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PECULIARITIES OF ALGINIC ACID HYDRATION IN THE AIR AND IN HYDROPHOBIC ORGANIC ENVIRONMENT

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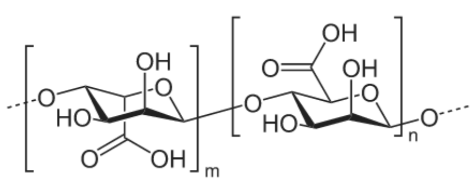
The effect of the medium on the parameters of water bound to the surface of alginic acid powder was studied by low-temperature ^{1}H NMR spectroscopy. The aim of this work was to study the effect of hydrophobic environment on the binding of water with alginic acid and to compare the parameters of the interfacial layers of water in air, in chloroform and chloroform with the addition of hydrochloric acid. It is shown that when adsorbed on the surface (500 mg/g H_2O), most of it is strongly bound. It is shown that for most dispersed systems, when replacing the air with chloroform, the interfacial energy of water increases from 11.8 to 15.2 kJ/mol, which is due to the capability of weakly polar organic molecules to diffuse on the surface of solid particles, thereby reducing the interaction energy with the adsorbed surface water clusters. It is concluded that chloroform molecules cannot diffuse on the surface of alginic acid particles and affect only the structure of water clusters localized in the outer adsorption layer. In the presence of hydrochloric acid on the surface of alginic acid, a system of water clusters is formed, most of which does not dissolve hydrochloric acid, and the radii of these clusters is 2 nm, which are likely to form in the gaps between the polymer chains of polysaccharide.

Keywords: *alginic acid, interfacial energy, strongly and weakly bound water, hydration*

INTRODUCTION

Alginic acid (AA) belongs to hydrophilic polymers of plant origin (brown algae) capable of binding a significant amount of water. Its hydrophilicity is due to the structure of molecules, which include the remains of polyuronic acids (*D*-mannuronic and *L*-guluronic) in different proportions, which vary depending on the specific type of algae. Alginates are not digested in the human body and excreted through the intestine. Alginic acid is insoluble in water and in most organic solvents. One part of the alginic acid adsorbs 300 mass parts of water, which causes its use as a thickener in the food industry, in particular in the preparation of ice cream, syrups, sauces and cheeses [1–4].



Usually hydrophilic properties of substances are considered in the context of interphase interactions in contact with water, air and non-polar organic substances (aliphatic hydrocarbons) [5, 6]. The efficiency of interactions of heterogeneous substances is determined by the total decrease in the free energy of the heterogeneous system [7]. At the same time, the fact that low-polar (non-polar) liquids do not mix with water does not mean the complete absence of their interpenetration. Thus, the solubility of water in hydrocarbons (and vice versa) can be from tenths to one percent [8]. In the case when hydrophilic powders or swollen polymers containing adsorbed water contact with a weak polar medium environment, the effect of joint adsorption of water and non-polar substances can be particularly strong. Thus, while studying the effect of weakly polar chloroform environment on water adsorbed in the interparticle gaps of hydrophilic and hydrophobic silica [9], it has been shown that chloroform can displace water from the interparticle gaps of not only hydrophobic but also hydrophilic material. This proves the fact that in a heterogeneous system a diffusion is observed of chloroform molecules on the surface of solid silica particles, and this reduces the possibility of contact with them clusters of adsorbed water.

Goal of this paper is to study the effect of hydrophobic environment on binding of water by alginic acid and comparison of parameters of the water interphase layers in the air, in the environment of $CDCl_3$ and $CDCl_3$ with addition of hydrochloric acid. Measurements have been carried out by the low-temperature ^1H nuclear magnetic resonance spectroscopy [10–12], which allows us to calculate the average number of hydrogen bonds in which each water molecule participates according to the results of the chemical shift of adsorbed water and by the depression of the freezing temperature, it is possible to calculate the radius of clusters of the water adsorbed and changes in the Gibbs free energy of water in the adsorption layer.

