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SORPTION PROPERTIES OF TECHNICAL AND PURIFIED CARBOXYMETHYL CELLULOSE

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ABSTRACT

In this paper, the interaction of technical and purified carboxymethyl cellulose (CMC) macromolecules with solvent molecules with the same degree of exchange and polymerization is comparatively studied. The thermodynamic parameters of technical and purified CMC samples were evaluated by sorption of solvent vapors.

KEYWORDS: *Technical, purified CMC, thermodynamics, capillary-porous structure, sorption, Gibbs energy, BET equation, Zimm-Landberg, Der Bur-Zwicker.*

In recent years, there has been a sharp escalation of interest in the study of natural macromolecular compounds due to the expansion of the practical use of biodegradable and environmentally friendly polymers. CMC plays an important role in its water solubility, biodegradability, suitability for the organism [1,2].

CMC is one of the most common simple ethers of cellulose compounds and are widely used in various industries today [3,4]. With the expansion of the use of CMC, the demand for it is growing [5]. Worldwide, the production of technical CMC is 580-590 thousand tons per year, which are widely utilized mainly in the oil and gas, construction, mining, metallurgy, textile, paper industries [6].

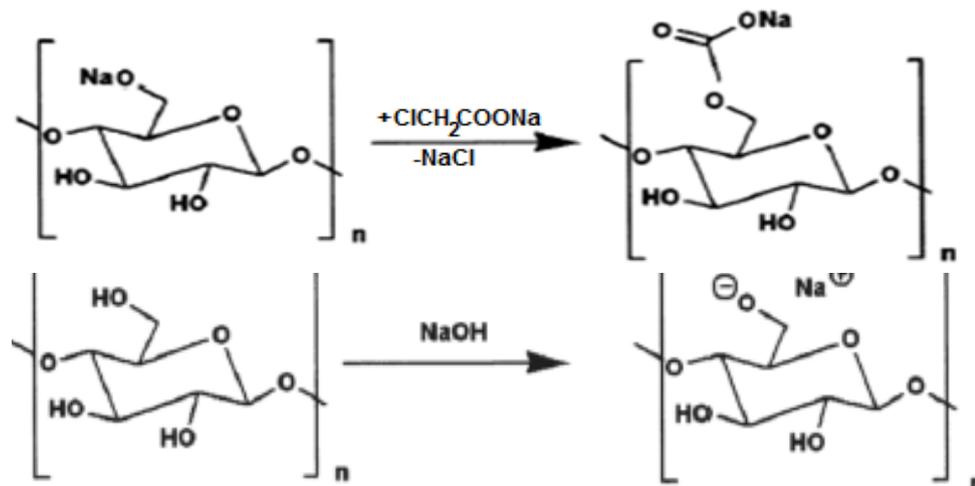
Refined CMC brands are widely used in food, pharmaceutical, medical, perfumery and cosmetics and other fields [7,8].

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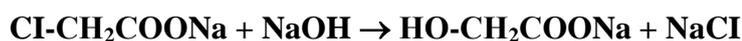
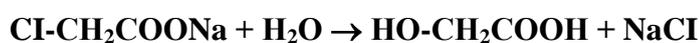
The process of synthesis of cellulose-based CMC consists of two stages [9]:

In step 1, the process of mercerization of cellulose with an alkaline solution is carried out;

In step 2, the alkaline cellulose is formed by the carboxymethylation reaction in the presence of an alkylating agent - monochloroacetic acid or its sodium salt.



During this reaction, chloride and glycolate salts are formed as supplement products [10,11].



Nowadays, the content of additives - organic and inorganic salts - in the composition of samples produced on an industrial scale is 40-50%, which sharply reduces the quality of the product [12].

We obtained purified samples on the basis of technical CMC obtained on an industrial scale and compared the thermodynamic parameters of these samples.

On the basis of physicochemical and thermodynamic studies, thermodynamic analysis of the water state in cellulose was performed. It was found that the effect of Gibbs energy, enthalpy and entropy mixing on the cellulose-water system on clustering and thermodynamic parameters is a light function of polar functional groups, more specifically a function of molecular packaging, submicroscopic capillary-porosity and crystal structure.

