Thermodynamics of the Process of Adsorption of Aliphatic Amidpolyamine on Cellulose

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Synopsis

The subject of this research is the thermodynamics of the adsorption equilibrium of three types of bleached pulp in water solutions of aliphatic amidpolyamine—Lamid-1, (L-1) in concentrations from 0.03 to 0.50 g/L in a temperature interval of 0–60°C and the influence of pH of the environment on the adsorption process. It was established that with the increase of temperature the quantity of adsorbed L-1 decreases. The values of the heat of adsorption are negative, do not depend on the quantity of adsorbed L-1, and are of the order 111.7–14.7 kJ/mol. The values of the entropy of adsorption are also negative and are of the order of 76.8 ÷ 84.5 J/mol·K. Adsorption equilibrium is described by ther adsorption isotherm of Langmuir. Optimum pH for lower concentrations of the solution is from 5 to 7. When the concentrations of the solution are higher ($C \cong 0.15$ g/L) the process can also take place very satisfactorily in an alkaline environment.

INTRODUCTION

The interaction between the synthetic product aliphatic amidopolyamine Lamid-1 (L-1) and pulp cellulose has hardly been studied, thus, until now, it has not been used in the cellulose and paper industry. The results of some studies,[1-3] however, show that L-1, as an organic polyelectrolyte has strongly expressed binding and retention properties, which can make it a desirable auxiliary in such production processes. Its effective utilization necessitates a more exhaustive and thorough study of processes and phenomena accompanying the interaction of L-1 and pulp cellulose and clarification of its mechanism.

The contemporary picture of the mechanism of interaction between cellulose and different polyelectrolytes is based on the awareness of the complex colloid-chemical adsorption processes taking place in the system "cellulose-water-polyelectrolyte." The aim of the present work is to analyze the thermodynamics of the adsorption equilibrium of the system "cellulose-water solutions of L-1" and the influence of pH on that equilibrium, revealing the mechanism of interaction taking place in the system.

EXPERIMENTAL

Three types of bleached pulp were used as sorbents: sulfate hardwood pulp, and sulfite and sulfate softwood pulp in their H-forms. The H-forms resulted from treating the initial pulp with 0.1n HCl to ash content of 0.05%. The L-1 used in the process was obtained by condensation of long fatty acids with diethylene triamine and is characterized by an amine num-

ber in the order of 190–220 mg KOH/g and viscosity 20 s at a temperature of 20°C.

The adsorption isotherms for the system cellulose-water-L-1 were obtained at temperatures of 0, 20, 40, and 60°C, respectively; module* 1:40, and concentrations of the solution ranging from 0.03 to 0.5 g/L, constantly stirred with a glass mixer (n = 50 revolutions/min) and pH = 4.5–5.0.

A test sample of 10 g absolutely dry cellulose was left to swell for 19 hours in distilled water (ratio 1:15) at room temperature after which it was subjected to tempering for 1 hour at the temperature at which the adsorption was to take place. After this time expired, a certain volume of the concentrated solution of L-1 was added to the system in order to achieve the necessary concentration of polyelectrolyte in the working solution. At the beginning and at the end of the process, the pH of the solution was measured with a LP-6 pH-meter. The moment in which adsorption equilibrium was reached was determined by taking test samples during the adsorption at intervals of 1–3 minutes. The quantity of L-1 in the samples was determined after reduction to ammonium distillates. Every sample was passed through a Schott filter G1 in order to avoid discharge of cellulose fibers in the solution. The time in which adsorption equilibrium was achieved was 4–40 min for the corresponding concentration interval and temperature range 0–60°C.

The concentration of L-1 before and during the adsorption was determined by establishing the quantity of NH_3 in the distillates spectrophotometrically by the method of Kehldal-Nesler with a SPEKOL ZV.[4] For this purpose, the adsorption spectrum of the complex ammonium Nesler reagent and, subsequently the working wavelength $\lambda = 390$ mm and a calibration curve "optical density (mkg)NH_3" were established. Standard solutions of $(NH_4)_2SO_4$ were used. By the experimentally established E and the calibration curve the quantity of NH_3 in the distillates and subsequently the concentration of L-1 in the solutions were calculated.

