of coatings to metallic implants to facilitate osteointegration. The biological behavior of such coatings depends largely on the chemical and phase composition of the material.

A preliminary thermodynamic model of the formation of dicalcium phosphate dihydrate (DCPD, $CaHPO_4 \cdot 2H_2O$) and octacalcium phosphate (OCP, $Ca_8H_2(PO_4)_6 \cdot 5H_2O$) coatings from α-tricalcium phosphate (α-TCP, $Ca_3(PO_4)_2$) is proposed in the present study. The Medusa software [2] was used to calculate phase equilibria and determine stable PC phases. Buffer solutions based on CH_3COO^-, Na^+, Ca^{2+}, and PO^{4-} (HPO_4^{2-} or $H_2PO_4^-$, depending on the pH value) were the initial components of the system. The concentration of buffer system components CH_3COO^- and Na^+ was 1.5 M, and the concentration of PO_4^{3-} (HPO_4^{2-} or $H_2PO_4^-$) fell within the $0.45-1.55$ M interval [3]. The concentration of Ca^{2+} was varied from 10^{-7} to 10^2 M (extreme limits in Medusa). The pH value of the medium varied from 1 to 13.

The ionic strength of solution was calculated as

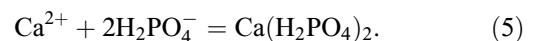$$I_c = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2, \qquad (1)$$
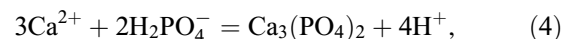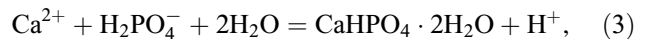
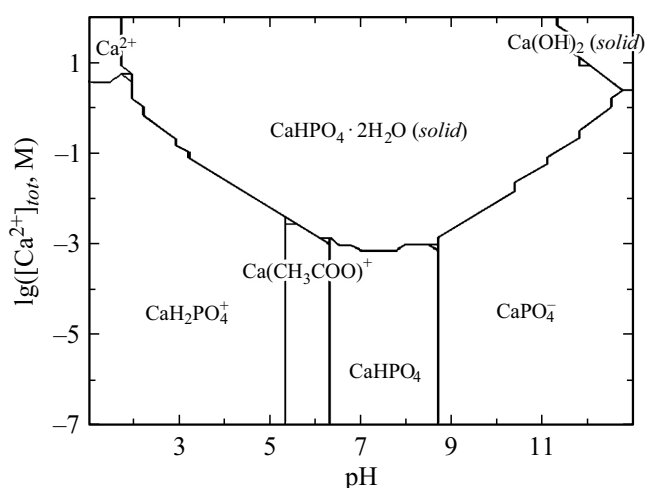and the Gibbs energy was determined using the reaction-isotherm equation

$$\Delta G = \Delta G^0 + RT \ln \Pi a, \qquad (2)$$

where ΔG^0 is the change of the standard Gibbs energy of reaction [kJ/mol], R is the universal gas constant ($8.31\, J/(mol \cdot K)$), T is temperature [K], and Πa is the product of activities of reaction components.

Figure 1 presents the calculated diagram of the region of energetically favorable CP phases in the process of recrystallization of α-TCP ceramics. It is evident that $CaH_2PO_4^+$ ions are dominant in the buffer solution when the concentration of Ca^{2+} ions is insufficient. As surface α-TCP layers dissolve, the concentration of Ca^{2+} increases, and the solution enters the region of DCPD stability. The region of DCPD stability corresponds to the interval of pH values from 5 to 10. As the pH value increases, dicalcium phosphate (DCP, $CaHPO_4$) starts to form.

According to the ternary ionic equilibrium of phosphate ions (Fig. 2), $H_2PO_4^-$ constitute the majority of phosphate ions in the conditions of dissolution of the surface of α-TCP ceramics. This enables the crystallization of the following poorly soluble PCs (DCPD, TCP, and monocalcium phosphate $Ca(H_2PO_4)$, respectively):

