Corrosion Behavior of Titanium in Simulated Body Solutions with the Addition of Biomolecules

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ABSTRACT: Titanium is one of the most used biomaterials for different applications. The aim of this study is to investigate the influence of adenine, thymine, and L-histidine as important biomolecules in the human body on the corrosion behavior of titanium in simulated body solutions. Open circuit measurements, potentiodynamic measurements, electrochemical impedance spectroscopy measurements, and quantum chemical calculations were employed during the investigation. All electrochemical methods used revealed that the investigated biomolecules provide better corrosion resistance to titanium in artificial body solutions. The increase in corrosion resistance is a result of the formation of a stable protective film on the metal surface. Also, quantum chemical calculations are in compliance with electrochemical test results and indicate that adenine, thymine, and L-histidine may act as corrosion inhibitors in the investigated solutions.

INTRODUCTION

Excellent corrosion behavior and high strength-to-density ratio are the most important characteristics of titanium (Ti) and its alloys, making them highly attractive for many industrial and technological applications, including chemical processing and aerospace industries.1−3 Beside titanium and its alloys are among the most important materials that have been used in medicine.4−10 Due to the broad range of applications of titanium, its properties were tested under different conditions. One of the mandatory properties for application in different aggressive media is considerable corrosion resistance. The satisfactory corrosion resistance of titanium and its alloys due to the formation of a protective oxide film on their surface has been confirmed in a number of papers.11−24 Nevertheless, for its application in medicine, in addition to good corrosion characteristics, it is essential that titanium has satisfactory levels of biocompatibility. Biocompatibility of titanium mainly depends on the chemical structure and morphology of the metal surface,25 which suggests that the formed TiO2 film can significantly affect biocompatibility. However, naturally formed TiO2 does not significantly improve the biocompatibility of titanium primarily because of its low thickness. Considering this fact, preferable methods for TiO2 formation are thermal annealing, chemical synthesis, physical vapor deposition, and anodic oxidation.26,27 In any case, formed TiO2 is very stable and resistant to dissolution in aggressive environments. Nonetheless, in biological solutions that are aggressive, the destruction and disappearance of the TiO2 film from the titanium surface occur with time.28 In addition to TiO2, other oxides (TiO, Ti2O3, Ti3O5, TiO3) may also be present on the surface of titanium, but the TiO2 form is the most stable.29−32 The appearance of several types of oxides on the surface of titanium results in the reduction of metal passivation.33 The TiO2 film formed influences the adsorption of ions from the solution on the metal surface because it is highly polar and easily attracts molecules of water and other substances soluble in water.34

It is very important to reduce the dissolution of metals as it leads to a decrease in the concentration of ions released from the metal surface. As a result, the useful lifetime of metals and alloys is prolonged. Available literature data show that numerous organic compounds can be used as corrosion inhibitors for different metals,35−42 but there are limited data on the effect of organic inhibitors on the electrochemical behavior of titanium.43,44 Titanium has dominant applications as a biocompatible material and, therefore, it is necessary to know the mechanisms
of action of Ti in solutions that simulate body fluids. However, the mechanism of the effect of biomolecules on the corrosion processes of titanium and its alloys is not yet fully revealed.\textsuperscript{44} Biomolecules such as proteins and amino acids can be adsorbed on the surface of metals. Further, biomolecules form a film or act as ligands and form metal complexes on the electrode surface and reduce corrosion processes.\textsuperscript{45,46}

The aim of this article is to examine the influence of different concentrations of adenine (AD), thymine (THY), and L-histidine (HIS), biomolecules that are components of the compounds in the human body, on the dissolution of titanium in BM-3 solution. Structures of adenine, thymine, and L-histidine are shown in Figure 1.

![Figure 1. Structures of (a) adenine, (b) thymine, and (c) L-histidine.](image)

- **RESULTS AND DISCUSSION**

  **Open Circuit Potential (OCP) Measurements.** Curves obtained during OCP measurements for 30 min in BM-3 solution with and without the presence of various concentrations of adenine, thymine, and L-histidine are shown in Figure 2a–c.