The quantity in mg (A) of polyelectrolyte adsorbed by 100 g of absolutely dry cellulose was calculated according to the formula:

$$A = (C_o - C_t) \cdot V \cdot B^{-1} \cdot 100 \qquad (1)$$

where: C_o and C_t are, respectively, initial and current concentration of the solution (g/l); V–volume of L-1 solution in liters; B–sample of absolutely dry cellulose in grams.

The maximum absolute error in calculating the quantity of adsorbed L-1 is: $\Delta A = \pm 25$ mg/100g cell.

The desorption of the polyelectrolyte by repeated treatment with distilled water was also studied with the purpose of gathering additional data necessary to explain L-1 and cellulose interaction.

Two kinds of bleached pulp were used to reveal the influence of pH on the adsorption process: sulfate hardwood pulp and sulfite softwood in buffered solutions of L-1 in concentrations of 0.05, 0.10, and 0.15 g/L with a pH of 2–12.[5] pH of the solution was measured with an LP-6 pH meter. The

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* Ratio of weight of fiber to weight of water.

concentration of L-1 was determined spectrophotometrically. The experiment was carried out at a temperature of 20°C and the other conditions were identical to those in which the adsorption isotherms were determined.

RESULTS AND ANALYSES

The adsorption isotherms for the three kinds of pulp in the temperature interval 0–60°C are graphically represented in Figures 1, 2, and 3. It is evident that the adsorption maximum for all three kinds of pulp is achieved in an equilibrium concentration $C = 0.10–0.15$ g/L. The disposition of the adsorption isotherms shows that with the increase of temperature the quantity of adsorbed polyelectrolyte decreases.

To determine the type of adsorption isotherm which describes the process of adsorption of L-1 on cellulose the adsorption isosteres have been drawn up, after which the values of isosteric heat were calculated according to Clausius-Clapeyron's equation in its integral form:

$$\lg C = \frac{\Delta S}{2,3R} - \frac{\Delta H}{2,3R} \cdot \frac{1}{T} \tag{2}$$

Equation (2) expresses the thermal relation of the equilibrium concentration when the quantity of the adsorbed substance remains constant ($A = $ const.).

Figures 4, 5, and 6 are graphic representations of the isosteres of adsorption of the three kinds of pulp under examination for different adsorbed quantities of L-1 at temperatures of 0, 20, 40, and 60°C. It is evident that the functions $1\,gC = f(\frac{1}{T})$ are approximately parallel straight lines, which shows that the heat of adsorption is not substantially influenced by the
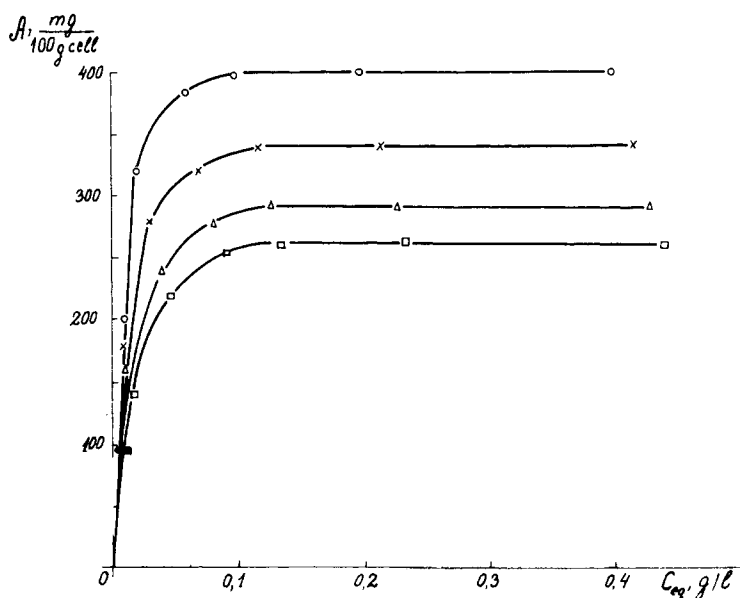

