NANO-SENSORS FOR MODELING OF RADIATION PROCESSES

Marsagishvili T., Machavariani M., Tatishvili G., Khositashvili R.,
Tskhakaia E., Ananiashvili N., Metreveli J., Kikabidze-Gachechiladze M.

Abstract. Dosimetry, which is based on registration of the products created as a result of the influence of radiation, has essential value in investigation of radiation processes. Application of sensitive methods and increase of the concentration by use of adsorbents allows to use the sensors based on registration of electro-conductivity. It is suggested to use given sensors for determination of some substances existent in biological liquids (with radioactive substances) and for determination of radioactive detrimental impurities in water ecosystems. Analytical expressions of kinetic parameters for charge transfer and electron excitation energy transfer processes between particles are obtained.

Keywords and phrases: Nano-sensors, quantum approach, charge transfer, Hamiltonian.

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Different processes occur in substances under the influence of high energy radiation (heavy charged particles, neutrons, electrons, X-ray beams, etc.). As a result of such influence different short-lived formations occur in the substance, such as excited molecules, free radicals, solvated electrons, etc.

Subject to environmental contamination by radionuclides a problem of fixing of radiation sources occurs. Because of very low concentrations of radionuclides their detection is connected with some difficulties. At the same time, long-term exposure of radiation sources, even at their low concentration, brings to essential changes in biological processes. Possibilities of modern technical registration facilities may be used during investigation of radiation sources, when their concentration is low. At the same time, one can increase concentration of radionuclides in liquid media with the help of synthetic or natural (zeolites) adsorbents.

We will consider the sensors based on registration of electro-conductivity [1]. Principle of operation of nano-sensors may be the following. Adsorption of molecule on the electrode coating takes place under the influence of radionuclide, electron or heavy particle. As a result, the magnitude of current transmitted between electrodes of the sensor changes. Among the components, used for creation of sensors' electrodes, there are no substances harmful for the environment (materials with repeated processing and regeneration possibilities will be used). The analytical signal of these sensors may be transmitted to large distances without any previous processing. That allows placement of these devices in such zones, which are inaccessible or dangerous for the maintenance personnel [2-6]. We suggested to use given sensors for determination of some substances existent in biological liquids (with radioactive substances).

The processes passing in the investigated system may be divided into several groups. (First group) - charge transfer processes between particles and between electrode and particle in condensed medium. (Second group) - electron excitation processes of some

particles and processes of electron excitation energy transfer between particles in condensed medium. Consequently,the process may be divided into two types. (First type processes) - charge transfer form electrode on particle takes place i.e. current, which passes between the electrodes of the sensor changes. (Second type processes) - molecule excitation occurs in the film on the surface of the electrode under the influence of radiation and transfer of excitation energy takes place.

Charge transfer processes from electrode on impurity particle may be described analytically, at selection of particular system, for which system's Hamiltonian will be written correctly. The principal complicity of research of electron transfer processes is connected with necessity of quantum approach. In frames of this approach there are no accepted models for charge transfer and energy transfer processes in nonregular condensed medium. Usage of mathematical physics apparatus of temperature Green function permits description of complex condensed systems and charge transfer processes in such systems. This method permits to unify theoretical approaches and to use different models for description of spatial and frequency effects of dispersion [7-14]. Hence, we have derived quantum expression for density of cathode current of the heterogeneous process for semiconductor electrode with Fermi distribution

$$i_c = e\pi |L_{fi}(\vec{R}^*, \Psi^*)|^2 \int d\epsilon kT \rho(\epsilon) exp(-\ln \sin(\pi\theta^*)) \Phi(\vec{R}^*, \Psi^*) U(\vec{R}^*, \Psi^*) \qquad (1)$$

$$exp\left\{-\beta\theta^* \Delta F - \Psi^m(\vec{R}^*, \Psi^*, \theta) - \sum_{k=1}^{N} \beta E_k \frac{\theta^*(1-\theta^*)\omega_k^i \omega_k^f}{(1-\theta^*)(\omega_k^i)^2 + \theta^*(\omega_k^f)^2} \theta^* \ln \prod_{k=1}^{N} (\omega_k^f/\omega_k^i)\right.$$

$$\left. - e\eta - \theta^* \ln[1 + \beta \sum_{k=1}^{N} (G_k(\vec{R}^*, \Psi^*) + (\omega_k^f/\omega_k^i)\bar{G}_k(\vec{R}^*, \Psi^*)](2E_{rk}\omega_k^i)^{1/2}(\omega_k^f)^{-1}\right\}$$

