Investigation on the Kinetics of the Adsorption Process of Aliphatic Amidpolyamine on Cellulose

MARGARITA PETKOVA NEDELCHEVA,* STEFKA MARINOVA MLADENOVA, and EVA TODOROVA VALCHEVA

Department of Pulp and Paper Chemistry, Higher Chemico-Technological Institute, Sofia 1756 Bulgaria

SYNOPSIS

Investigation has been carried out on the kinetic dependences of the adsorption process of aliphatic amidpolyamine (lamide-1, L-1) on three kinds of bleached pulp (sulfate pulp of hard wood and sulfate and sulfite pulp of soft wood) at temperatures of 0, 20, 40, and 60°C within a concentration interval of 0.030 g/liter + 0.500 g/liter. It has been established that the kinetic process can be described by the Elovich–Tyomkin exponential kinetic equation. The activation energy is of the order of 4.12–4.42 kJ/mol and the entropy factors substantially affect the process speed. The coefficients of the correlations describing the effect of the L-1 solution concentrations on the coefficient of heterogeneity (α) and the initial adsorption speed (V_0) have been determined.

INTRODUCTION

During the past years, increasing attention has been paid[1-5] to theoretical studies aiming at the elucidation of the mechanism of processes taking place in the system fiber–water–polyelectrolyte (PE). Knowledge of the complex interactions between the fibrous suspension and the different PEs is necessary with a view to ensuring efficient control on the technological processes in a series of industry branches and optimum conditions of PE application.

The purpose of this article is to study the kinetics of the adsorption process of aliphatic amidpolyamine (lamide-1, L-1) on bleached pulp in order to clarify the mechanism of colloid–chemical processes taking place in the system pulp–water–L-1.

EXPERIMENTAL

Three kinds of bleached pulp were used as adsorbents: sulfate pulp of hard wood and sulfate and sulfite pulp of soft wood. The pulp was prepared in an unashed (H–) form by treatment with 0.1 nHCl to an ash content below 0.05%. The investigations were carried out on aqueous solutions of L-1 with a concentration ranging from 0.030 to 0.500 g/liter at a 1 : 40 ratio (pulp : solution) and temperatures of 0, 20, 40, and 60°C. To control the process and the concentration–adsorption equilibrium, samples were withdrawn at time intervals of 1–3 min. The quantity of PE in the samples was established spectrophotometrically by a SPECOL ZV using the Kehldal-Nesler method.[6] The initial (C_0) and current (C_t) concentrations of the solutions were determined by a method described in detail in Ref. 7. The quantity of L-1 adsorbed for a definite period of time on the same amount of adsorbent (for all three kinds of cellulose) was expressed by the $C_0 - C_t$ difference.

RESULTS AND DISCUSSION

To eliminate diffusion as a possible rate-controlling step, the experiments were carried out on preliminary beaten dry cellulose with continuous stirring of the solution (50 rpm). Preliminary investigations of the system cellulose–water–L-1 carried out with different stirring speeds showed the process to be adsorption controlled. From the data on the C_t of the solutions, the quantity (in g/liters) of adsorbed L-1 ($C_0 - C_t$) per 10.0 g absolutely dry cellulose was calculated, and the kinetic curves of the adsorption

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 42, 985–992 (1991)
 CCC 0021-8995/91/040985-08$04.00

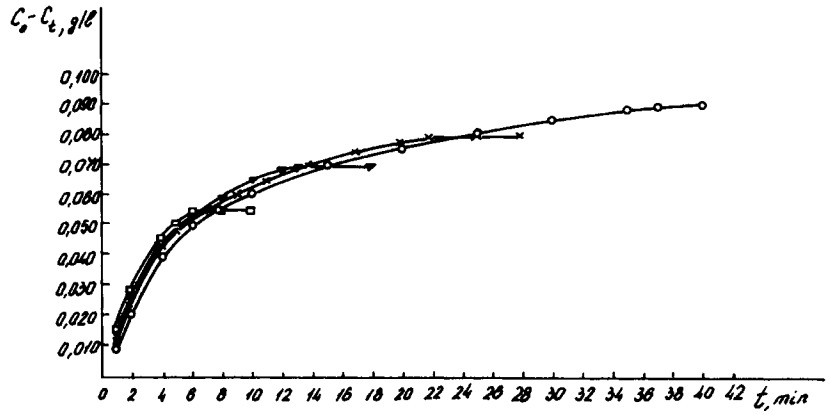

Figure 1 Kinetic curves of L-1 adsorption on bleached sulfate pulp of soft wood at C_0 = 0.200 g/liter and temperatures of: (○) 0°C, (×) 20°C, (▲) 40°C, and (□) 60°C.

process were plotted for the three kinds of cellulose at temperatures of 0, 20, 40, and 60°C and a solution concentration ranging from 0.030 to 0.500 g/liter.

According to Figure 1, the higher the temperature, the shorter the time needed for attaining adsorption equilibrium (33–40 min at 0°C, 5–7 min at 60°C).