Fig. 1. Adsorption isotherms of bleached sulfate hardwood pulp at temperatures: (○) 0°C, (x) 20°C, (△) 40°C, (□) 60°C.
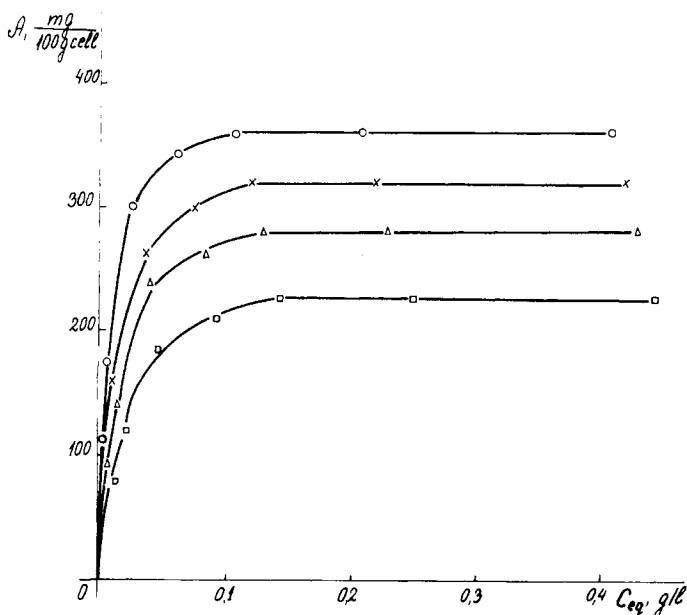
Fig. 2. Adsorption isotherms of bleached sulfate softwood pulp at temperatures: (○) 0°C, (x) 20°C, (△) 40°C, (□) 60°C.

quantity of adsorbed L-1. The slope coefficient of the linear functions (Figs. 4–6) helps establish the values of the isosteric heat of adsorption (ΔH). These values are negative and nearly identical. The average values for each kind of pulp are contained in Table I.

The similarity between the values of isosteric heat ($\Delta H \approx$ const.) gives sufficient grounds to accept that the surface of the cellulose fibers is energetically homogeneous, therefore, the adsorption isotherm of Langmuir can be applied to the process of adsorption under study.

It is accepted that as a general case the value and the size of the charge of the cellulose fiber depend on the donor-acceptor properties of the functional groups of cellulose and the molecules of the liquid environment or its components. In accordance with the theory of donor-acceptor interactions[6] t' ɔ basic functional groups of cellulose can be arranged in the following o. .er considering their donor strength:

$$C_3-OH > C_6-OH > C_2-OH > C\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagup\atop\diagdown}}$$
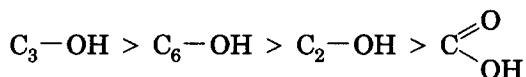
During the adsorption of L-1, the molecules of which contain $-NH_2$, $=NH$, and $=N-$ groups, the conditions for donor-acceptor interaction between the polyelectrolyte and the cellulose fibers, are evidently favourable. This is confirmed by the place which their functional groups occupy when they are arranged according to their donor strength:
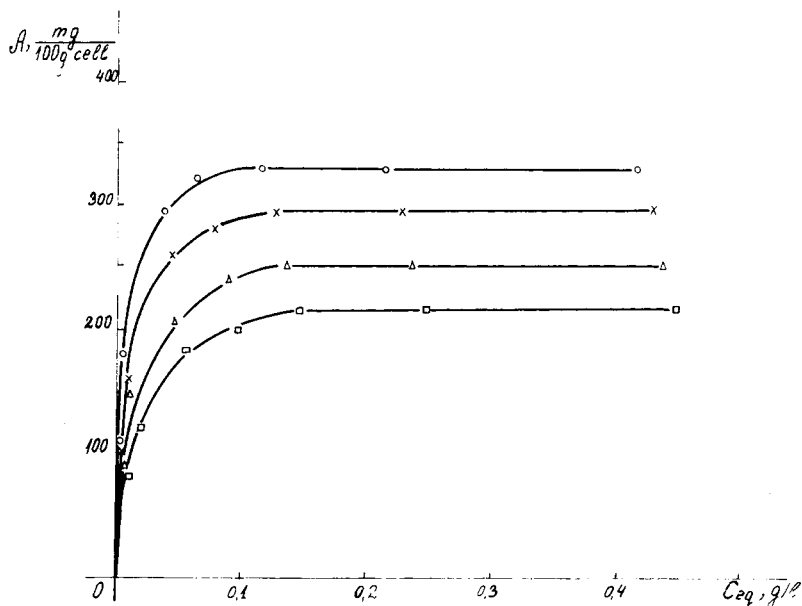
$$-NH_2 > -OH > -OCOR > C_6H_5 > -Cl$$
$$> -COOH > -CN > -C = C-$$
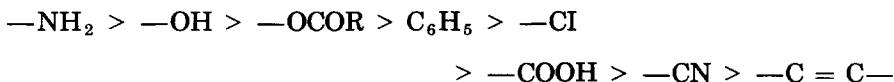
Fig. 3. Adsorption isotherms of bleached sulfite softwood pulp at temperatures: (○) 0°C, (x) 20°C, (△) 40°C, (□) 60°C.
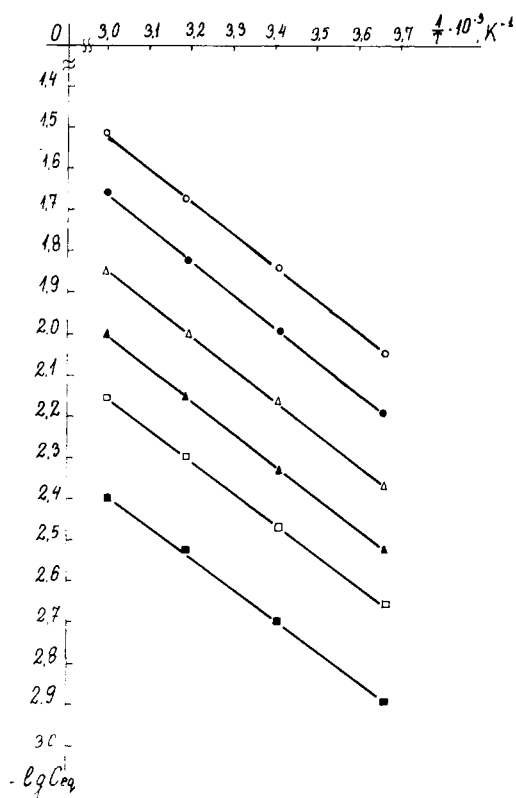

Fig. 4. Isosteres of adsorption of L-1 on bleached sulfate hardwood pulp in a temperature interval of 0–60°C, at A = const.: (○) 200 mg/100g cell, (●) 175 mg/100g cell, (△) 150 mg/100g cell, (▲) 125 mg/100g cell, (□) 100 mg/100g cell, (■) 50 mg/100g cell.

Bearing in mind the low values and the symbol of isosteric heat (ΔH) and the influence of temperature on the adsorption of L-1, it is evident that adsorption of L-1 takes place in accordance with the theory of H-bond formation and the electrostatic mechanism as explained by the theory of donor-acceptor interaction between the functional groups of cellulose and L-1.

The adsorption isotherms for the three kinds of pulp under examination are similar in character, and are described by Langmuir's equation:

$$A = \frac{A_{max} \cdot K \cdot C}{1 + K \cdot C} \tag{3}$$

where:

