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ELECTROCAPILLARY PROPERTIES OF HYDROGELS

Based on the thermodynamic theory of electrocapillarity, a formula has been obtained that relates the surface tension coefficient of a hydrogel and the surface concentration of ionic impurities in it. The relative coefficients of surface tension in a hydrogel on the basis of hydroxypropyl cellulose with ionic impurities of chlorides of Group I alkali metals (Li, Na, K, Rb, and Cs) have been experimentally determined. The obtained formula is used to calculate the relative surface concentrations of ions in the corresponding samples. It is shown that the surface tension coefficient and the surface concentration of ions depend on the size of ions, and those dependences are non-monotonic. A mechanism responsible for this non-monotonicity has been proposed.

K e y w o r d s: hydrogel, ions, surface tension.

1. Introduction

As is known [1], there exists a near-surface layer at the interface between two media, with its structure and physical properties being different from those of the contacting media. An important thermodynamic parameter of the near-surface layer is the surface tension coefficient α. The presence of ions in the mentioned media changes the value of α. The phenomena associated with the influence of ions on the surface tension coefficient are usually combined under the name "electrocapillarity" [2–4].

The concentration n of ions in the near-surface layer, as a rule, differs from the average concentrations of ions in the bulk of contacting media. Note that the concentration n, along with the coefficient α, is another important thermodynamic parameter of surface tension. However, unlike α, there is no direct method to determine n from experiment. At the same time, as was already mentioned, α depends on n. So, having the dependences $\alpha(n)$ at our disposal, we can

calculate n on the basis of experimentally determined α values.

The first goal of this work is to determine the analytic dependence $\alpha(n)$. To our knowledge, this task has not been considered earlier in the literature. The corresponding problem arose in connection with the research of properties of hydrogels. According to the definition [5], the gel is a phase of a polymer solution in which polymer chains form a network. In the case where water is the solvent, the term "hydrogel" is used. Another phase of a polymer solution, the sol, contains polymer chains that do not form a network.

The relevance of the indicated problem is associated, first of all, with the medical application of hydrogels for wound treatment [6–10]. Hydrogels created for this purpose often contain medical substances in the form of ions. Since the hydrogel surface is in direct contact with the damaged tissue, the therapeutic effect depends on the state of this surface. Currently, it is not clear how the size of ions affects the parameters α and n. Searching for an answer to this question is another goal of this work, which is a continuation of our previous research on hydrogels [11–15].

2. Thermodynamic Theory of Electrocapillarity

The thermodynamic theory of electrocapillarity was developed in the work by Gibbs [16]. Despite that more than a hundred years have passed since its creation, it remains relevant till now, which is evidenced by the fact that this theory, practically unchanged, is presented in modern monographs and textbooks [17–19]. This theory will also be used in this work to consider the formulated problem.

The thermodynamic potential Φ in the near-surface layer is written in the form

$$\Phi = \alpha Q, \tag{1}$$

where Q is the area of the interface simulating the near-surface layer, i.e., the contact interface between both media.

Let this interface be a plane. Let X denote the coordinate axis directed perpendicularly to this plane. As the coordinate origin $x = 0$, we choose the intersection point between the mentioned plane and the axis X. As ϕ' and ϕ'', we denote the potentials and, as q' and q'', the charges of both media at the point $x = 0$. The differential of the thermodynamic potential Φ looks like [3]

$$d\Phi = \alpha dQ - q'd\phi' - q''d\phi''. \tag{2}$$

The interface is assumed to be electrically neutral, i.e.,

$$q' + q'' = 0. \tag{3}$$

Introducing the notations

$$q = q' = -q'', \tag{4}$$

$$\phi = \phi' - \phi'', \tag{5}$$

we obtain

$$d\Phi = \alpha dQ - qd\phi. \tag{6}$$

Differentiating expression (1), we obtain

$$d\Phi = \alpha dQ + Qd\alpha. \tag{7}$$

Comparing Eqs. (6) and (7), we arrive at the equality

$$\sigma = -\frac{d\alpha}{d\phi}, \tag{8}$$

where $\sigma = q/Q$ is the surface charge concentration.

3. Dependence of the Surface Tension Coefficient on the Surface Concentration of Ions

Let us expand the function $\alpha(\phi)$ in a series up to the second-order term,

$$\alpha = \alpha_0 + \frac{d\alpha}{d\phi}\bigg|_{\phi=0} \phi + \frac{1}{2}\frac{d^2\alpha}{d\phi^2}\bigg|_{\phi=0} \phi^2. \tag{9}$$

It is obvious that, at $\phi = 0$, there are no surface charges, i.e., $\sigma = 0$. Taking equality (8) into account, we have

$$\frac{d\alpha}{d\phi}\bigg|_{\phi=0} = 0. \tag{10}$$

Using the notation

$$\frac{d^2\alpha}{d\phi^2}\bigg|_{\phi=0} = -M, \tag{11}$$

let us rewrite expression (9) in the form

$$\alpha_0 - \alpha = \frac{1}{2}M\phi^2. \tag{12}$$

As was shown in work [14], the inequality $d^2\alpha/d\phi^2 < 0$ holds. Accordingly, the inequality $M > 0$ also holds.