  Shapes of the obtained curves and higher values of OCP at the end of measurements as compared to those at the beginning of measurements reveal that titanium is passivated in the presence of adenine, thymine, and L-histidine in the investigated solutions.\textsuperscript{47–50} In BM-3 solution, with the addition of THY and HIS at a certain concentration, a sharp increase of OCP values is evident, which indicates the formation of a layer on the electrode surface. Afterward, a decrease of OCP values reveals that the formed layer dissolves due to the action of aggressive ions. The shift of OCP values to a negative direction in the presence of AD, THY, and HIS when compared to the blank solution indicates that the layer formed in the presence of these biomolecules inhibits cathodic reactions.\textsuperscript{51} This will be discussed in more detail later.

  **Potentiodynamic Polarization Measurements.** Polarization curves of titanium obtained in BM-3 solution with the addition of a certain amount of biomolecules are shown in Figure 3. It is evident that the \( E_{\text{corr}} \) values move toward the negative direction in the presence of AD, THY, and HIS, which is in agreement with OCP measurements. This shift of \( E_{\text{corr}} \) values reveals the adsorption of biomolecules on cathodic active sites on the titanium surface, thus preventing the diffusion of ions and molecules to the surface of titanium and reducing cathodic corrosion processes.\textsuperscript{52} The shift of the \( E_{\text{corr}} \) values in all tested solutions is in the negative direction, and the most pronounced shift is achieved in the solution with the addition of L-histidine. This behavior indicates better adsorption of histidine molecules on cathodic active sites as compared to adenine and thymine and more noticeable inhibition of cathodic processes.

  ![Figure 2. Open circuit potential curves of titanium in BM-3 solution without and with the addition of (a) adenine, (b) thymine, and (c) L-histidine.](image)
solution. This probably means that the passive layer is formed at a more negative potential in the presence of biomolecules. In the anodic branches of the polarization curves, the current density is higher in the presence of biomolecules even in the passivated region, indicating that the passive film is less stable compared to the passive film formed in the bare BM-3 solution. However, in any case, in the observed range of potentials, there was no breakdown or dissolution of the protective film. Based on the above, molecules of AD, THY, and HIS engage in the formation of the passive film on the titanium surface, but their protective effect is observed only in the vicinity of the corrosion potential and in the cathodic region. From this, it can be said that AD, THY, and HIS act like cathodic-type inhibitors in BM-3 solution. Anodic polarization curves obtained in the solution with the addition of biomolecules approach the curve obtained in the bare BM-3 solution. This indicates that the process of formation and growth of the TiO$_2$ layer and the process of incorporation of Ca$^{2+}$ and PO$_4^{3-}$ ions are not limited by the diffusion of ions and molecules through a layer of biomolecules on the surface of titanium. Formation of TiO$_2$ on the electrode surface is represented by the following equation:

$$\text{Ti} + 2\text{H}_2\text{O} = \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^-$$  (1)

In addition, adsorption and incorporation of ions and molecules from the solution on and into the oxide film, respectively, contribute to the complexity of the film formed on the titanium surface. The adsorption of ions is facilitated by the OH$^-$ bridges formed on the surface of titanium during hydroxylation, which are highly polarized and easily replaceable by the cations located in their surroundings. Ca$^{2+}$ and PO$_4^{3-}$ are the most common ions in artificial body fluids that adsorb easily on the surface and greatly affect the biocompatibility of titanium. Concentrations of Ca$^{2+}$ and PO$_4^{3-}$ ions on the titanium surface depend on their concentrations in solution. Adsorption of these ions on the TiO$_2$ surface causes an increase in the film thickness, providing an even better barrier and preventing aggressive ions from the solution from coming in contact with titanium. The interaction between the titanium surface and phosphate ions in solution can be represented by the following equations:

$$\text{Ti(OH)}_3^{3+} + \text{H}_2\text{PO}_4^{(aq)} = \text{Ti}^{4+} \cdot \text{HPO}_3^{2-} + \text{H}_2\text{O}$$  (2)

$$\text{Ti}^{4+} \cdot \text{HPO}_3^{2-} + \text{OH}^- = \text{Ti}^{4+} \cdot \text{PO}_4^{3-} + \text{H}_2\text{O}$$  (3)

$$\text{Ti(OH)}_3^{3+} + \text{HPO}_4^{2-} = \text{Ti}^{4+} \cdot \text{PO}_4^{3-} + \text{H}_2\text{O}$$  (4)