A = the quantity of adsorbed L-1, g/100g cell
C = the equilibrium concentration of the L-1 solution, g/L
K = the equilibrium constant of the adsorption equilibrium
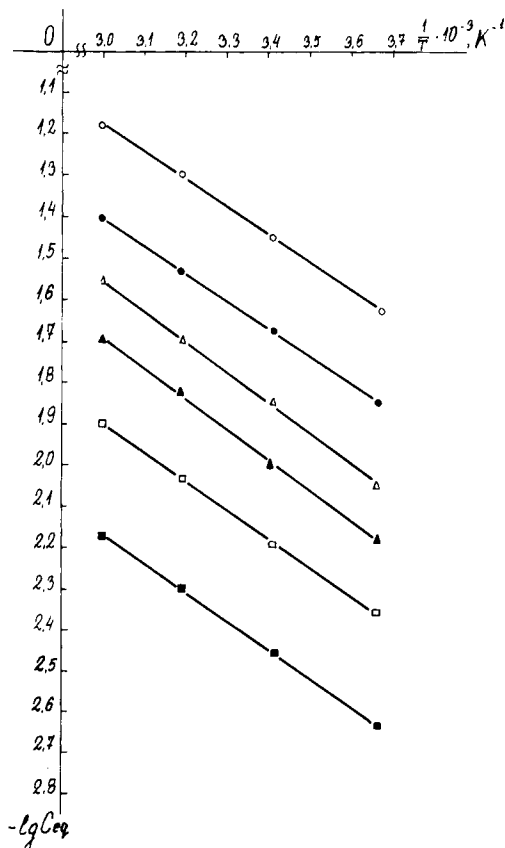A_{max} = the maximum quantity of adsorbed L-1, g/100 g cell

Fig. 5.   Isosteres of adsorption of L-1 on bleached sulfate softwood pulp in the temperature interval of 0–60°C, at A = const.: See Figure 4 for key.

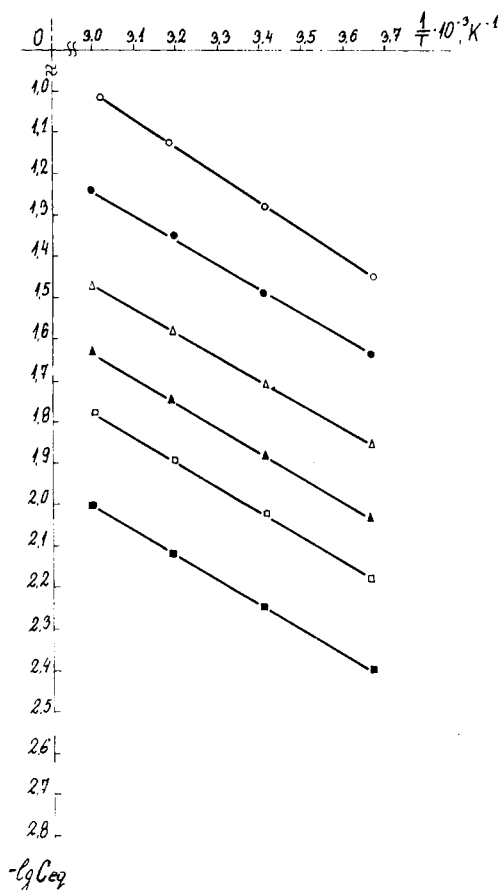Fig. 6.   Isostere of adsorption of L-1 on bleached sulfite softwood pulp in the temperature interval of 0-60°C, at A = const.: See Figure 4 for key.

TABLE I

Thermodynamic Characteristics of the Process of Adsorption of L-1 on Cellulose in Relation to Temperature

Type of cellulose	T (°C)	A_{max} (mg/100g cell)	K	ΔG^0 (kJ/mol.K)	ΔH_a[a] (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
Bleached	0	418	149.44	−11,355			
sulfate	20	358	96.24	−11,099			
Hard-	40	314	66.29	−10,958	−14.74	−14.71	−84.58
wood							
pulp	60	283	51.90	−10,893			
Bleached	0	380	130.00	−11,042			
sulfate	20	345	93.00	−11,032			
Softwood	40	305	64.29	−10,826	−13.55	−13.34	−80.55
pulp	60	226	49.00	−10,766			
Bleached	0	354	112.80	−10,718			
sulfite	20	312	81.30	−10,698			
Softwood	40	275	60.66	−10,677	−11.79	−11.95	−76.84
pulp	60	237	46.85	−10,645			

[a] Average isosteric heat of adsorption.