$$\times (2\pi)^{1/2}[\prod_{k=1}^{N} \omega_k^i((1-\theta)(\omega_k^i)^2 + \theta^*(\omega_k^f)^2)^{-1/2}][1 + (\theta^*(\beta\theta^* - F_\omega(\theta^*)))]$$

$$\times \sum_{k=1}^{N} [(G_k(\vec{R}^*, \Psi^*) + (\omega_k^f/\omega_k^i)\bar{G}_k(\vec{R}^*, \Psi^*)](2E_{rk}\omega_k^i)^{1/2}(\omega_k^f)^2[(1-\theta^*)(\omega_k^i)^2 + \theta^*(\omega_k^f)^2]^{3/2}],$$

where ΔF is free energy of the process, including particle's electron excitation energy in final state, E_m is reorganization energy of n-th intramolecular degree of freedom of the particle,ω_n^i and ω_n^f are frequencies of intramolecular oscillation at the beginning and at the end of the process correspondingly. The functions $G_k(\vec{R}^*, \Psi^*)$ and $\bar{G}_k(\vec{R}^*, \Psi^*)$ are connected with interaction of intramolecular oscillations of impurity particle with fluctuations of molecule polarization of electrolyte and are given by the formulas

$$G_k(\vec{R}^*, \Psi^*) = -\frac{1}{2} \int d\vec{r} d\vec{r}' \frac{\partial E_i(\vec{r}, \vec{R}^*, \Psi^*)}{\partial Q} g_{ik}^R(\vec{r}, \vec{r}', \omega) \Delta E_k(\vec{r}', \vec{R}^*, \psi^*)), \ \omega = 0, \quad (2)$$

$$\bar{G}_k(\vec{R}^*, \Psi^*) = -\frac{1}{2} \int d\vec{r} d\vec{r}' \Delta E_i(\vec{r}, \vec{R}^*, \psi^*) g_{ik}^R(\vec{r}, \vec{r}', \omega) \frac{\partial E_i(\vec{r}', \vec{R}^*, \Psi^*)}{\partial Q}.$$

ΔE is change of electric field intensity of impurity particle and electrode during charge transfer process. In the formulas (1), (2) star signifies the value of this coordinate in point of maximum by taking of corresponding integral by method of saddle point. Saddle point θ^* may be found from the equation

$$e\eta + \beta\Delta F + \frac{\partial\Psi^m(\vec{R}^*,\Psi^*,\theta)}{\partial\theta} + \frac{\partial}{\partial\theta}\sum_{k=1}^{N}\beta E_{rk}\frac{\theta(1-\theta)\omega_k^i\omega_k^f}{(1-\theta)(\omega_k^i)^2 + \theta(\omega_k^f)^2} + \ln\prod_{k=1}^{N}(\omega_k^f/\omega_k^i)$$

$$+\ln[1 + \beta\sum_{k=1}^{N}(G_k + (\omega_k^f/\omega_k^i)G_k^-)](2E_{rk}\omega_k^i)^{1/2}(\omega_k^f)^{-1} + \pi ctg(\pi\theta) = 0. \qquad (3)$$

In this formula L_{fi} is resonance integral of interaction of particle with the surface of semiconductor electrode.

In the formulas (1)-(3) the function $U(\vec{R}^*,\Psi^*)$ is calculated for concrete processes with consideration of geometry of particles and electrodes. $\Psi^m(\vec{R}^*,\Psi^*)$ is function of medium reorganization given by

$$\Psi^m(\vec{R}^*,\psi^*,\theta) = \frac{1}{\pi}\int d\vec{r}d\vec{r}'\Delta E_1(\vec{r},\vec{R}^*,\psi^*)\Delta E_k(\vec{r}',\vec{R}^*,\psi^*))\int\limits_{-\infty}^{\infty} d\omega\,\mathrm{Im}\,g_{ik}^R(\vec{r},\vec{r}',\omega)$$

$$\frac{sh\dfrac{\beta\omega(1-\theta)}{2}sh\dfrac{\beta\omega\theta}{2}}{\omega^2 sh\dfrac{\beta\omega}{2}}.$$

As conducted estimations show, realization of analytical calculations is not possible completely. So, it is necessary to carry out numerical integration.

