

Polyethylenimine Adsorption by Cellulose

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Synopsis

The behavior of cellulose materials in aqueous solutions of polyethylenimine was investigated. Sulfite-bleached cellulose, sulfite unbleached, sulfate unbleached, and monocarboxylcellulose were used. The adsorption kinetics of polyethylenimine by monocarboxylcellulose were studied in detail. The velocity constants of the process, the velocity temperature coefficients, and the activation energies were calculated. The reaction order was established. The physical type of polyethylenimine adsorption by cellulose was established, and it was shown that the adsorption isotherms comply with the equation of Langmuir. On the basis of the data and on the dependencies obtained, the equations of adsorption in the temperature interval of 0°C to 60°C were derived.

INTRODUCTION

The polyelectrolyte ability to modify the surface of cellulose fibers finds great application in paper production. For such purposes, most suitable are the cationic polyelectrolytes and, among them, polyethylenimine (PEI). The investigations carried out in this area are dedicated mostly to the establishment of PEI influence on paper pulp properties and finished paper, or on some technological factors governing PEI retention such as the properties of fibrous materials, paper composition, type of the paper obtained, PEI type, etc.¹⁻¹¹

The reports which refer to the study and establishment of the interaction mechanism between cellulose materials and PEI are very limited.⁷⁻⁹ For this reason, there is no universally accepted theory about the PEI retention mechanism by fibrous materials.

The aim of the present work is to investigate the complete behavior of cellulose materials in PEI water solutions and to establish the type of processes taking place in the system.

EXPERIMENTAL

Materials

The investigations were carried out with sulfite-bleached, sulfite unbleached, sulfate unbleached, and monocarboxylcellulose (MCC), obtained

from softwood. The results of the analyses of the initial celluloses are given in Table I. MCC was obtained from sulfite-bleached cellulose after oxidation with NO_2^{12} until 3.11% COOH groups were obtained.

The three initial technical celluloses were previously ash-freed after several treatments with 0.1N HCl and washed with distilled water to free them from chloride ions. The water-soluble impurities were removed from the ash-freed material by hot water extraction for 1 hr, which was repeated three times, after which the celluloses were filtered and air dried.

The PEI was a product of BASF (West Germany), trademark Polymin SN, supplied as a 20% solution. The exact polymer concentration was controlled by a quantitative nitrogen determination according to a modified method of Kjeldahl.¹³ Solutions of desired concentration were prepared from the initial solution by dilution.

Methods

A determined sample of 10 g o.d. cellulose, after being weighed at 0.0001 g accuracy, was transferred into a glass-topped jar, distilled water was poured over it (ratio 1:20), and the sample was then left to swell at the required temperature until complete equilibrium resulted with respect to the temperature and the swelling of the cellulose material. A certain volume of PEI solution was then added by pipet, which was of such a concentration as to secure the desired polymer concentration in the solution at solid:solution ratio equal to 1:40.

The sample was well dispersed and thermostated at the required temperature until an adsorption equilibrium was reached. At regular intervals, the sample was intensively mixed. It was established in advance that the equilibrium adsorption did not depend on the manner of mixing, either continuously or sporadically. After reaching an adsorption equilibrium, the dispersion was filtered through a coarse filter. Part of the filtrate was further filtered through a Schott filter (G_5) for complete removal of any fibers, after which the clarified solution was analyzed for PEI content. The blank runs that were carried out showed no polymer loss due to adsorption by the vessels and filters.