Differentiating in equality (8), we obtain

$$\sigma = M\phi. \tag{13}$$

Substituting this equality into expression (12), we have

$$\alpha_0 - \alpha = \frac{\sigma^2}{2M}. \tag{14}$$

As was mentioned above, in the framework of the thermodynamic approach, the near-surface layer is considered as a surface. For the sake of simplicity, in Section 2, this surface was assumed to be a plane. According to the thermodynamic theory, the surface charges $q' = q$ and $q'' = -q$ from both contacting systems are located at this plane. It is clear that such a model is idealized, because the charges q' and q'' are separated by a certain distance equal to the near-surface layer thickness (the so-called electric double layer).

By definition, the following identities are satisfied:

$$\sigma' = q'/S = n'e', \quad \sigma'' = q''/S = n''e'', \tag{15}$$
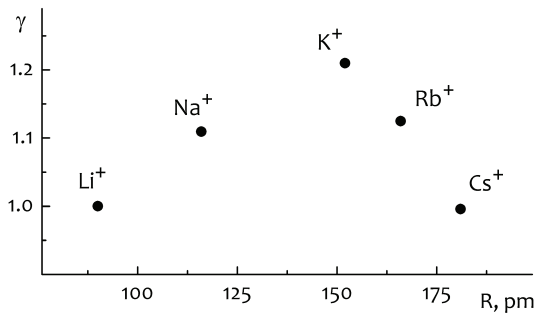
Dependence of the relative surface concentration of ions on their size

Relative surface tension coefficient β in aqueous solutions of hydroxypropyl cellulose with ionic impurities

Ions	β
Li	0.653 ± 0.203
Na	0.573 ± 0.178
K	0.492 ± 0.165
Rb	0.561 ± 0.193
Cs	0.656 ± 0.201

where S is the surface area; and n' and n'' are the surface concentrations of ions with the corresponding charges e' and e''. Let us assume that the absolute charge values of the ions that form the electric double layer are identical. Then, according to expression (4), we have the equality

$$n' = n''. \tag{16}$$

Therefore, in this article, we use the same notation n for the surface concentrations of both positively and negatively charged ions. So,

$$\sigma = ne. \tag{17}$$

Taking Eq. (17) into account, formula (14) reads

$$\alpha_0 - \alpha = \frac{e^2 n^2}{2M}. \tag{18}$$

Let us consider the relative surface tension coefficient

$$\beta = \frac{\alpha}{\alpha_0} \tag{19}$$

and rewrite formula (18) in the form

$$n = A(1 - \beta)^{1/2}, \quad A = e^{-1}(2M\alpha_0)^{1/2}. \tag{20}$$

4. Experimental Part

Aqueous solutions of hydroxypropyl cellulose (2 wt.%) produced by the Alfa Aesar company [20] with admixtures of alkali metal ions of Group I (chlorides of Li, Na, K, Rb, and Cs) were studied. The molar salt concentrations in all samples were the same and amounted to 0.154 mol/l.

The indicated salts dissociate in the aqueous solution to form negative ions Cl^- and corresponding positive ions (Li^+, Na^+, K^+, Rb^+, and Cs^+). According to equality (16), the concentrations of positive and negative ions were the same. In what follows, the quantity n means the surface concentration of positive ions.

Following the procedure described in works [14,15], the quantity β was determined for interfaces between the sol and gel phases. The values obtained for β in the experiment are quoted in Table.

Let us denote the surface concentration of Li^+ ions by n_1 and consider the relative surface concentration of ions, γ, as the ratio

$$\gamma = \frac{n}{n_1}. \tag{21}$$

The values of γ calculated using formula (20) are shown in Figure, where R is the effective size of the positive ion (the values of R were taken from work [21]). The experimental points depicted in Figure form a dependence $\gamma(R)$, which we are going to determine below.

5. Discussion of Experimental Results

As follows from the analysis of the results given in Table and Figure, the dependences $\beta(R)$ and $\gamma(R)$ have a non-monotonic character, namely:

$$\begin{aligned} d\beta/dR < 0, \quad d\gamma/dR > 0, \quad (R < 150\,\text{pm}); \\ d\beta/dR > 0, \quad d\gamma/dR < 0, \quad (R > 150\,\text{pm}). \end{aligned} \tag{22}$$

In the framework of the thermodynamic approach, this fact can be explained as follows.

