Effect of electrolyte conductivity and local electric field inhomogeneity on heating of an aqueous suspension of solid-state nanoparticles

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Abstract. This work theoretically investigates the process of heat release in an electrolyte near a solid-state nanoparticle when exposed to an external radio-frequency electromagnetic field. The effect on the heat release of the effect of a change in the electrical conductivity of the electrolyte near the nanoparticle due to the redistribution of the ion concentration and the inhomogeneity of the electric field caused by the difference in the dielectric constants of the electrolyte and the nanoparticle is taken into account. The proposed model can be useful for choosing the optimal parameters of nanoparticles and radio frequency radiation when used in biomedicine for tumor hyperthermia.

1 Introduction
Thermal heating of nanoparticles is used in various applied problems, in particular, therapeutic hyperthermia is one of the most important applications. Hyperthermia is a promising method for treating oncological diseases, and is a general or local heating of the body. There are various ways to achieve hyperthermia, however, in this work, heating using radio frequency radiation is considered, since it is able to penetrate deeply into human tissues. If the local body temperature is raised to 45°C, it is possible to guarantee the destruction of cancer cells. Hyperthermia can also be used in conjunction with chemotherapy for greater therapeutic effect [1,2].

However, the clinical use of hyperthermia is difficult due to the lack of equipment and techniques for local heat delivery. The use of nanoparticles capable of accumulating in a tumor and causing thermal damage to nearby tissues under the influence of external fields opens up new possibilities in tumor hyperthermia [3]. The advantage of using nanoparticles is that nanoparticles can act as multimodal agents and be used in both therapy and diagnosis of tumors.

The effect of heating aqueous suspensions of biocompatible weakly conductive silicon nanoparticles was published in [4, 5], which describe both the theoretical description of the suspension heating process and the experimental results.
The article [4] proposes a description of the mechanism of operation of nanoparticles as thermosensitizers, and experimentally shows a direct correlation between the concentration of nanoparticles in a solution and the rate of its heating. In [4], the efficiency of using nanoparticles in radiofrequency therapy for cancer was shown, as well as the ability of Si nanoparticles to biodegradability, which makes this type of particles preferable. However, work [4] does not describe the model of the interaction of a radio-frequency field with a suspension.

Article [5] proposes a model of heating an aqueous HCl solution containing silicon nanoparticles by an external radio frequency field. This model is based on the following assumptions: the displacement of electrolyte ions under the action of an external field occurs along one spatial coordinate (one-dimensional case), the dielectric constant of the electrolyte is equal to the dielectric constant of water and does not depend on the concentration of ions and the frequency of the applied field, acceleration of ions under the action of an external field is absent due to viscous friction, the skin effect in the electrolyte is ignored.

In [5], preliminary results were obtained that qualitatively describe the process of heating the electrolyte, but due to some simplifications proposed in the model, this result may not be entirely accurate.

This article proposes the development of the described model taking into account some corrections, namely: the oscillations of ions occur in three spatial coordinates, the inhomogeneity of the local field around the nanoparticle is taken into account.

2 Model

A spherical silicon nanoparticle with radius $a$ is in an aqueous solution of HCl with a specific conductivity $\sigma_0$ in an external electromagnetic field of the radio frequency range, amplitude of the alternating electric field in the medium $E_0$.

Under the action of an external field, electrolyte ions are set in motion, which can be considered as the appearance of an electric current in the electrolyte, and, consequently, Joule heating. The thermal power released in the electrolyte is calculated [5] as follows (1).

$$P = \frac{1}{2} \omega \varepsilon_0 \varepsilon''(\omega) E_0^2$$

Where $\omega$ – is the circular frequency of the external field, rad/s, $\varepsilon_0$ – the dielectric constant, $\varepsilon''(\omega)$ – is the imaginary part of the dielectric constant of the electrolyte, which is sought in the form (2).

$$\varepsilon''(\omega) = \frac{i \varepsilon_w \Omega_0 \omega}{\Omega_0^2 + \omega^2}$$

where, $\varepsilon_w$ – dielectric constant of water, $\Omega_0 = \frac{\sigma_0}{\varepsilon_w \varepsilon_0}$ – inverse Maxwell relaxation time, $\sigma_0$ – electrolyte conductivity.

Specific thermal power released in the electrolyte is determined by the expression (3).

$$P = \frac{1}{2} \varepsilon_0 \varepsilon_w \frac{\Omega_0 \omega^2}{\Omega_0^2 + \omega^2} E_0^2$$

The heating of the electrolyte $Q_{el}$ under the action of an external field in a certain volume outside the particle can be written in the following form (4).

$$Q_{el} = 2\pi |E_0|^2 \int_a \frac{\Omega_0 \omega^2}{\Omega_0^2 + \omega^2} r^2 dr$$
where $L$ – distance of overlapping thermal fields of nanoparticles.