The study of the process of interaction of a polar sorbent with a polar sorbent is based on the adsorption theory of De Boer and Zwicker in a water-soluble acetylcellulose fiber-water system. [13]The water absorption of the polymer is calculated based on Zimm-Landberg's theory [14].

Thermodynamic proximity $\Delta\mu_i$ between polymers, changes in the chemical potential of the components, Gibbs's energy of mixing ΔG , Flori - Haggins interaction parameters χ_i were determined. The thermodynamic parameters of technical and purified CMC samples were evaluated by sorption of solvent vapors.

Research in this area is of practical importance in the study of the biodegradability of CMC samples in the body, the ability of drug substances to bind in the macromolecule, the solvent-polymer and polymer-polymer effects.

Research methodology

The object of research was a sample of technical CMC produced by "Promxim Impeks" LLC.

Table 1. Quality indicators of technical and purified CMC samples

Indicators Name	Technical CMC	Purified CMC
Water solubility,%	98,5	98,9
Amount of base substance,%	63,0	99,4
Humidity,%	9,8	9,3
Exchange rate	0,86	0,86
PH of 1.5% solution	8,7	8,1
Degree of polymerization	810	800

In determining the thermodynamic parameters of CMC samples were studied on the basis of its sorption properties. At the same time, the change in the mass of the sample was detected on high-vacuum MAK-BEN scales, quartz springs with a sensitivity of 3.69 mg/mm. In the experiments, the sorption cells were kept at $25^{\circ}\text{C} \pm 1$.

Measurements were performed using a catheter KM-8 with a residual pressure of $10^{-3} - 10^{-4}$ Pa. Sorption experiments were performed at the required high vacuum, changes in quartz springs were recorded, and the catheter pressure readings at and above were determined using the following equation:

$$g_c = g_{BT} - \left(r \Delta h_0 / 1000 \right) \quad (1)$$

Here:

g_c -is the polymer mass after sorption

g_{vI} -is the polymer mass before sorption

r -is the sensitivity of the spring mm/mg

Δh_0 -is the difference between catheter readings before and after sorption

To determine the amount of sorbate, ie water vapor sorbed into the polymer, a constant is determined during the measurement of each sample:

$$K = r / g \cdot 1000 \quad (2)$$

K -is the percentage of vapor that is sorbed to lengthen the spring by 1 mm.

The sorption percentage for each pressure is found by the following equation:

$$\% C = K \Delta h \quad (3)$$

Here:

Δh - is the difference between the reading on the catheter at high vacuum and the reading of P_i / P_i^0 at equilibrium of the sorbate used.

P_i -is the vapor pressure of the sorbent in the sorption measurement

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P_i^0 is the saturated vapor pressure of sorbate.

To measure the vapor pressure of a solvent in a polymer solution, a graph is drawn based on the following relationship:

$$X/M=f(P_i/P_i^0) \quad (4)$$

The chemical potential of the solvent is calculated on the basis of the following relationship:

$$\Delta\mu_1 = RT/M_1 \ln(P_i/P_i^0) \quad (5)$$

$\Delta\mu_2$ is needed to determine the average critical mixing energy. Of course, the chemical potential of the polymer at the same temperature is $\Delta\mu_2$ and the chemical potential of the polymer at the same temperature is $\Delta\mu_1^0$.

To determine the value of $\Delta\mu_2$ it is sufficient to know the value of $\Delta\mu_1^0$ of the other component in the solution (of course for two-component systems).

$$\Delta\mu_2 = \int_a^\infty \omega_1 / \omega_2 (\partial\Delta\mu_1) \quad (6)$$

Δg^m we find the value of as follows:

$$\Delta g^m = \Delta\mu_1\omega_1 + \Delta\mu_2\omega_2 \quad (7)$$

The value of Δg^m is determined at all pressures and

$$\Delta g^m = f(\omega_2) \quad (8)$$

The graph is drawn on the basis of dependence. From this graph, the value of the Gibbs energy ΔG_i is found.