$$Ca^{2+} + H_2PO_4^- + 2H_2O = CaHPO_4 \cdot 2H_2O + H^+, \quad (3)$$

$$3Ca^{2+} + 2H_2PO_4^- = Ca_3(PO_4)_2 + 4H^+, \qquad (4)$$

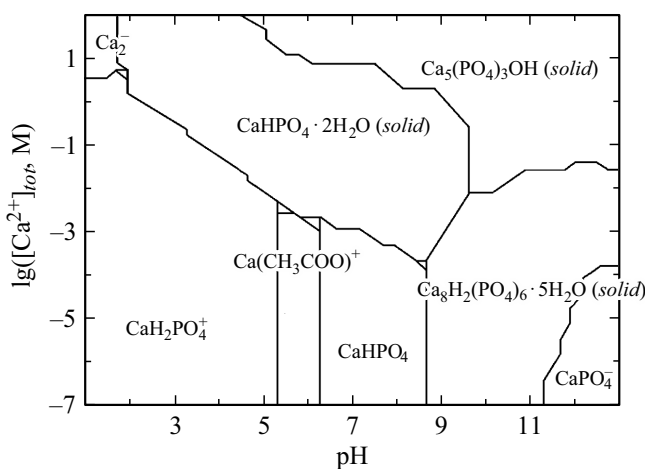$$Ca^{2+} + 2H_2PO_4^- = Ca(H_2PO_4)_2. \qquad (5)$$

Figure 1. Diagram of the PC phases region upon recrystallization of TCP ceramics.
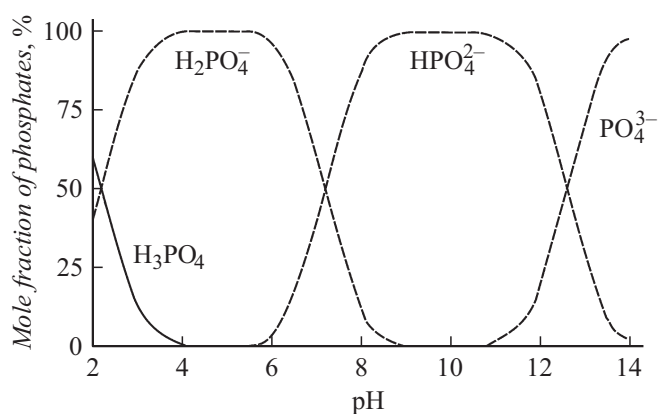
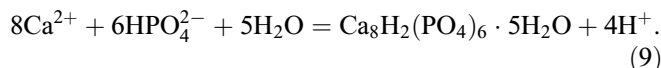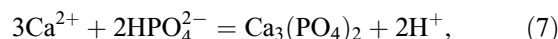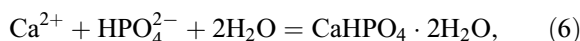**Figure 2.** Diagram of dissociation of phosphoric acid at different pH values.

Figure 3. Diagram of the PC phases region upon recrystallization of DCPD into OCP.

Gibbs energy values

PC	ΔG, kJ/mol	
	α-TCP substrate	DCPD substrate
$CaHPO_4 \cdot 2H_2O$	-546.6	-83.20
$Ca_3(PO_4)_2$	-77.0	-75.90
$Ca(H_2PO_4)_2$	-26.8	$-$
$Ca_8H_2(PO_4)_6 \cdot 5H_2O$	-220.7	-265.32
$CaHPO_4$	$-$	-45.50

The calculated Gibbs energies for poorly soluble PCs are listed in the table.

When coatings based on OCP from DCPD are being formed, HPO_4^{2-} is the major solution component (Fig. 3). This enables the crystallization of the following poorly soluble PCs (DCPD, TCP, DCP, and OCP, respectively):

$$Ca^{2+} + HPO_4^{2-} + 2H_2O = CaHPO_4 \cdot 2H_2O, \qquad (6)$$

$$3Ca^{2+} + 2HPO_4^{2-} = Ca_3(PO_4)_2 + 2H^+, \qquad (7)$$

$$Ca^{2+} + HPO_4^{2-} = CaHPO_4, \qquad (8)$$

$$8Ca^{2+} + 6HPO_4^{2-} + 5H_2O = Ca_8H_2(PO_4)_6 \cdot 5H_2O + 4H^+. \qquad (9)$$

The calculated ΔG values (see the table) were used to determine that the OCP stability region is reached at pH = 9 and a Ca^{2+} ion concentration of 10^{-3} M.

Thus, a preliminary thermodynamic model and preliminary calculations of the total Gibbs energy for ceramic coatings based on PCs, which may be used in the engineering of implant surfaces with a given composition of the end product, were presented.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

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[3] A.Yu. Fedotov, A.A. Kotyakov, I.V. Smirnov, Yu.V. Zobkov, O.V. Baranov, A.A. Egorov, A.Yu. Teterina, E.A. Rad'kova, Yu.B. Tyut'kova, S.M. Barinov, V.S. Komlev, Inorg. Mater.: Appl. Res., **12**, 940 (2021). DOI: 10.31044/1684-579X-2020-0-10-43-48

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