The kinetics investigations of PEI adsorption were carried out with solutions of initial concentrations of 0.142, 0.194, 0.305, and 0.395 g/l. at temperatures of 0°C and 40°C, and with monocarboxylcellulose, which proved appro-

TABLE I
Characteristics of Initial Cellulose Materials

Type of cellulose	Ash %	α -Cellulose, %	Lignin, %	Pentosanes, %	CHO groups, %	COOH groups %	Degree of beating, °SR
Sulfite bleached	0.19	99.2	1.52	1.09	0.07	0.30	14
Sulfite unbleached	0.15	86.7	6.33	4.70	0.84	0.75	16
Sulfate unbleached	0.19	90.1	4.70	7.20	0.91	0.62	17

ropriate for the purpose because of its increased adsorption ability. The temperatures of 0°C and 40°C were chosen because they secured a sufficiently great PEI concentration difference before and after the experiments. At smaller temperature intervals, the concentration differences approached the error of the method, while at greater ranges (higher temperatures), the adsorption equilibrium was established so fast that the process went out of control.

In determining the adsorption kinetics, 10 g o.d. cellulose was taken which, after swelling and homogenization, was thermostated to the required temperature. The corresponding quantity of polymer solution was thermostated in a measuring flask. The polymer solution was then quickly added to the cellulose dispersion, mixing was started, and the time was recorded.

Mixing was carried out continuously at low speed, which secured complete dispersion and homogenization of the whole sample without any damage to the fibers. At regular intervals, 10-ml samples were taken out by means of a filter-fitted pipet. These aliquots were filtered through a Schott filter (G₅), and the PEI concentration was determined in 5 ml of the solution.

The quantitative polymer determinations were carried out spectrophotometrically by a SPEKOL-ZV, designed by C. Zeiss, at 635 nm. Determinations were based on the colored chelate complex formed between PEI and 0.1N solution of Cu(CH₃COO)₂.¹⁴ A standard curve was drawn for the dependence between optical density and polymer solution concentrations, by means of which the concentrations of the investigated solutions were determined.

Under the working conditions used, the accuracy of determining the PEI concentrations was $\Delta C = \pm 0.001$ g/l. The adsorbed quantity was calculated by the formula:

$$A = (C_0 - C_\tau) \cdot V \cdot 100/B \quad (1)$$

where A is PEI quantity (mg) adsorbed by 100 g cellulose, C_0 is initial polymer concentration (g/l.), C_τ is polymer concentration at the moment (g/l.), V is the total volume of the solution (ml), and B is o.d. cellulose sample (g).

From eq. (1), after differentiation, the absolute error of the method for determining the PEI quantities adsorbed was calculated: $\Delta A = \pm 9$ mg/100 g.

RESULTS AND DISCUSSION

In Figures 1 and 2 are shown the kinetics curves at 0°C and 40°C for $C_0 = 0.142$ and $C_0 = 0.395$ g/l. It can be seen that polymer solution concentrations decrease extremely fast in the first minute after the adsorption begins, and equilibrium is reached in about 6–7 min at 40°C and in 13–15 min at 0°C. For the other two concentrations, $C_0 = 0.194$ and $C_0 = 0.305$ g/l., similar dependencies are obtained (Table II). The fast establishment of the adsorption equilibrium is evidently due to the MCC accessibility for PEI molecules.

In Figures 3 and 4 are shown the dependencies between the reciprocal values of the equilibrium concentrations and the duration of the process. In the case of a second-order reaction, the dependence must comply with the equation

$$K \cdot \tau = 1/C_\tau - 1/C_0 \quad (2)$$

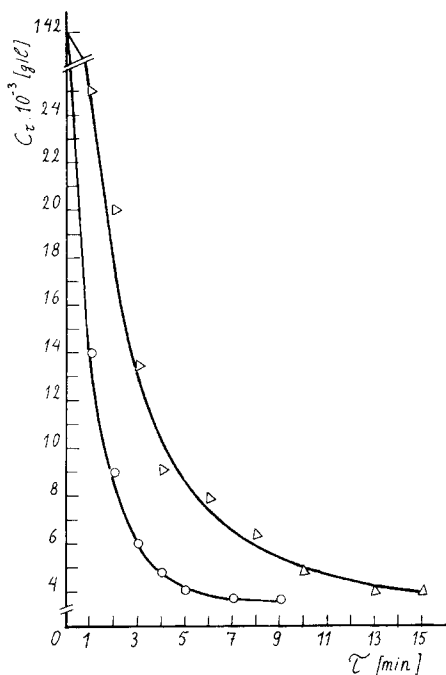


Fig. 1. Kinetics dependencies for $C_0 = 0.142$ g/l.: (O) 40°C; (Δ) 0°C.