Also, the Flory-Huggins thermodynamic parameter is calculated by the following equation:

$$\chi_{is} = \ln a_s - \ln \varphi_s - (1 - \varphi_s)/(1 - \varphi_s)^2 \quad (9)$$

Here

$a_s = P_i/P_i^0$ – is the activity of the solvent

$\varphi_s = x/m/(x/m + d_s/d_p)$ volume fraction of solvent

d_s – is the density of the solvent

d_p – is the density of the polymer

$(1-\varphi_s) = \varphi_2$ – is the volume fraction of the polymer.

Flori-Huggins polymer solution theory: The mixing energy has a shape similar to a mixture of two low molecular weight liquids. Consider a solution g consisting of G solution molecules and N_2 polymer molecules; the total number of solvent molecules and monomer units is $H = N + N_{ir}$.

Analysis and results

The following table determines that the sorption properties and capillary-porous structure of technical and purified CMC samples relative to water vapor.

Table 2. Sorption properties of technical and purified CMC samples

Sample	Technical CMC	Purified CMC
Relative humidity%	Sorption, %	
10	0,60	0,30
30	1,40	0,80
50	2,00	1,60
65	3,20	5,00
80	5,30	14,00
90	8,00	29,00
100	13,00	43,00

Table 3. Capillary-porous structure of samples of technical and purified CMC

№	Indicators	Technical CMC	Purified CMC
1	$X/m, \text{ r/r}$	0,006	0,003
2	$S_{y\text{д}} \text{ m}_2/\text{ r}$	48,18	31,54
3	$W_o \text{ sm}^3/\text{ r}$	0,13	0,43
4	$r_k \text{ A}^\circ$	53,96 A°	272,66 A°

It can be seen from these tables that as a result of purification of technical CMC from additional salts, there are changes in the capillary-porous structure of the product and its specific surface area decreases slightly, the volume sum and radius of pores increase sharply.

Based on the results of sorption, several thermodynamic parameters Gibbs energy, average free energy of mixing $-\Delta g^m$, chemical potentials $-\Delta\mu_1, \Delta\mu_2$ were determined. The following tables illustrate the thermodynamic properties of the calculated technical and purified CMC based on the sorption results.

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The BET theory states that the molecules of the first layer are adsorbed on the adsorbent surface as a result of the intermolecular interaction of the adsorbent. Each adsorbed molecule of the first adsorption layer can, in turn, be the adsorption center of the molecules of the second layer, and so on. Thus, the second and subsequent sorption layers are formed. The adsorption heat in the first layer is determined by the adsorption-adsorbent interaction, in all subsequent layers by the adsorption-adsorption interaction.

To measure the vapor pressure of a solvent in a polymer solution, a graph is drawn based on the relationship $X/m=f(P_i/P_i^0)$.

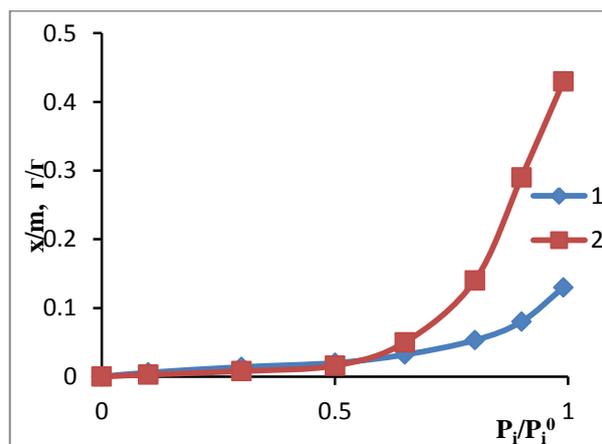


Figure 1. Isotherm of water vapor sorption

(1 technical CMC, 2 purified CMC)

As can be seen from this graph, the sorption properties of the technical and purified CMC samples differ from each other. The smaller S-shaped appearance for technical CMC indicates its lower water solubility and porosity compared to purified CMC. It can be seen from the figure that the removal of additional organic and inorganic salts from the sample leads to an increase in its sorption properties.