The linear form of Eq. (3) is:

$$\frac{C}{A} = \frac{1}{A_{max} \cdot K} + \frac{1}{A_{max}} \cdot C \tag{4}$$

The adsorption isotherms of the three kinds of pulp are represented linearly within the coordinates $\frac{C}{A} = f(C)$; Figure 7 demonstrates this function for bleached sulfate hardwood pulp. The slope coefficient and the segment of the straight lines help determine the constant from Langmuir's equation
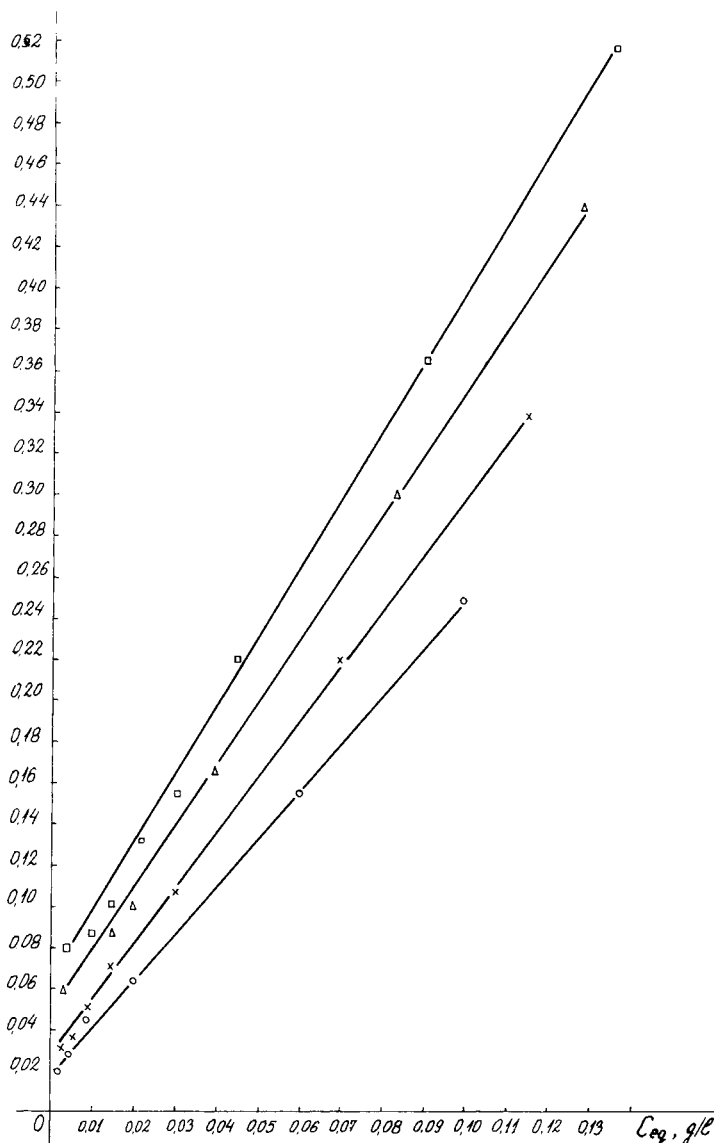

Fig. 7. Linear representation of adsorption isotherms of bleached sulfate hardwood pulp at temperature of: (○) 0°C, (x) 20°C, (△) 40°C, (□) 60°C.

(3)—A_{max} and K (Table I). The values of A_{max} are similar—within the error limit—to the experimentally established values. The values of K that were obtained show that K depends on the type of adsorbent and the temperature. With the increase of temperature K decreases, which is another proof that the process of adsorption of L-1 on cellulose is an exothermic process. The relation between the equilibrium constant and the temperature is described by the equation of the reaction isobar in its integral form:

$$lgK = \frac{\Delta S}{2,3 \cdot R} + \frac{\Delta H}{2,3 \cdot R} \cdot \frac{1}{T} \tag{5}$$

In accordance with Eq. (5) the relation between K and the temperature for the three kinds of pulp is depicted graphically within the coordinates $lgK = F(\frac{1}{T})$ in Figure 8. Through the slope coefficient and the segment of the straight lines, the heat of the process of adsorption (ΔH) and the entropy of adsorption (ΔS) were determined (Table I).