EXPERIMENTAL PART

A powdered sample of commercial alginic acid was investigated, which in its initial state contained no more than 5 wt. % of water. Then 500 mg/g of distilled water was added to it and left to balance for the period of 3 days. To measure the weight gain, the sample of 200 mg was placed in a 5 mm NMR ampoule, on the basis of which ^1H NMR spectra were measured at a temperature range of 200–280 K (in the air). Then 0.5 ml of deuterochloroform was added to the sample and measurements were repeated in $CDCl_3$. After that, 200 mg/g of hydrochloric acid was added to the sample, thoroughly mixed and left for 30 min for balancing, and then measured in the presence of HCl.

NMR spectra were obtained by the help of a high-resolution NMR spectrometer (Varian “Mercury”), operating frequency of which is 400 MHz. A 90° interrogation pulse with duration of 3 μs was used. Temperature in the sensor was regulated by a thermal insert Bruker VT-1000 with accuracy of ±1 degree. Signal intensities were determined by measuring the area of peaks using the procedure of signal decomposition into its components under the assumption of the Gaussian shape of line, optimization of the zero line and phase with accuracy not worse than ±10 %. To prevent overcooling of water in the studied objects, measurements of concentration of the non-freezing water were carried out by heating the samples previously cooled to the temperature of 210 K.

RESULTS AND DISCUSSION

Spectra of ^1H NMR of water adsorbed by alginic acid (C_{H2O} = 500 mg/g) in the air, $CDCl_3$ and $CDCl_3$ with HCl additive, which have been taken at different temperatures are shown in Fig. 1 *a*, *b* respectively. In the air environment (Fig. 1 *a*) spectrum consists of a single signal, the chemical shift of which is $\delta_H = 5$ ppm at $T = 280$ K, which is slightly more than that for liquid water [10]. Temperature dependence of the chemical shift is shown in Fig. 2. As the temperature decreases, the value of chemical shift increases to $\delta_H = 8$ ppm at $T = 210$ K. Immersion of the alginic acid sample in the chloroform environment (Fig. 1 *c*) leads to a certain decrease in the δ_H value, which indicates a partial destruction of net of hydrogen bonds of adsorbed water. At the same time, the range of changes in the chemical shift is 3.5–6 million parts (Fig. 2). When adding HCl to a sample, the spectra kinds change (Fig. 1 *c*). In addition to the signal with a chemical shift $\delta_H = 3.5$ ppm in weak magnetic fields, a wide signal appears, the center of which is located at $\delta_H = 8$–10 ppm. Besides, at low temperatures a weakly intense signal can be observed at $\delta_H = 0$–2 ppm (Fig. 1 *d*) in the spectra, which can be classified as weakly associated water [10]. As the temperature decreases, the intensity of all signals decreases due to partial freezing of adsorbed water.

Regardless of the observation environment, the chemical shift of adsorbed water increases with decreasing temperature (Fig. 2). In the air, the value δ_H reaches a value of 7.5–8 ppm, which is typical for tetracoordinated water [10, 11]. We should note that the value of the chemical shift can be contributed by the protons of carboxylic groups of polyuronic acids that are part of the polymer, because the rapid proton exchange between them and the molecules of adsorbed water can significantly increase the measured value of average chemical shift. In the presence of hydrochloric acid, the amount of chemical shift is contributed also by “acidic” HCl protons, chemical shift of which can reach 11 million parts.

Taking in account that chemical shift of the signal 1 in Fig. 1 *c* is close to the value of chemical shift of the water signal under conditions of absence of HCl, it can be concluded that a significant part of the adsorbed water is in a state of clusters that practically do not dissolve the acid. At the same time, the chemical shift of signal 2 is appropriate to the water HCl solution. A large signal width can be associated with the presence of several proton signals belonging to different clusters of adsorbed water, capable of dissolving a different amount of HCl [13, 14]. Another reason may be the rapid proton exchange with mobile protons of polymer molecules, the mobility of which is significantly less than those for water and acid molecules in the adsorption layer.