The process of adsorption of Ca$^{2+}$ and PO$_4^{3-}$ ions is rapid, but the saturation of the surface is a slow process that requires a longer exposure time of the electrode to the solution. Also, the test solution contains Cl$^-$ ions, and therefore, adsorption of chloride ions occurs on the titanium surface, leading to the formation of the chemisorbed complex according to the equation:

$$\text{Ti} + 4\text{Cl}^- = [\text{TiCl}_4]^$$  (5)

Further, the formed complex ion is transformed into TiCl$_4$:

$$[\text{TiCl}_4]^ = \text{TiCl}_4 + 4\text{e}^-$$  (6)

After that, TiCl$_4$ hydrolyzes according to the equation:

$$\text{TiCl}_4 + 2\text{H}_2\text{O} = \text{TiO}_2 + 4\text{Cl}^- + 4\text{H}^+$$  (7)

In the presence of biomolecules, such as AD, THY, and HIS, adsorption of these molecules occurs on the TiO$_2$ layer. L-Histidine, similar to other amino acids, contains a carboxyl group in its structure, through which it binds with TiO$_2$. Adenine and thymine react with titanium and form a bond with a metal ion through a nitrogen atom in their structure.
Nevertheless, the dissolution of the TiO$_2$ film occurs in aggressive media, and after that, the biomolecules interact with the metal and form a complex. If chloride ions exist in the solution, formation of metal chloride and a metal/biomolecule/chloride complex is observed on the surface during repassivation of the oxide layer. However, more definite characterizations of titanium surface morphology in the presence of biomolecules in artificial body solutions will be performed in the future via some new investigations using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) and atomic force microscopy (AFM).

On the basis of polarization curves, electrochemical parameters of titanium oxidation were determined. Values of corrosion potential ($E_{corr}$), corrosion current density ($j_{corr}$), as well as the anodic and cathodic Tafel slopes ($b_a$ and $b_c$) are presented in Table 1. In addition to the electrochemical parameters shown in Table 1, the dependence of inhibition efficiency (IE) on biomolecule concentrations is also shown. The inhibition efficiency was calculated according to the following equation:

$$\text{IE} = \frac{j_{corr} - j_{lab}}{j_{corr}} \times 100$$  
(8)

where $j_{corr}$ and $j_{lab}$ represent the corrosion current density in the absence and presence of the inhibitor, respectively.

The change of values of anodic and cathodic Tafel slopes in the presence of biomolecules suggests the formation of the protective film on the titanium surface. The shift of the corrosion potential in the presence of inhibitors is more than 85 mV relative to the corrosion potential obtained in the bare solution, which also indicates that adenine, thymine, and L-histidine act as cathodic corrosion inhibitors of titanium in BM-3 solution. The presence of a higher amount of AD, THY, and HIS in BM-3 solution leads to a higher decrease of $j_{corr}$ and an increase of IE, suggesting greater inhibition efficiency of corrosion processes.

### Table 1. Electrochemical Parameters Calculated According to the Polarization Curves of Titanium Recorded in BM-3 Solution with the Addition of Adenine, Thymine, and L-Histidine

| solution   | $E_{corr}$ (V vs SCE) | $i_{corr}$ (A/cm$^2$) | $b_a$ (V/dec) | $b_c$ (V/dec) | IE (%) |
|------------|----------------------|-----------------------|---------------|---------------|--------|
| BM-3       | $-0.097$             | $1.95 \times 10^{-4}$ | $0.281$       | $0.332$       |        |
| $1 \times 10^{-3}$ M AD | $-0.0297$ | $6.19 \times 10^{-7}$ | $-0.232$      | $0.151$       | $68.2$ |
| $5 \times 10^{-5}$ M AD | $-0.182$  | $3.6 \times 10^{-7}$  | $-0.106$      | $0.108$       | $81.5$ |
| $1 \times 10^{-5}$ M AD | $-0.195$  | $3.48 \times 10^{-7}$ | $-0.075$      | $0.089$       | $82.2$ |
| $1 \times 10^{-4}$ M HIS | $-0.250$  | $7.5 \times 10^{-7}$  | $-0.267$      | $0.082$       | $61.5$ |
| $5 \times 10^{-4}$ M HIS | $-0.282$  | $5.4 \times 10^{-7}$  | $-0.150$      | $0.086$       | $72.3$ |
| $1 \times 10^{-4}$ M THY | $-0.3$    | $5.09 \times 10^{-7}$ | $-0.108$      | $0.108$       | $73.9$ |
| $1 \times 10^{-4}$ M THY | $-0.175$  | $7.75 \times 10^{-7}$ | $-0.246$      | $0.211$       | $60.2$ |
| $5 \times 10^{-4}$ M THY | $-0.154$  | $6.82 \times 10^{-7}$ | $-0.203$      | $0.207$       | $65.0$ |
| $1 \times 10^{-4}$ M THY | $-0.180$  | $3.86 \times 10^{-7}$ | $-0.095$      | $0.074$       | $80.2$ |

### Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy was used to investigate the changes at the passive film/electrolyte interface upon exposure of the Ti samples to BM-3 solution with the addition of different amounts of adenine, thymine, and L-histidine.

IVIUM software was used for precise fitting of the obtained results. Equivalent circuits are shown in Figure 4. In the presented equivalent circuits, $R_1$ represents the solution resistance, and $R_2$ is the resistance of the passive film formed on the metal surface (barrier layer). CPE$_1$ is a constant phase element, which consists of film capacitance $C_1$ and deviation parameters $n_1$, that represents the deviation of the ideal capacitive behavior of the passive film, which is attributed to the roughness and defects on the surface of the electrode.$^{51-63}$ A constant phase element (CPE) was used to improve the fitting quality instead of the ideal capacitance.$^{64}$ The constant phase element is dominantly used in systems with surface heterogeneity.$^{65-67}$ Electrochemical impedance spectroscopy parameters are presented in Table 2.

CPE values decrease in the presence of adenine, thymine, and L-histidine, most likely due to the adsorption of their molecules on the titanium surface, indicating the increase of thickness of the passive film on the electrode surface. Nonetheless, the increase of $n$ values implies a certain decrease of the surface inhomogeneity due to the biomolecule adsorption and formation of the passive layer on the metal surface.$^{68}$ Furthermore, $C_1$ values were calculated according to the equation$^{68}$

$$C_1 = \frac{(\text{CPE}_1 \times R_2^{1-n})}{n_1}$$  
(9)

$C_1$ values presented in Table 2 decrease in the presence of biomolecules, whereby the most pronounced reductions were observed in the BM-3 solution with adenine. A decrease of $C_1$ values indicates adsorption of biomolecules on the metal surface and a lower value indicates better adsorption of the molecule. Accordingly, adenine adsorbed to a greater extent on the titanium surface compared to other biomolecules, providing the best protection. Besides, $R_2$ values increase in the presence of biomolecules, which is a sign of the growth of the passive film on the electrode surface.

The Nyquist diagram obtained in the BM-3 solution with the addition of AD, THY, and HIS (Figure 5) showed only one capacitive loop with a high polarization resistance, which is typical for passivated surfaces. Evaluation of the Nyquist diagram leads to the conclusion that the semicircle diameter increases in the presence of AD, THY, and HIS, suggesting that oxidation processes decrease. The diameters of the capacitive loops increase in the order $AD > THY > HIS$, revealing that in the presence of adenine, the formed protective layer on the titanium surface increases the corrosion resistance.
and reduces the oxidation of the metal to a greater extent than the film formed in the presence of thymine and L-histidine. Further, in the bare BM-3 solution, one capacitive loop is also observed, which suggests that in this solution, titanium oxidizes and forms a layer of products on the surface. Figures 6 and 7 represent the Bode phase angle and Bode module diagrams, respectively, and it can be seen that at higher frequencies in all examined solutions, the values of absolute impedance $|Z|$ are constant, whereby the phase angle is 0°, which corresponds to the resistive region. Nevertheless, Bode module diagrams indicate a purely capacitive behavior in the medium and in one part of the low-frequency region, which is reflected in the negative slope of curves, with a slope of $-1$ in the log $|Z|$–log $f$ form, and in maximum values of phase angle. At low frequencies, absolute impedance values lose their linearity and the values of phase angle do not reach 0°, which indicates the absence of the resistive region. This highly capacitive behavior is typical for passive materials with a high corrosion resistance.