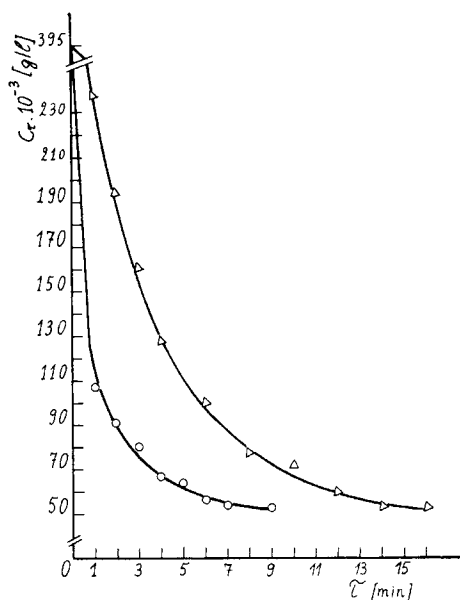


Fig. 2. Kinetics dependencies for $C_0 = 0.395$ g/l.: (O) 40°C; (Δ) 0°C.

where K is total velocity constant and τ is duration of the process.

The linear character of the dependencies obtained confirms that the process of PEI adsorption by cellulose is of second order.

On the basis of the experimental results and the slopes of the straight lines (Figs. 3 and 4), the velocity constants of the process were determined and the

velocity temperature coefficients calculated (Table III). It can be seen that with the increase in polymer concentrations, the values of the velocity constants decreased and the velocity temperature coefficients also decreased when PEI was adsorbed at 40°C and at 0°C. The decreased values of the velocity constants give evidence that the system approaches a condition of complete PEI saturation. The decrease of the temperature coefficients shows that a molecule diffusion has started into the volume of the cellulose, i.e., the process gradually passes from its kinetics phase to an inner diffusional phase. Owing to the different influence of the rise in temperature on the adsorption and diffusion, the temperature coefficients (Table III) differ essentially from the coefficient of Van't Hoff.

The apparent activation energy of the process is calculated according to the equation

$$E = \frac{\lg K^{40} - \lg K^0}{1/T_1 - 1/T_2} \tag{3}$$

where E is activation energy, and T_1 and T_2 are temperatures in °K for 40°C and 0°C. The values obtained for E , which exclude the heat of adsorption, are in the range of 200–900 cal/mole.

In Figure 5 is shown the activation energy change which is dependent on PEI concentration. It can be seen that with the increase of the polymer concentration in the solution from about 0.14 to about 0.40 g/l., the activation energy decreases from approximately 900 to 250 cal/mole. Such a change in the activation energy indicates that an apparently small number of adsorption centers correspond to the higher PEI concentrations, which active centers are of a decreased reaction activity, while the lower concentration values correspond to a greater number of active centers, which are of a higher total activity.

If the equation of Arrhenius describing the velocity constant dependence on temperature is logarithmic, we shall obtain

$$\lg K = \lg K_0 - E/2.303 RT \tag{4}$$

where K_0 is fore-exponential multiplier, and R is gass constant.