According to formula (1), the surface tension coefficient α is, in essence, the density of the surface thermodynamic potential, which allows us to write the formula

$$\alpha = U + \Psi - TS, \tag{23}$$

where U is the density of the surface potential energy at the temperature $T = 0$, Ψ is the density of the surface vibrational free energy, and S is the density of the surface configurational entropy. Substituting formula (18) into expression (23) and performing the differentiation with respect to R, we obtain

$$-\frac{e^2}{M}\,n\frac{\partial n}{\partial R} = \frac{\partial \alpha}{\partial R} = \frac{\partial U}{\partial R} + \frac{\partial \Psi}{\partial R} - T\frac{\partial S}{\partial R}. \tag{24}$$

When penetrating into the near-surface layer of the gel, the ion deforms it. Obviously, the larger the size of the ion, the higher the energy of this deformation. This fact corresponds to the inequality

$$\frac{\partial U}{\partial R} > 0. \tag{25}$$

It is also evident that, as the size of the ions increases, the number of ways for the possible arrangement of the ions at the surface decreases. From whence, it follows that

$$\frac{\partial S}{\partial R} < 0. \tag{26}$$

For the density of the surface vibrational free energy, we have the formula [3]

$$\Psi = \frac{k_{\rm B}T}{Q}\sum_J \ln\left(2\,\mathrm{sh}\,\frac{\hbar\omega_J}{2k_{\rm B}T}\right), \tag{27}$$

where $k_{\rm B}$ is the Boltzmann constant, $\hbar$ Planck's constant, and ω_J the frequency of normal vibrations. The parameter Ψ is practically determined by low-frequency vibrations. Accordingly, the near-surface layer can be considered as a continuous medium and can be assigned a certain value of the shear modulus G (a specific feature of the gel, as is known, consists in that, in contrast to the liquid, the value of G for it differs from zero). Therefore, the vibrational thermal motion of the gel surface can be considered as a set of Rayleigh surface waves propagating with the velocity C, which can be approximately determined by the formula [22]

$$C = 0.9(G/\rho)^{1/2}, \tag{28}$$

where ρ is the density of the medium that simulates the near-surface layer.

In our experiment, the density of impurities exceeds the gel density. Accordingly, the density ρ increases

with the growth of R, which leads to a decrease of the velocity C. The frequencies ω_J are proportional to C, so the reduction of C is accompanied by a frequency reduction. As a result, as is required by formula (27), Ψ decreases, i.e., the following inequality is obeyed:

$$\frac{\partial \Psi}{\partial R} < 0. \tag{29}$$

Hence, from the thermodynamic viewpoint, the non-monotonicity of the dependences $\beta(R)$ and $\gamma(R)$ is a consequence of various relationships between the derivatives of the quantities that enter the right-hand side of equality (23) in different media, namely:
• for medium 1,

$$\frac{d\beta}{dR} > 0, \quad \frac{d\gamma}{dR} > 0, \quad \left|\frac{\partial \Psi}{\partial R}\right| < \frac{\partial U}{\partial R} - T\frac{\partial S}{\partial R};$$

• for medium 2,

$$\frac{d\beta}{dR} > 0, \quad \frac{d\gamma}{dR} < 0, \quad \left|\frac{\partial \Psi}{\partial R}\right| > \frac{\partial U}{\partial R} - T\frac{\partial S}{\partial R}.$$

6. Conclusions

The practical value of this work is determined, first of all by the application of hydrogels created on the basis of cellulose derivatives with ionic impurities in medical practice. The therapeutic effect of such hydrogels essentially depends on their surface, the physical state of which is determined by the surface tension coefficient and the surface concentration of ions.

It is shown that the presence of ionic impurities – e.g., the components of medicinal drugs – in hydrogels substantially changes the surface tension coefficient. It is also found that the value of this coefficient is affected not only by the ionic charge, but also by the ionic size R. There exists a certain critical size of ions, R_c, such that an increase of the ionic size R leads to a decrease of the surface tension coefficient if $R < R_c$, and to its increase, if $R > R_c$. At the same time, the surface concentration of ions behaves itself differently: an increase of the ionic size leads to an increase of this concentration, if $R < R_c$, and to its decrease, if $R > R_c$. For hydrogels created on the basis of hydroxypropyl cellulose, the critical value of the ionic radius of the alkali metals belonging to the elements of Group I is approximately equal to 150 pm.

Thus, by introducing ions into hydrogel, it is possible to modify the electrocapillary properties of the

polymer and the state of its surface, which is an important factor for the application of hydrogels in medical practice.

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ЕЛЕКТРОКАПІЛЯРНІ ВЛАСТИВОСТІ ГІДРОГЕЛІВ

На підставі термодинамічної теорії електрокапілярності одержано формулу, що зв'язує коефіцієнт поверхневого натягу гідрогелю та поверхневу концентрацію іонних домішок у полімері. Експериментально визначено відносні коефіцієнти поверхневого натягу гідрогелю, створеного на основі гідроксипропілцелюлози з домішками іонів лужних металів I-ї групи (хлориди Li, Na, K, Rb і Cs). За допомогою отриманої формули обчислені відносні поверхневі концентрації іонів у відповідних зразках. Показано, що коефіцієнт поверхневого натягу і поверхнева концентрація іонів залежать від розміру іонів, і що ці залежності мають немонотонний характер. Запропоновано механізм, який віповідальний за вказану немонотонність.

К л ю ч о в і   с л о в а: гідрогель, іони, поверхневий натяг.