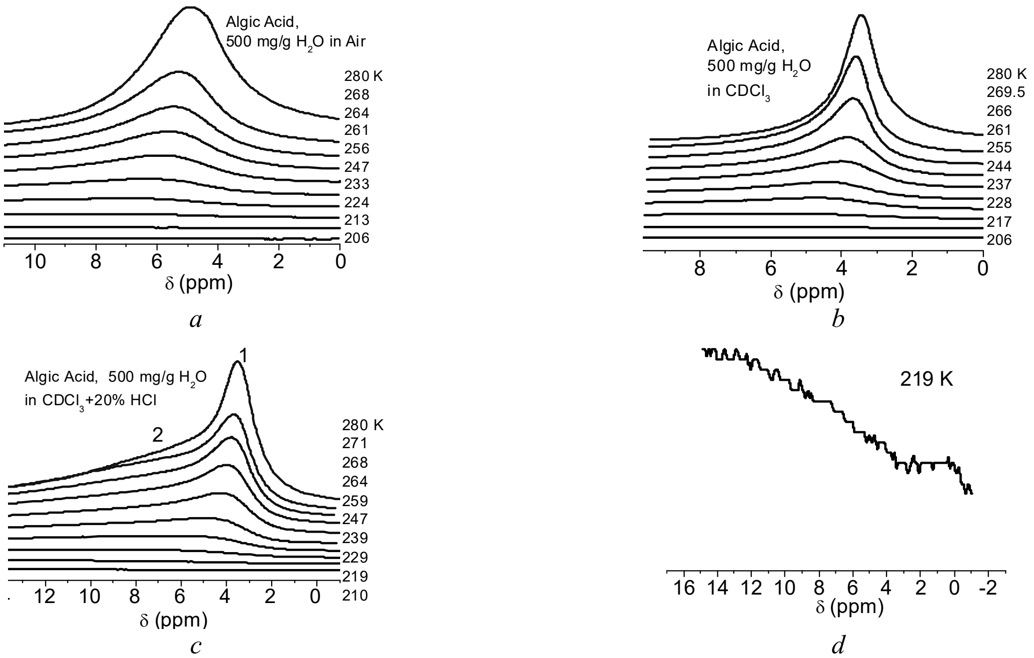


Fig. 1. Taken at different temperatures spectra of ^{1}H NMR water adsorbed by alginic acid (C_{H2O} = 500 mg/g) in the air environment (*a*), in the environment of $CDCl_3$ (*b*) and the $CDCl_3$ environment with addition of HCl (*c*, *d*)

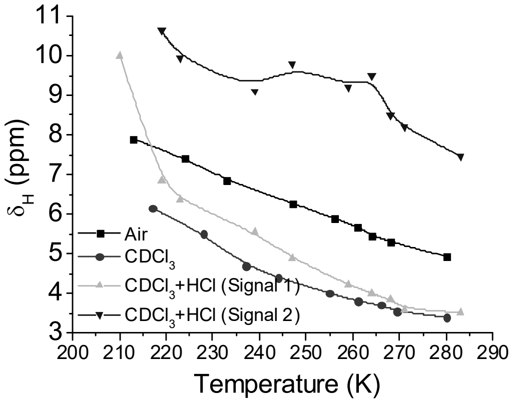


Fig. 2. Temperature dependences of chemical shift of water adsorbed by alginic acid in different environment

Whereas the water concentration in the samples is known, based on the measurement of the values of integral intensity of the water signals, the concentrations of non-freezing water (C_{uw}) can be calculated for each temperature and dependences of $C_{uw}(T)$ can be constructed. Water in the adsorption layer freezes at temperatures below 273 K. Depression of freezing point (273–T) is determined by decrease of free water energy due to adsorption interactions. The condition of adsorbed water freezing is the equality of the Gibbs free energies for water and ice [10–12]. Then, for the difference in the Gibbs free energies (ΔG) at 273 K and measurement temperature (T), the following ratio is true:

$$\Delta G = -0.036 \cdot (273 - \mathrm{T}), \qquad (1)$$

in which the numerical coefficient is determined empirically from the temperature dependence of the thermodynamic functions of ice [15].

