

ISOTHERMS OF PARTICLE ADSORPTION ON MEMBRANES
ON ACCOUNT OF ADSORPTION CENTER CHANGESV. B. ARAKELYAN^{1*}, K. S. ARAMYAN², V. M. ARUSTAMYAN², H. K. GEVORGYAN¹,
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In this work the isotherms of particle adsorption on membranes are evaluated theoretically. The changes of adsorption center structure and the process of particle adsorption are considered in a consistent way. It is shown that the account of potential well deformation at adsorption process may result in qualitatively different regimes of adsorption. Dependence on the parameters of particle interaction with the adsorption center allows to obtain either Langmuir or S-shaped isotherms of adsorption.

Keywords: membranes, isotherm, adsorption.

Introduction. The running of a number of essential membrane processes and in the first instance the transport of particles through membranes and reception is closely related with the particle-membrane adsorption [1, 2]. Commonly, the cell responds to the increase in the quantity of particles adsorbed on the membrane depending on the type of adsorption isotherm. In turn, the isotherm type depends on both the character of interaction of adsorbed particles and the adsorption center, and interaction of adsorbed particles. The overwhelming majority of works focuses on the impact of interactions between adsorbed particles upon the adsorption isotherm [3–5]. As shown, allowing such an interaction leads to the adsorption isotherm different from Langmuir's isotherm provided, interaction of adsorbed particles is dominated by force of attraction, then the adsorption isotherm assumes an S-shaped form, and such a case is frequently referred to as cooperative adsorption [6]. However, this article suggests one more way of deriving an S-shaped adsorption curve with regard only to interaction of the adsorbed particle and the adsorption center. The work [7] highlights a theoretical study of reversible particle membrane adsorption with regard for changes in the adsorption center during interaction of the adsorbed particle and the adsorption center. As demonstrated, a cooperative consideration of adsorption and changes in the structure of the adsorption center lead to a bistable adsorption regime and S-shaped form of adsorption isotherms.

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Theoretical Part. In this work the adsorption process is considered as an adsorbed particle transition to a free potential well of the adsorption center from a potential well, located nearby the adsorption center. We assume that during adsorption the particle deforms the potential profile of the adsorption center to slightly deepen the potential well. A potential well depth value is proportional to a generalized conformation variable.

To determine the adsorption isotherm one should firstly define a conformation variable stationary distribution that accounts its fluctuations in relation to stationary values. The equation for a dimensionless conformation variable x is given in works [7, 8]:

$$\tau \frac{dx}{dt} = -x + \beta \cdot \frac{\gamma}{\exp(-x) + \gamma}, \quad (1)$$

where τ is the relaxation time of conformation changes, $\beta = x_\infty$ determines the value of a maximal change in the conformation variable, and $\gamma = K_0 c$ depends on the quantity of c particles in near-membrane area (K_0 is a quasi-chemical adsorption reaction equilibrium constant). The effective conformation potential of a system $U_{eff}(x, \gamma, \beta)$ is determined by equation

$$\tau \frac{dx}{dt} = - \frac{\partial U_{eff}(x, \gamma, \beta)}{\partial x}. \quad (2)$$

After integrating the right side of the equation (2) and with regard for (1), we derive the following effective conformation potential expression:

$$U_{eff}(x, \gamma, \beta) = \frac{x^2}{2} - \beta(x + \ln|\gamma + \exp(-x)|). \quad (3)$$

Let us demonstrate that the conformation potential (3) brings to the non-Longmuir's isotherms adsorption of particles. One should note that the density of equilibrium distribution of a conformation variable $P(x, \gamma, \beta)$ is as follows:

$$P(x, \gamma, \beta) = Z^{-1} \exp(-U_{eff}(x, \gamma, \beta)), \quad (4)$$

$$Z = \int_0^{x_\infty} \exp(-U_{eff}(x, \gamma, \beta)) dx.$$

The work [7] contains calculation of the adsorption center θ , filling at a given value of the conformation variable:

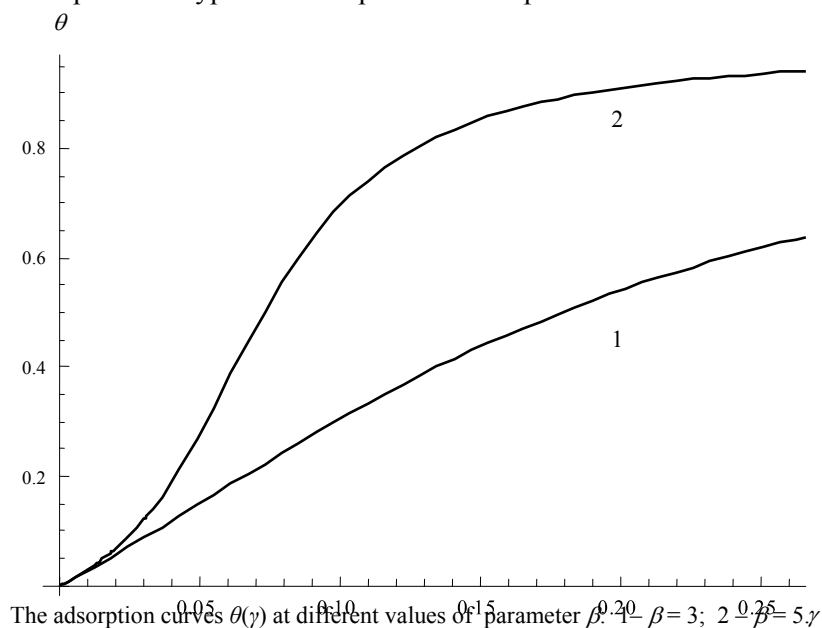
$$\theta = \frac{\gamma}{\gamma + \exp(-x)}. \quad (5)$$