From eq. (4) are calculated the fore-exponential multipliers. The dependence between $\lg K_0$ and the activation energy is shown in Figure 6. The dependence is a linear one, which shows a possible existence of a compensation effect.^{15,16} The presence of a compensation effect explains to a certain degree the insignificant influence of PEI concentration on the velocity of the

TABLE II
PEI Adsorption Depending on the Duration of the Process

C_0 , g/l.	t , °C	$C_\tau \times 10^{-3}$, g/l.										
		$\tau =$ 1 min	2 min	3 min	4 min	5 min	6 min	8 min	10 min	12 min	13 min	15 min
0.194	0	40	26	—	17	—	14	11	8	7	7	7
	40	17	13	9	8	7	7					
0.305	0	182	125	71	59	—	48	38	26	22	20	20
	40	55	43	35	25	23	20	20				

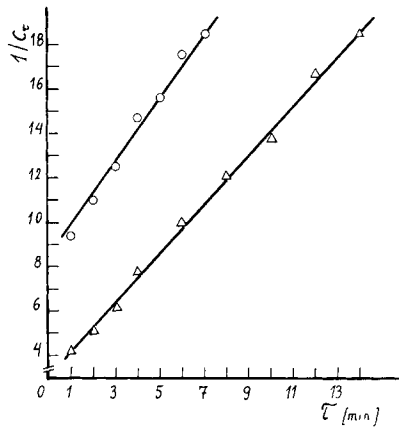


Fig. 3. Dependence of reciprocal values of PEI concentrations on the duration of the process for $C_0 = 0.142$ g/l.: (O) 40°C; (Δ) 0°C.

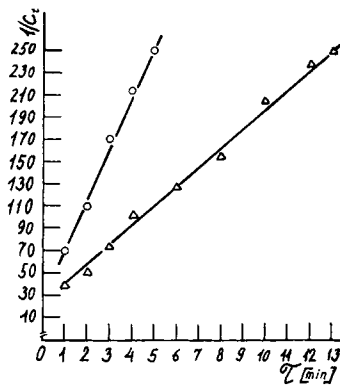


Fig. 4. Dependence of reciprocal values of PEI concentrations on the duration of the process for $C_0 = 0.395$ g/l.: (O) 40°C; (Δ) 0°C.

process. Such an effect of the PEI concentration in the solution is due to (1) the complicated nature of PEI, which determines its interaction with the adsorbent, as well as the interaction among the polymer macromolecules, and (2) the no less complex polymer structure of the cellulose.

The results of the PEI adsorption kinetics investigations with respect to the three initial cellulose show that equilibrium takes place almost in the same manner and at the same time as for MCC. All dependencies investigated are of the same character as those obtained for MCC.

TABLE III
Velocity Constants and Velocity Temperature Coefficients
at PEI Adsorption by Cellulose

C_0 , g/l.	K		K^{40}/K^0
	40°C	0°C	
0.142	45.00	17.50	2.57
0.194	20.80	9.83	2.12
0.305	6.40	3.71	1.72
0.395	1.42	1.10	1.29

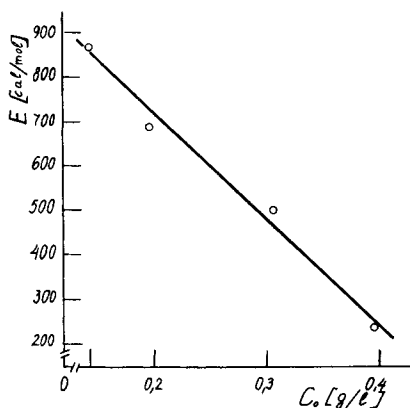


Fig. 5. Change of the apparent activation energy with the PEI solution concentrations.

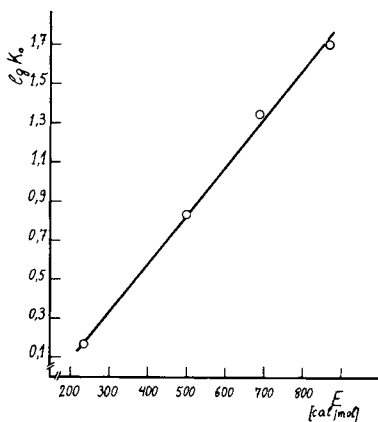


Fig. 6. Dependence of logarithm of the pre-exponential multiplier on the activation energy.