Fig. 3 shows the dependence of concentration of non-freezing water on the temperature and changes in the Gibbs free energy from the concentration of non-freezing water in the coordinates $\Delta G(T)(C_{\text{uw}})$. Integration of dependences $\Delta G(C_{\text{uw}})$ allows us to determine the value of interfacial energy (γ_S) which determines the total reduction of free energy due to adsorption interactions for the entire layer of bound water

$$\gamma_S = -K \int_0^{C_{\text{uw}}^{\max}} \Delta G(C_{\text{uw}})dC_{\text{uw}} \, . \qquad (2)$$

Table shows thermodynamic parameters of the non-freezing water layers in the studied systems. At the same time, strongly bound (SBW) was considered the part of non-freezing water that melts at $T < 265$ K ($\Delta G < -0.5$ kJ/mol) [10]. The ΔG^S value determines the maximum reduction of free energy in the layer of bound water [10]. This decrease can be determined by interaction with the phase boundaries (adsorption interactions) and with dissolved substances (solvation). Close values of ΔG^S for the adsorbed HCl solution and water may be due to the fact that main mechanism for lowering the freezing point is solvation (dissolution), and not the interaction with solid particles of alginic acid. A large amount of both weakly and strongly bound water (C_{uw}^W and C_{uw}^S, respectively), as well as the value of γ_S in the alginic acid containing 500 mg/g of H_2O proves the fact of its high tendency to hydration.

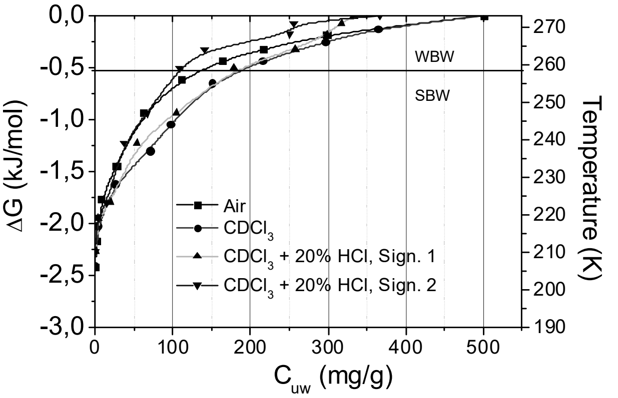


Fig. 3. Dependences of concentration of non-freezing water on the temperature and changes in the Gibbs free energy on concentration of the non-freezing water in coordinates $\Delta G(T)(C_{\text{uw}})$ for hydrated alginic acid in different environment

Table. Characteristics of water layers adsorbed by alginic acid in different environment

Environment	$-\Delta G^S$, kJ/mol	C_{uw}^S, mg/g	C_{uw}^w, mg/g	γ_S, J/g
Air	2.4	110	390	11.8
$CDCl_3$	2.4	175	325	15.2
$CDCl_3$ +HCl (1)	2.4	150	75	13.9
$CDCl_3$ +HCl (2)	2.4	85	190	9.4

To determine the geometric sizes of the adsorbed water clusters, the equation of Gibbs-Thomson, binding the radius of the spherical or cylindrical water cluster or domain (R) with the magnitude of depression of freezing point was used [16, 17]:

$$\Delta T_m = T_m(R) - T_{m,\infty} = \frac{2\sigma_{sl}T_{m,\infty}}{\Delta H_f \rho R} \, , \qquad (3)$$

where $T_{\text{m}}(R)$ is the melting temperature of ice localized in the pores of radius R, $T_{\text{m},\infty}$ is the melting temperature of bulk ice, ρ is the density of the solid phase, σ_{sl} is the interaction energy of a solid object with a liquid and ΔH_f is the volume enthalpy of melting. For practical use equation (1) can be used as $\Delta T_m = (k/R)$, in which the constant k for many heterogeneous systems containing water is close to 50 degrees·nm [16]. Distribution by radii of the adsorbed water clusters for hydrated alginic acid in different environments is shown in Fig. 4.