Since the nanoparticle has a certain surface charge, the electric field created by the nanoparticle attracts ions of the opposite sign, which leads to an increase in the concentration of charge carriers near the nanoparticle. The electrolyte conductivity takes the form (5).

$$
\sigma(r) = \sigma_0 + \sigma_a \frac{a}{r} \exp \left( \frac{a-r}{L_D} \right)
$$

(5)

where $\sigma_a = \frac{\sigma_0}{\mu+1} (\mu \exp \left[ -\frac{e \zeta}{kT} \right] + \exp \left[ \frac{e \zeta}{kT} \right])$, $L_D$ – Debye length, $\zeta$ – zeta potential, $e$ – elementary charge, $k$ – Boltzmann constant, $T$ – medium temperature, $\mu = \mu_+ / \mu_-$ – the ratio of the mobility of positive and negative ions.

Thus, the electrolyte heating in the presence of a nanoparticle is determined by the expression (6).

$$
Q_{ex} = 2\pi \left| \bar{E}_0 \right|^2 \int_{a}^{L} \frac{\Omega \omega^2}{\Omega^2 + \omega^2} r^2 dr
$$

(6)

where, $\Omega = \frac{\sigma(r)}{\varepsilon_0 \varepsilon_{r\text{q}}}$

Since the field near the nanoparticle is inhomogeneous, it is necessary to take into account the effect of this inhomogeneity on heat release. The local field near the particle $E_{inh}$ is represented as a combination of two components of the electric field (7): directed along the external field $E_z$ and directed orthogonally to the external field $E_r$.

$$
\bar{E}_{inh}(r, \theta) = \sqrt{\left| \bar{E}_r(r, \theta) \right|^2 + \left| \bar{E}_z(r, \theta) \right|^2}
$$

(7)

$E_z$ and $E_r$ have the form, respectively (8) and (9) [6].

$$
\bar{E}_z(r, \theta) = \bar{E}_0 \left( 1 + \frac{\text{Re}(s)/\text{Re}(s)+2}{\text{Re}(s)+2} \right)^{-1} a^3 \sin(2\theta) / r^3
$$

$$
\bar{E}_r(r, \theta) = \bar{E}_0 \left( \frac{\text{Re}(s)/\text{Re}(s)+2}{\text{Re}(s)+2} \right)^{-1} a^3 \sin(2\theta) / 2r^3
$$

(8)

(9)

where, $\varepsilon_p$ – dielectric constant of a nanoparticle.

The final formula for calculating heat release is (10).

$$
Q_{tot} = 2\pi \int_{a}^{L} \int_{0}^{\pi} r^2 dr d\theta \cdot \Omega \omega^2 / \Omega^2 + \omega^2 \sin(\theta) r^2 d\theta
$$

(10)

3 Calculation results and comparison with experiment

The contribution $\Delta Q/Q_{el}$, where $\Delta Q = Q_{tot} - Q_{el}$, of the nanoparticle to the heating of the electrolyte medium has been calculated. Nanoparticle size 7.5 nm, zeta potential -30 mV at external field frequencies of 1 MHz, 10 MHz and 100 MHz figure 1.
Figure 1. Dependence of the relative contribution of nanoparticles to the heating of the solution on the conductivity of the electrolyte.

Figure 1 shows the calculation of the relative contribution of the nanoparticle to the heating of the electrolyte at different values of the field frequency. It is shown that the relative contribution to the total heating decreases with an increase in the electrolyte conductivity, however, tends to a nonzero value at infinity, which is achieved due to the inhomogeneity of the local field near the nanoparticle.

Figure 2. Dependence of heat release in a solution of nanoparticles under the action of an electric field with a frequency of 27 MHz on the specific electrical conductivity of the electrolyte in a container with a volume of 3 and 8 ml.

Figure 2 shows the experimental and calculated values of the contribution of silicon nanoparticles with a radius of 7.5 nm under the action of an electric field of 27 MHz from the specific electrical conductivity of the electrolyte. 27 MHz is a characteristic frequency used in the treatment of various diseases. The experiment was carried out for volumes of the heated suspension of 3 and 8 ml. The experimentally obtained
results of heating the electrolyte by nanoparticles are in agreement with the chosen model (solid line) in the region of low electrolyte conductivities. At high conductivity of the electrolyte, there is a discrepancy with theory, which may be associated with field inhomogeneities that arise at the boundaries of the walls of the container with the solution. You can see that with a larger volume of the container, this effect is smoother.

4 Conclusion

The heating of aqueous solutions of electrolytes in the presence of solid-state nanoparticles in an electric field of the radio-frequency range is investigated. A model has been developed that takes into account the processes of heat release in the electrolyte layer around the nanoparticle, which are caused by the inhomogeneity of the local electric field near the nanoparticle. The theoretical dependence, which takes into account the inhomogeneity of the electric field near nonconducting nanoparticles with a radius of 7.5 nm, agrees with the experimentally obtained data.

References

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