The investigations carried out about the temperature influence on PEI adsorption for the four celluloses, within the temperature range of 0°C to 40°C, show that in this range PEI adsorption practically does not depend on temperature, i.e., a positive heat effect is not present, which is typical of physical adsorption. Evidently, this fact is due to the change taking place in the polymer structure of the PEI solution with the increase of temperature, as a result of the destruction of molecular aggregates and the significant increase of the molecular mobility, which ultimately eliminates the high-temperature negative influence on the investigated process.¹⁷

In Figure 7 are shown the adsorption isotherms of the investigated celluloses in the temperature range of 0°C to 60°C. In expressing Langmuir's equation for adsorption from solutions,

$$A = A_{\max} \cdot C / (K_1 + C) \tag{5}$$

in its linear form:

$$C/A = K_1/A_{\max} + 1/A_{\max} \times C \tag{6}$$

the dependence $C_{eq}/A = f(C_{eq})$ can be derived.

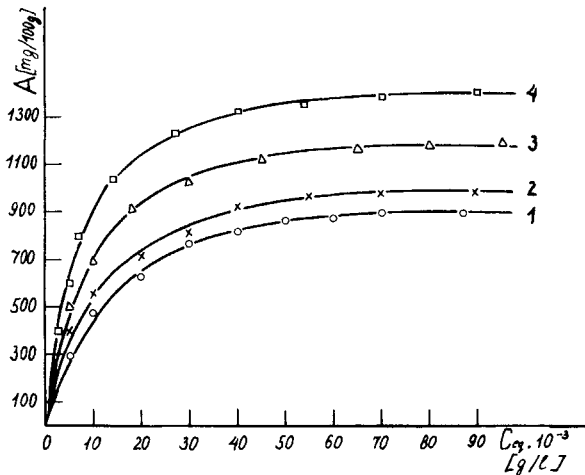


Fig. 7. Adsorption isotherms in the temperature interval of 0°C to 60°C of: (1) sulfite bleached; (2) sulfate unbleached; (3) sulfite unbleached; and (4) MCC.

The dependencies thus obtained are linear for all celluloses (Fig. 8), which proves that PEI adsorption from aqueous solutions by cellulose is of Langmuir's type. On the basis of the experimental results, the slopes and the intersections of the straight lines in Figure 8 can be calculated the constants A_{\max} and K_1 given in eq. (6).

After substituting these constants in eq. (5), the adsorption eqs. (7)–(10) are obtained, which describe the change of the adsorbed PEI quantity as a function of the equilibrium concentration of its aqueous solutions in the temperature range of 0°C to 60°C:

For sulfite bleached,

$$A = \frac{1055 \cdot C}{0.0121 + C} \quad (7)$$

For sulfite unbleached,

$$A = \frac{1120 \cdot C}{0.0101 + C} \quad (8)$$

For sulfate unbleached,

$$A = \frac{1300 \cdot C}{0.0078 + C} \quad (9)$$

For MCC,

$$A = \frac{1500 \cdot C}{0.0060 + C} \quad (10)$$

All this shows that PEI retention on cellulose fibers takes place mostly at the expense of the formation of hydrogen bonds between the polymer amino groups and the hydroxyl and carboxyl groups of the cellulose. The pH values (4–5) at which adsorption was achieved show that under the experimental conditions adopted, no ion exchange results, which excludes any presence of ion bonding between the cellulose and PEI.

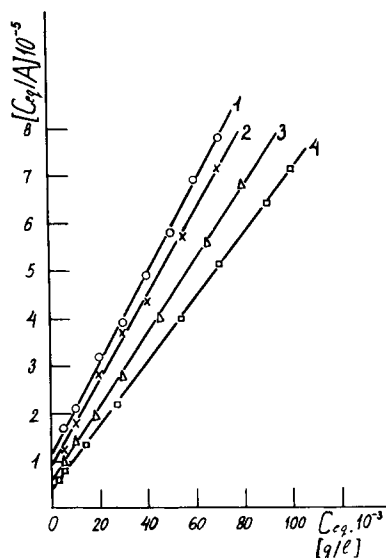


Fig. 8. Linear form of Arrhenius equation for: (1) sulfite bleached; (2) sulfate unbleached; (3) sulfite unbleached; and (4) MCC.