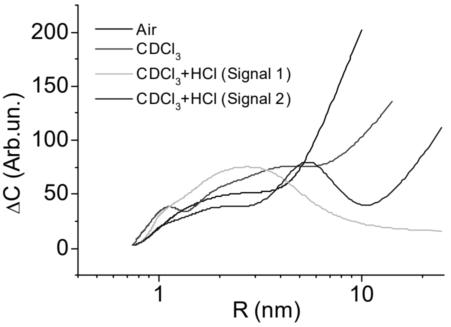


Fig. 4. Distribution by radii of the adsorbed water clusters for hydrated alginic acid in different environments

For hydrated alginic acid powders, high values of interphase energies are observed, that is due to the high hydrophilicity of the polymer studied. When replacing the air with a weakly polar environment ($CDCl_3$) γ_S increases from 11.8 to 15.2 kJ/mol, the acid additive increases it up to 22.3 kJ/mol (sum of values for signals 1 and 2), which is caused by the effect of water solvation of HCl molecules. The value of γ_S is controlled mainly by the amount of strongly bound water. It should be noted that for most disperse systems [10, 11] replacement of air by $CDCl_3$ environment is accompanied by decrease in the interaction of water with the surface. This is due to the possibility of weakly polar organic molecules to diffuse over the surface of the solid phase particles, thereby reducing the interaction energy with the surface of adsorbed water clusters. In the case of alginic acid this does not occur probably due to the formation in the interparticle gaps of a system of water clusters associated with surface carboxyl groups of acid residues. In this case, the penetration into the interparticle gaps of chloroform molecules thermodynamically is not profitable.

According to the data in Fig. 4, chloroform environment stabilizes smaller radius water clusters, which also indicates the lack of penetration of chloroform molecules to the surface and its effect on the structure of water clusters localized in the outer adsorption layer. Thus, effective binding of water by polymer prevents adsorption of weakly polar molecules and leads to the formation of significant number of water clusters that do not dissolve strong acid (HCl). The radius of such clusters is about 2 nm. Probably, they are formed in the gaps between the polymer chains of the polysaccharide.

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Особливості гідратації альгінової кислоти на повітрі та в гідрофобному органічному середовищі

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Методом низькотемпературної ^{1}H ЯМР-спектроскопії вивчено вплив середовища на параметри води, зв'язаної з поверхнею порошка альгінової кислоти. Метою даної роботи було вивчення впливу гідрофобного середовища на зв'язування води альгіновою кислотою та співставлення параметрів міжфазних шарів води на повітрі, в середовищі хлороформу та хлороформу з додаванням соляної кислоти. В роботі показано, що при адсорбції на поверхні 500 мг/г H_2O, більша її частина є сильнозв'язаною. Показано, що для більшості дисперсних систем при заміні повітряного середовища середовищем хлороформу, міжфазна енергія води *збільшується від 11.8 до 15.2 кДж/моль, що пов'язано з можливістю слабкополярних органічних молекул дифундувати по поверхні частинок твердої фази, тим самим зменшуючи енергію взаємодії з поверхнею адсорбованих кластерів води. Зроблено висновок про те, що молекули хлороформу не можуть дифундувати по поверхні частинок альгінової кислоти і впливають лише на будову кластерів води, локалізованої у зовнішньому адсорбційному шарі. В присутності соляної кислоти на поверхні альгінової кислоти формується система кластерів води, значна частина якої не розчиняє соляну кислоту, а радіус даних кластерів складає 2 нм, які ймовірно формуються в проміжках між полімерними ланцюгами полісахариду.*

***Ключові слова**: альгінова кислота, міжфазна енергія, сильно- та слабкозв'язана вода, гідратація*

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