Activation energy of the process can be determined by formula

$$E_a = -\ln(\sin\pi\theta^*) + \theta^*(1-\theta^*)E_r^m - \Delta F\theta^* + \sum_{k=1}^{N}E_{rk}\theta^*(1-\theta^*)\omega_k^i\omega_k^f[(1-\theta^*)(\omega_k^i)^2 + \theta^*(\omega_k^f)^2]^{-1}$$

$$-e\eta - kT\theta^*\ln[1 + \beta\sum_{k=1}^{N}(G_k + (\omega_k^f/\omega_k^i)G_k^-)](2E_{rk}\omega_k^i)^{1/2}(\omega_k^f)^{-1} + \theta^*\sum_{k=1}^{N}\ln(\omega_k^f/\omega_k^i). \quad (4)$$

If interaction of intramolecular oscillations of particle with fluctuations of medium polarization will be neglected, then expression (4) will be simplified

$$E_a = -\ln(\sin\pi\theta^*) + \theta^*(1-\theta^*)E_r^m - e\eta - \Delta F\theta^*$$

$$+\sum_{k=1}^{N}E_{rk}\theta^*(1-\theta^*)\omega_k^i\omega_k^f[(1-\theta^*)(\omega_k^i)^2 + \theta^*(\omega_k^f)^2]^{-1}.$$

$$(5)$$

According to (5) equation (3) for determination of θ^* becomes

$$e\eta + \beta\Delta F - \ln(\sin\pi\theta^*) + (1-2\theta)E_r^m + \frac{\partial}{\partial\theta}\sum_{k=1}^{N}\beta E_{rk}\frac{\theta(1-\theta)\omega_k^i\omega_k^f}{(1-\theta)(\omega_k^i)^2 + \theta(\omega_k^f)^2} = 0.$$

If intramolecular reorganization of particle of neglected or if particle is monoatomic, we obtain

$$E_a = -\ln(\sin \pi\theta^*) + \theta^*(1 - \theta^*)E_r^m - e\eta - \Delta F\theta^*.$$

R E F E R E N C E S

1. Marsagishvili T, Ananiashvili N., Metreveli J., et all. Applications of Georgian Zeolites for the Extraction of Useful Components from Natural and Waste Waters. *ECB1260*, (2014), 102-103.

2. Melnikov M.J., Ivanov V.L. Experimental Methods of Chemical Kinetic (Russian). *Fotokhimia, Moscow*, 2004.

3. Hernandez R., Valles Cr., Benito A., Maser W., et all. Graphene-based potentiometric biosensor for the immediate detection of living bacteria. *J. Biosensors and Bioelectronics*, (2013), 553-557.

4. Fu Y., Forman M., Leznoff C., Lever A. Effect of stearic acid on molecular orientation in metal-free 2,9,16,23-tetra-tert-butyltetrabenzotriazaporphine Langmuir-Blodgett Films. *J. Phys. Chem.*, **98** (1994), 85-89.

5. Goldenberg L.M. Application of Electrochemical Methods for Study of Electroactive Langmuir-Blodgett Films (Russian). *Uspekhi Khimii*, **98** (1997), 11-41.

6. Fu Y., Jayaraj K., Lever A., Langmuir L. Langmuir-Blodgett Films of Bis (stearyl Pyridine-4-carboxylate)-Phthalocyaninatoiron (II). *J. Phys. Chem.*, **10** (1994), 36-38.

7. Abrikosov A.A., Gorkov L.P., Dzyaloshinski I.E. Methods of Quantum Field Theory in Statistical Physics. *Dover Publ. INC. New York*, 1963.

8. Plattsman F., Volf P. Waves and Interactions in Plasma of Solid (Russian). *Mir; Moscow*, 1975.

9. Dogonadze R.R., Marsagishvili T.A. The Chemical Physics of Solvation, Part A. *Elsevier, Amsterdam*, 1985.

10. Agranovich V.M., Galanin M.D. Electron Excitation Energy Transfer in Condensed Medium (Russian). *Nauka, Moscow*, 1978.

11. Ermolaev V.L., Bodunov E.N., Sveshnikov E.B. et all. Nonradiative Electron Excitation Energy Transfer (Russian). *Nauka, Leningrad*, 1977.

12. Dogonadze R.R., Kuznetsov R.R., Marsagishvili T.A. The present state of the theory of charge transfer processes in condensed phase. *Electrochimica Acta*, **25** (1980), 1-28.

13. Flugge Z. Practical Quantum Mechanics II., Vol.2, *Springer-Verlag, Berlin-Heidelberg-New York*, 1971.

14. Kubo R. Statistical Mechanics. *North-Holland Publishing Company - Amsterdam*, 1965.

Authors' addresses:

T. Marsagishvili, M. Machavariani, G. Tatishvili, R. Khositashvili,
E. Tskhakaia, N. Ananiashvili, J. Metreveli, M. Kikabidze-Gachechiladze
R. Agladze Institute of Inorganic Chemistry and Electrochemistry of
Iv. Javakhishvili Tbilisi State University
2, University St., Tbilisi 0186
Georgia
E-mail: tatigia@yahoo.com