The negative variation values of ΔS show that, as a result of the adsorption, the degree of freedom of L-1 macromolecules decreases and the structure of the adsorbent acquires greater stability.[7]

The approximately identical values of ΔS show the equal influence the three kinds of pulp have on the mobility of the molecules of L-1, which testifies to the existence of adsorption centers of the same type. The standard
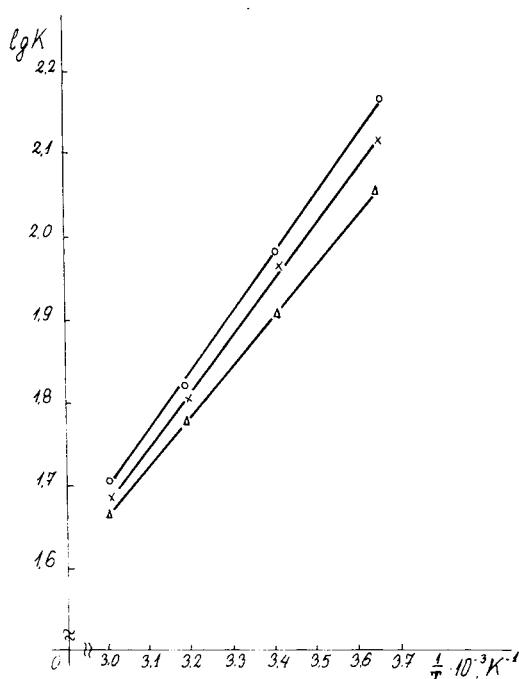

Fig. 8. Temperature function of the equilibrium constant for the bleached pulp under research: (◯) sulfate hardwood, (x) sulfate softwood, (△) sulfite softwood.

affinity (ΔG^o) was calculated from the values of K (Table I) according to the formula:

$$\Delta G^o = -R \cdot T \cdot \ln K \qquad (6)$$

The figures from Table I show that the values of ΔG_o within the temperature interval under study are similar, and there is a weak tendency of decrease in similarity with the increase in temperature. There are no substantial differences between the values of ΔG^0 for the different kinds of pulp. This leads to the conclusion that the active centers of the cellulose fibers have nearly the same adsorption capacity in respect to L-1. The figures from Table I show, too, that in respect to the values of ΔG_0 the three kinds of pulp are arranged in the same order as in respect to the adsorption capacity toward L-1.

Figures 9 and 10 show the variation in the quantity of L-1 adsorbed by sulfate hardwood and sulfite softwood pulp in respect to different pH of the environment for different concentrations of L-1 in the solution. It is evident that the type of pulp is not related to the type of isotherm. The character of the curves leads to the conclusion that for both types of pulp there exist two types of isotherms determined by the concentration of the solution of L-1.

The maximum adsorption for the different concentrations and pH = 5 $\div$ 7[10] is for the bleached sulfate hardwood pulp in the order of 150 to 300
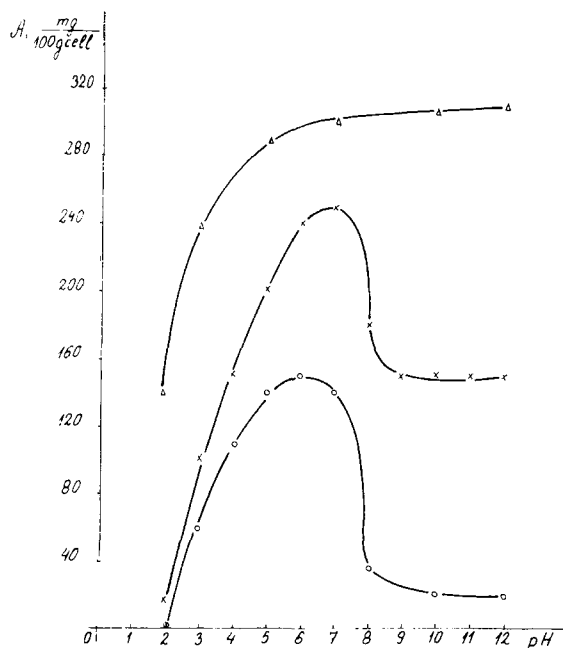