In all examined BM-3 solutions, with the addition of biomolecules, max values of phase angle were close to each other, indicating that the stability of the formed protective films was similar. Values of phase angle are slightly higher in adenine and thymine solutions, which indicates that the formed film in L-histidine solution provides less protection during exposure of titanium to an aggressive environment. Also, the order of inhibition efficiency obtained by EIS measurements is in accordance with those obtained from polarization measurements.

**Quantum Chemical Calculations.** Quantum chemical calculations represent a very important tool used to establish a correlation between the molecular structure and the inhibition efficiency of inhibitors. Quantum chemical calculations and molecule geometry optimization were realized by the PM3-SCF method. The software used for calculation and visualization was ArgusLab 4.0, which has already been proved to be very helpful for this purpose. The proposed spatial distribution of HOMO and LUMO is presented in Figure 8. Values of the highest occupied molecular orbital energy ($E_{\text{HOMO}}$), the lowest unoccupied molecular orbital energy ($E_{\text{LUMO}}$), and the energy gap as indicators of the reactivity and adsorption ability of the inhibitor molecules on the metal surface ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) are presented in Table 3.

Lower values of $\Delta E$ reveal higher reactivity and adsorption ability of the examined biomolecule on the metal surface. Ionization energy ($I = -E_{\text{HOMO}}$) and electron affinity ($A = -E_{\text{LUMO}}$) correspond to negative values of the highest

**Table 2.** Electrochemical Impedance Spectroscopy Parameters for Titanium in BM-3 Solution without and with the Addition of Adenine, Thymine, and L-Histidine

|        | $R_1$ (Ω/cm²) | $R_2$ (Ω/cm²) | CPE$_1$ (Ω$^{-1}$ cm$^{-2}$ s$^n$) | $n_1$ | $C_1$ (F/cm²) | IE (%) |
|--------|--------------|--------------|-----------------|-------|-------------|--------|
| BM-3   | 41           | 7.9 $\times$ 10$^3$ | 1.805 $\times$ 10$^{-4}$ | 0.85  | 1.91 $\times$ 10$^{-4}$ |        |
| 1 $\times$ 10$^{-3}$ M AD | 22           | 3.5 $\times$ 10$^4$ | 8.05 $\times$ 10$^{-5}$ | 0.86  | 9.51 $\times$ 10$^{-5}$ | 77.4   |
| 1 $\times$ 10$^{-3}$ M HIS | 28.4         | 2.2 $\times$ 10$^4$ | 1.02 $\times$ 10$^{-4}$ | 0.88  | 1.14 $\times$ 10$^{-4}$ | 64.1   |
| 1 $\times$ 10$^{-3}$ M THY | 34           | 2.55 $\times$ 10$^4$ | 1.0 $\times$ 10$^{-4}$ | 0.87  | 1.15 $\times$ 10$^{-4}$ | 69.0   |
occupied molecular orbital energy and lowest unoccupied molecular orbital energy, according to Koopmans’s theorem. Electronegativity (χ), global hardness (η), and number of transferred electrons (ΔN) may be calculated according to equations 8

\[
\chi = 0.5 \times (I + A) \\
\eta = 0.5 \times (I - A) \\
\Delta N = \frac{(\chi_{\text{Ti}} - \chi_{\text{adh}})}{2 \times (\eta_{\text{Ti}} + \eta_{\text{adh}})}
\]

According to the literature data, some authors pointed out that the inhibitor with the lowest values of η has the highest inhibition efficiency.79,80 The obtained values for IE and η of adenine, thymine, and L-histidine confirmed this statement.

At the beginning of the inhibitor action, inhibitor molecules approach the titanium. After that, electrons flow from the molecule with a lower electronegativity to the molecule with a higher electronegativity until their electronegativities become equal.81–83 Therefore, a high value of electronegativity indicates that the compound is less capable of donating its electrons to the acceptor molecule.84,85 Ionization energy is one of the most important indicators of the reactivity of compounds. High values of ionization energy point to chemical inertness of the molecule, while small values of ionization energy confirm high reactivity of the compound.86 The obtained results of the ionization energy of AD, THY, and HIS indicate that adenine is more reactive and has higher inhibition efficiency than thymine and L-histidine, which is in agreement with electrochemical tests.