The physical type of the adsorption is also confirmed by the results obtained after carrying out polymer desorption. To this aim, a certain cellulose sample, which was saturated in advance with PEI (A_{eq}) at $C_0 = 0.360$ g/l., $t = 20^\circ\text{C}$, and at ratio 1:40, was washed four times with distilled water under the following conditions: $t = 20^\circ\text{C}$, $\tau = 1$ hr, and ratio 1:40. In Table IV are given the results from the PEI desorption experiments, where A_{res} is quantity of PEI retained by the cellulose after the washing and D is polymer quantity which has passed into the water. As can be seen from the data in Table IV, after the fourth washing with distilled water, irreversibly bonded polymer is present, which is evidently due to its mechanical retention owing to sterical effects.¹⁷

The contention that irreversibly bonded polymer is present in the cellulose is also confirmed by the results of the three successive washings, of three cellulose samples, with distilled water at 20°C for 24 hr, which are carried out after the four 1-hr washings. No PEI was analyzed in the filtrates.

TABLE IV
Polyethylenimine Desorption

Type of cellulose	A_{eq} , mg/ 100 g	pH_{eq}	1st Washing		2nd Washing		3rd Washing		4th Washing	
			A_{res}	D	A_{res}	D	A_{res}	D	A_{res}	D
Sulfite bleached	902	4.865	544	458	359	185	292	67	290	0
Sulfate unbleached	984	4.698	590	394	296	294	244	52	238	0
Sulfite unbleached	1180	4.237	808	372	490	318	382	108	370	0
MCC	1220	3.751	432	788	194	238	168	26	160	0

There is evidence for a certain contradiction between the established second order of the process and the physical type of adsorption. It is due to the PEI ability to flocculate cellulose fibers by which it is adsorbed. Consequently, during PEI adsorption two parallel processes take place: (1) adsorption of polymer molecules by single cellulose fibers, and (2) adsorption of fibers which have already adsorbed PEI, by other cellulose fibers—a result of the ability of the PEI molecules to bridge several cellulose fibers in one complex (bundle).^{2,5} Evidently, this is the case of an adsorption process in which the reacting substance and the product of the reaction are strongly adsorbed. Such a process can be described generally by the equation

$$dx/d\tau = k \cdot \theta_a \cdot \theta_b \quad (11)$$

where x is quantity of the substance which has reacted for time τ , and θ is area occupied by the adsorbed substance over 1 cm² of the adsorbent surface.

Since $\theta = f(C)$, it appears that PEI adsorption by cellulose is a process of second order as regards the polymer concentration.

CONCLUSIONS

1. The kinetics of PEI adsorption by MCC was investigated at 0°C and 40°C. It was established that the reaction is of second order as regards the polymer concentration, which was due to a great degree to its flocculation ability.

2. It was established that when increasing the polymer solution concentration the velocity of reaction practically does not change, which may be due to the presence of a compensation effect.

3. When increasing the concentration, the velocity temperature coefficients decreased, which showed that the process passed into its diffusion area.

4. PEI adsorption by four celluloses was studied. It was established that adsorption practically does not depend on temperature in the investigated temperature range. The adsorption isotherms obtained were of Langmuir's type.

5. The obtained values of the activation energies were in the range of 250 to 1000 cal/mole.

6. The PEI desorption from cellulose into pure water was investigated. A mobility of the adsorption equilibrium was established.

7. On the basis of conclusions 4, 5, and 6, it was found that the investigated adsorption process was of a physical type.

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