Using (4) and averaging (5) by all the configurations of the conformation variable, we derive the following expression for the adsorption isotherm:

$$\theta(\gamma, \beta) = \int_0^{x_\infty} \frac{\gamma}{\gamma + \exp(-x)} P(x, \gamma, \beta) dx, \quad 0 \leq \theta \leq 1. \quad (6)$$

Results and Discussion. A noteworthy result of the suggested adsorption theory is the fact that consideration of a potential well deformation during adsorption leads to a possibility of realization of diverse-type adsorption curves. Adsorption isotherms, determined by expression (6) at different values of parameter β , are given in Figure. As seen from curves 1 and 2, an increase in β parameters brings to a qualitative change in the shape of the curve. Analysis of the system

$U_{eff}(x, \gamma, \beta)$ indicates that the β parameter values, that result in Longmuir's isotherm (curve 1), conform to a monostable adsorption regime. In the case of realization of bistable adsorption regime, the adsorption isotherm (curve 2) assumes an S-shaped form typical for cooperative adsorption.



Commonly, a cooperative adsorption isotherm is derived through introducing interaction of adsorbed particles, as earlier performed by Frumkin [8]. An S-shaped adsorption isotherm origination mechanism is different for these two variants. Obviously, should a mean distance between adsorbed particles be large, then interaction of the adsorbed particles is weak and a probability of cooperative adsorption regime realization, according to Frumkin, is low. In the case of the suggested mechanism the effect of cooperative adsorption regime is independent on the mean distance between the adsorbed particles. Such a fact can underlay identification of a mechanism of cooperative particle binding to the adsorption center.

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REFERENCES

1. **Tatulyan S.A.** Bio. Membranes, 1985, v. 2, № 4, p. 383–394 (in Russian).
2. **Koslov M.M., Cherniy V.V., Sokolov V.S., Yermakov Yu.A., Markin V.S.** Biofizika, 1983, v. 28, № 2, p. 61–66 (in Russian).
3. **Kotelnikova T.A., Ageev Y.P.** JPhCh, 1999, v. 33, № 8, p. 856–859 (in Russian).
4. **Ostrovski V.Y.** Usp. Khimii, 1976, v. 45, № 5, p. 849–876 (in Russian).
5. **Lopatkin A.A.** Theory of Physical Adsorbtion. M.: MSU, 1983, 250 p. (in Russian).
6. **Kantor Ch., Shimmel P.** Biofizicheskaya Khimia, 1985, v. 3. M.: Mir, 534 p. (in Russian).
7. **Arakelyan V.B., Aramyan K.S., Arakelyan H.V., Avanaesyan E.V.** Uch. Zapiski YSU, 2008, № 2, p. 53–56 (in Russian).
8. **Christophorov L.N., Holzwarth A.R., Kharkianen V.N., Mourik F.** Chemical Physics, 2008, v. 256, № 1, p. 45–60.

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Թաղանթների վրա մասնիկների ադսորբման իզոթերմերը ադսորբման կենտրոնի կառուցվածքային փոփոխությունների առկայությամբ

Աշխատանքում բերված են թաղանթների վրա մասնիկների ադսորբման իզոթերմերի տեսական հաշվարկներ, որտեղ ինքնահամաձայնեցված կերպով նկարագրվում են մասնիկների ադսորբումը և ադսորբման կենտրոնի կառուցվածքային փոփոխությունը: Ցույց է տրված, որ ադսորբման դեպքում պոտենցիալային փոսի դեֆորմացիայի առկայությունը ադսորբման տարբեր ռեժիմների իրականացման հնարավորություն է տալիս: Ցույց է տրված նաև, որ կախված ադսորբման կենտրոնի հետ փոխազդող մասնիկների պարամետրերից, կարելի է ստանալ ինչպես Լենգմյուրի իզոթերմը, այնպես էլ ադսորբման S-նման կոր:

Изотермы адсорбции частиц на мембранах с учетом изменений структуры адсорбционного центра

В работе приведены теоретические вычисления изотерм адсорбции частиц на мембранах, где самосогласованным образом описываются адсорбция частиц и изменение структуры адсорбционного центра. Показано, что учет деформации потенциальной ямы при адсорбции приводит к возможности реализации различных режимов адсорбции. Показано также, что в зависимости от параметров взаимодействия частицы с адсорбционным центром можно получить как изотерму Ленгмюра, так и S-образную кривую адсорбции.