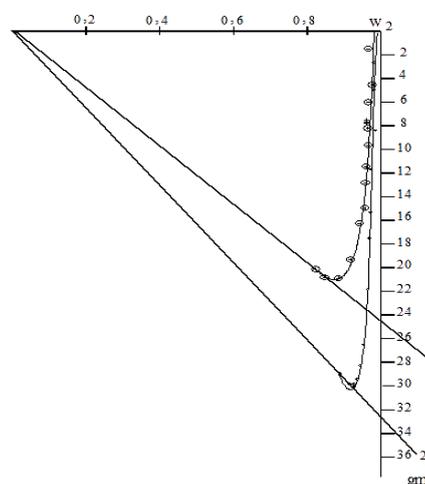


Figure 2. Dependence of the average free energy concentration in the CMC-water system on the exchange rate

(1-technical CMC, 2-purified CMC)

To quantify the thermodynamic activity of aquatic systems of technical and purified CMC, Gibbs

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potentials ΔG_i were calculated based on the average free energy and concentration dependence of the polymer solvent Δg^m based on the chemical potential calculation of $\Delta\mu_1$ solvent and $\Delta\mu_2$ polymer.

As can be seen from Figure 2, the purified CMC and water system illustrate more negative Gibbs energy than the technical sample. This result can be confirmed by the polymer-solvent interaction χ_{is} Flory-Huggins parameter.

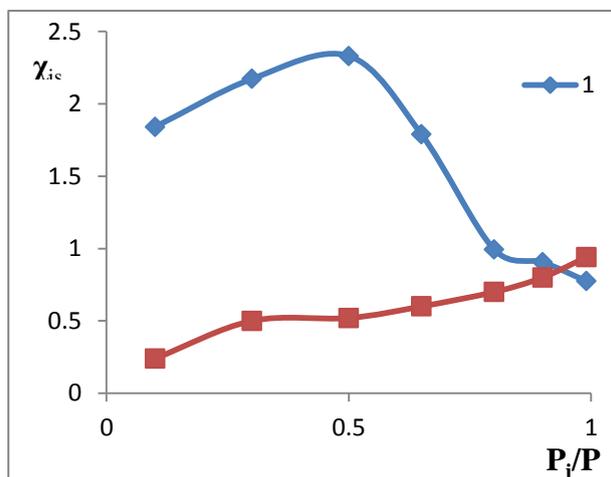
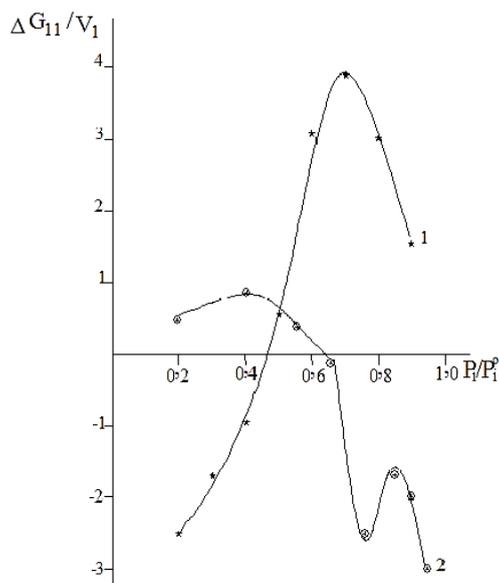


Figure 3. Correlation of thermodynamic propensity of water vapor activity with the χ_{is} parameter (1 technical CMC, 2 purified CMC)

As shown in Figure 3, the value of the polymer-solvent Flory-Huggins parameter of purified CMC is $\chi_{is} < 0,5$ at the initial pressure. At relative pressure $P_i/P_1^0 = 0,3 - 0,65$, the Flory-Huggins parameter is $\chi_{is} \leq 0,5$, ie it is a thermodynamically good solvent. At high relative pressures, it is $\chi_{is} > 0,5$. This is explained by the solvent-solvent interaction condensation process. From this result, the value of the Flory-Huggins parameter of the polymer-solvent interaction of technical CMC differs sharply from the value of the purified sample.

This situation can be explained by the fact that the presence of various organic and inorganic additives formed as a result of additional reactions in the composition of technical CMC leads to a decrease in the force of interaction between CMC and the solvent.