Fig. 9. Adsorption of L-1 on bleached sulfate hardwood pulp in regard to pH at a initial solution concentration of: (○) 0.5 g/L; (x) 0.10 g/L; (△) 0.15 g/L.
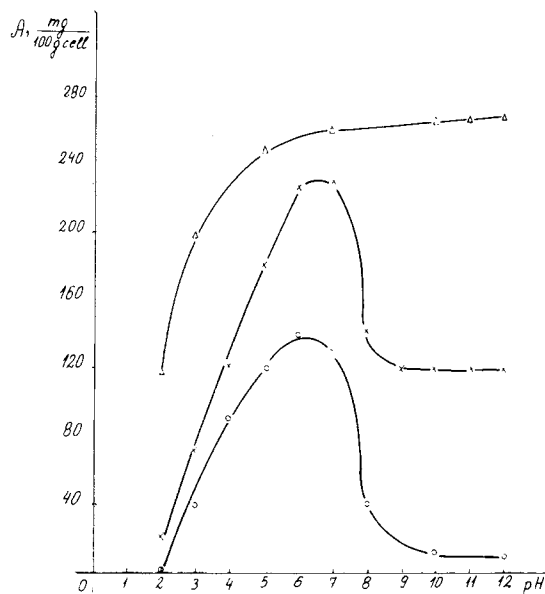
Fig. 10. Adsorption of L-1 on bleached sulfite softwood pulp in regard to pH at a initial solution concentration of: (○) 0.05 g/L; (x) 0.10 g/L; (△) 0.15 g/L.

mg/100 g cell, and for the bleached sulfite softwood pulp from 140 to 250 mg/100 g cell.

The comparatively lower values of A obtained at 20°C and pH = 4.5–5.0 in comparison to A from Figures 1 and 3 are obviously due to the ion-exchange processes taking place in the system cellulose-buffered solutions of L-1.

The data from the study of desorption of L-1 in water is displayed in Table II. The figures show that under the comparatively mild conditions accepted, nearly 30.6% of the adsorbed polyelectrolyte is desorbed.

CONCLUSIONS

1. The subject of the research was the adsorption of L-1 on bleached sulfate hardwood pulp and bleached sulfate and sulfite softwood pulp at temperatures of 0, 20, 40, and 60°C. It was established that the maximum of adsorption occurred under the following conditions: C_o = 0.15–0.20 g/L, temperature = 20°C, equilibrium pH ≈ 5; and is of the order of 310–360 mg/100 g cell. With the increase of temperature the quantity of adsorbed L-1 decreases. The resulting heat values of adsorption are negative and are independent of the quantity of adsorbed L-1. They are of the order of 11.7–14.7 kJ/mol. The adsorption equilibrium is represented by the adsorption isotherm of Langmuir.

2. It was established that the values of the equilibrium constant and the chemical affinity decrease with the increase of temperature.

3. The values of the entropy of adsorption for all three kinds of pulp are negative and relatively identical (76.8–84.5 J/mol).

4. The existence of 30.6% desorption of L-1 in water was established.

5. It was established that adsorption capacity in respect to L-1 for the

TABLE II
Desorption of L-1 from Bleached sulfate Hardwood Pulp in Distilled Water at 20°C; L-1 was
Adsorbed at 20°C from a Solution with a Concentration C_0 = 0.20 g/L

Number of washings with distilled H_2O	A_0[a] (mg/100g cell)	D (mg/100g cell)
0	358.0	—
1	325.6	32.4
2	309.7	15.9
3	297.2	12.5
4	286.8	10.4
5	276.4	10.4
6	266.7	9.1
7	257.6	9.1
8	251.9	5.7
9	248.3	3.6
10	248.3	0
Total amount (mg/100g cell)	248.3	109.7
Total amount (%)	69.4	30.6

[a] Amount of L-1 left after desorption.

three types of pulp under examination compares as follows: bleached sulfate hardwood > bleached sulfate softwood pulp > bleached sulfite softwood pulp. This order is determined by their chemical composition and the physical state.

6. It was established that the most favorable pH of the environment for the adsorption process is from 5 to 7 for the lower concentrations of the solution and above 5 for the higher concentrations. Difference in pulp type does not influence the pH isotherms.

These conclusions make possible the determination of the most favorable conditions for the utilization of L-1 in minimum quantities with the necessary high effect on the properties of the cellulose for paper production.

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