The dipole moment (μ) is also an important parameter that shows the polarization ability of the inhibitor molecules. Accumulation of inhibitor on the metal surface is more intense in the case when the inhibitor has a lower value of dipole moment. In this case, the inhibition efficiency increases, which is also in agreement with polarization and EIS measurements.87,88 Further, negative values of the number of transferred electrons (ΔN) indicate the transfer of electrons from the metal surface to the biomolecule.76,89

### Table 3. Quantum Chemical Parameters

|          | adenine | thymine | L-histidine |
|----------|---------|---------|-------------|
| E_HOMO (eV) | −8.835 | −9.533 | −9.141 |
| E_LUMO (eV) | −0.449 | −0.523 | −0.010 |
| ΔE (eV) | 8.386 | 9.01 | 9.131 |
| μ (D) | 2.47498272 | 3.86771172 | 12.47957269 |
| I (eV) | 8.8350561 | 9.53353716 | 9.140810132 |
| A (eV) | 0.448617032 | 0.522796944 | 0.010122864 |
| χ (eV) | 4.641836566 | 5.02816533 | 4.575466498 |
| η (eV) | 4.193219534 | 4.505368386 | 4.565343634 |
| ΔN | −0.142 | −0.175 | −0.123 |

### CONCLUSIONS

Adenine, thymine, and L-histidine act as cathodic corrosion inhibitors of titanium in BM-3 solution. Polarization measurement results reveal adsorption of biomolecules on cathodic active sites on the titanium surface, thus preventing the diffusion of ions and molecules to the surface of titanium. Adsorption of biomolecules leads to the formation of a protective film on the titanium surface. The formed barrier layer provides protection in the vicinity of the corrosion potential and inhibits cathodic corrosion processes. Also, potentiodynamic measurements show that the passive layer was formed at more negative potentials in the presence of the inhibitor. Besides, in aggressive media, such as BM-3 solution, a certain amount of TiO₂ dissolves and AD, THY, and HIS are capable of reacting with the metal and forming a complex that provides protection to the metal surface from aggressive ions.

EIS measurements also reveal that a surface film was formed in the presence of biomolecules in simulated body solutions. Furthermore, the stability of the formed films is similar in the presence of all tested biomolecules.

Quantum chemical calculations were used for a better understanding of the interaction between titanium and biomolecules, and the obtained results are in accordance with the results obtained by electrochemical studies.

### MATERIALS AND METHODS

During the experiments, the titanium electrode was used as the working electrode. The titanium electrode was made of CP-Ti grade 2, and the dimension of the electrode was 10 mm × 10 mm × 1 mm. Before each measurement, the Ti electrode was abraded with SiC paper (grade 250, 1500, and 2000), then washed with distilled water and dried. A platinum electrode was applied as an auxiliary electrode, and a standard calomel electrode (SCE) was utilized as the reference electrode. An electrochemical workstation (IVIUM XRE, IVIUM Technologies) with adequate software was used for electrochemical tests.

Open circuit potential (OCP) measurements, potentiodynamic polarization, and electrochemical impedance spectros-
copy (EIS) are the electrochemical methods that were used in the investigation. Open circuit potential measurements were carried out in a time period of 30 min. Then, LV and EIS measurements were carried out. Potentiodynamic curves were recorded at a scan rate of 1 mV/s from the open circuit potential up to −0.6 V in the cathodic direction and 1.0 V in the anodic direction. Afterward, electrochemical impedance spectroscopy measurements were conducted at the open circuit potential in the frequency range from 100 kHz to 0.01 Hz, with a 10 mV amplitude of the excitation signal. All measurements were done at ambient temperature. Also, all measurements were repeated at least three times, and the presented curves represent the mean value of the measurements.

ArgusLab 4.0 software and the density functional theory (DFT) method for geometrical optimization were used for molecular structure examination, and accordingly, quantum chemical parameters were calculated.

The electrochemical tests of titanium behavior were performed in the artificial body fluid BM-3. The composition of BM-3 solution is shown in Table 4.

| Table 4. Composition of BM-3 Solution |
|--------------------------------------|
| compound | NaCl  | KCl  | MgCl₂·6H₂O | CaCl₂·2H₂O | NaH₂PO₄·2H₂O | NaHCO₃ |
| concentration (g/dm³) | 4.7865 | 0.5975 | 0.1655 | 0.2646 | 0.1250 | 3.7005 |

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**Notes**

The authors declare no competing financial interest.

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