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Figure 4. Technical (1) and purified (2) cluster formation function for water vapor activity dependence for CMC-water system

Figure 4 illustrates the results of an integrated calculation of the dependence of cluster formation on the G_{11}/V_1 sorbent volume fraction. Theoretically, when $G_{11}/V_1 \geq -1$, water molecules aggregate into clusters. As can be seen from this graph, the value of the cluster formation function for the technical CMC-water system indicates that the transition to a positive field when the water vapor activity is $P_i/P_i^0 < 0,45$ indicates the beginning of cluster formation in the initial relative pressure areas.

For purified CMC-water systems, negative values of cluster formation function are observed, indicating that water molecules interact well with macromolecules at moderate relative pressures of water vapor.

The results of the study illustrate that the clustering for the studied samples is manifested in the field of high activity of water vapor and is consistent with the data in the literature on the formation of clusters of hydrophilic polar polymers. Cluster formation in low relative pressure areas is associated with the formation of polymer-water and water-water hydrogen bonds.

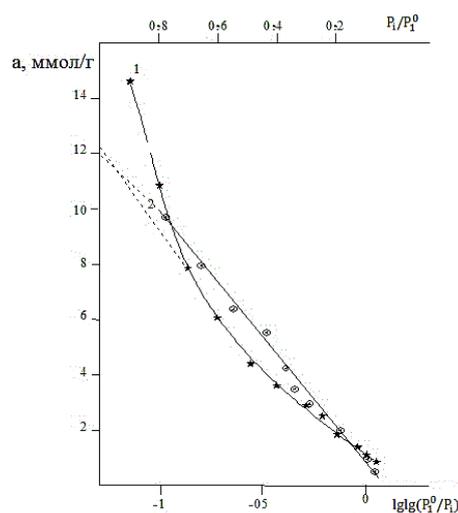


Figure 5. Water vapor sorption isotherms for CMC-water system in De Boer-Zwicker coordinate (1-technical CMC, 2-purified CMC)

According to the ideas of De Boer-Zwicker (1929), the surface of a polar adsorbent polarizes non-polar adsorbent molecules in the first adsorption layer. In 1929, according to De Boer-Zwicker, the adsorption of a non-polar adsorbent on the first adsorbed layer excites surface dipoles, resulting in dipoles in the next layer. The second theory is based on the assumption that the same forces that cause condensation are also responsible for the binding energy of the polymolecular adsorption. This theory is called the polymolecular adsorption theory. De Boer-Zwicker pointed out that the induced dipoles in the arbitrary layer polarize the first layer and at the same time create the connecting dipoles.

De Boer and Zwicker adsorption theory, which describes the processes of interaction of polar sorbents with polar sorbents, can be applied in the case of cellulose esters-water system. This theory is suitable for both adsorption and absorption mechanisms of water binding processes. The results of the experimental study of the De Boer and Zwicker equations are shown in Figure 5, and the linearization of the water vapor sorption isotherm allows to determine the “true” sorption value, which

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is not complicated by capillary coding and clustering of water. As can be seen from the figures, the isotherm is linear for the technical CMC-water system in areas with a relative pressure of 0.7. linerization occurs for the purified CMC-water system and the isotherm is linear in all areas of relative pressure. According to De Boer and Zwicker's theory, there is no "free" water in the specified activity range in the purified CMC-water system, all of the water is absorbed by the active groups of the polymer. Therefore, the Tsimm-Landberg values of the sample are negative and no cluster formation is observed in all areas of relative pressure. (Figure 4).

Conclusion

Using thermodynamic methods, it is possible to obtain the necessary information about the intermolecular interactions of components of different natures. In this case, the sorption properties and capillary-porous structure of technical and purified CMC samples with the same quality parameters were studied. As a result of the removal of additional salts from the technical CMC, it was found that the specific surface area of the purified product is slightly reduced, leading to a sharp increase in the volume and radius of the pores. Based on these results, their thermodynamic parameters $\Delta\mu_1$, $\Delta\mu_2$, Δg^m and ΔG_i were calculated and it was found that the purified CMC macromolecule interacts better with solvent molecules than the technical sample.

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