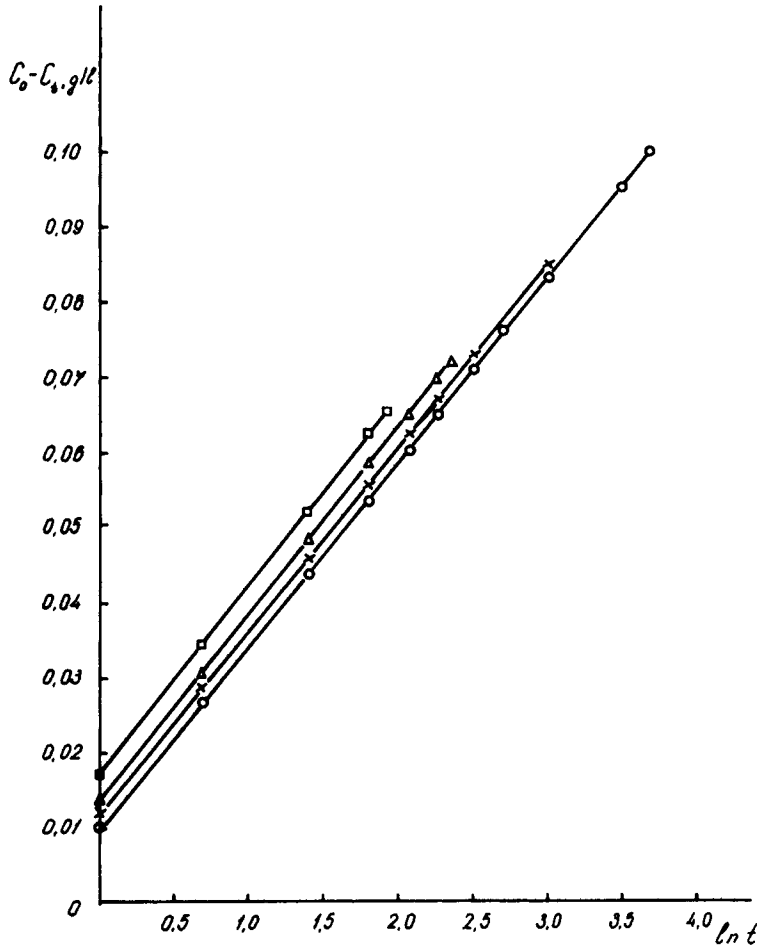

Figure 2 Amount of L-1 adsorbed on bleached sulfate pulp of hard wood at C_0 = 0.200 g/liter depending on ln t at temperatures of: (○) 0°C, (×) 20°C, (△) 40°C, and (□) 60°C.

The kinetic curves obtained, which are linearized in coordinates $C_0 - C_t = f(\ln t)$, are presented graphically in Figures 2–4. They are described by

$$C_0 - C_t = \frac{1}{\alpha} \ln(\alpha V_0) + \frac{1}{\alpha} \ln t \qquad (1)$$

Equation (1) represents an approximate integral form of an exponential kinetic equation[8]:

$$V = V_0 e^{-\alpha(C_0 - C_t)} \qquad (2)$$

where $V = dC/dt$ is the process speed at a given moment t (g/liter min), V_0 denotes the process speed at the initial moment t_0 when $C_0 - C_t \to 0$, and α is the coefficient of heterogeneity characterizing ths surface and depending, in the general case, on temperature and concentration.

Equation (2) describes processes occurring in real adsorption layers on energetically uniform heterogeneous surfaces.[8] The regularities characteristics of these processes are attributed to the mutual effect of species adsorbed on a homogeneous surface or to the presence, on the solid phase surface, of adsorption centers or regions possessing different adsorption abilities.

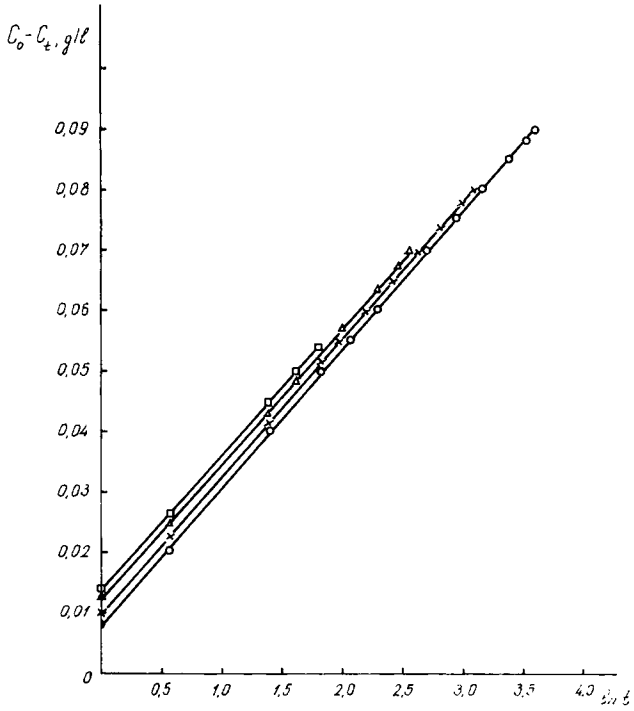

Figure 3 Quantity of L-1 adsorbed on bleached sulfate pulp of soft wood at $C_0 = 0.200$ g/liter in regard to ln t at temperatures of: (○) 0°C, (×) 20°C, (△) 40°C, and (□) 60°C.

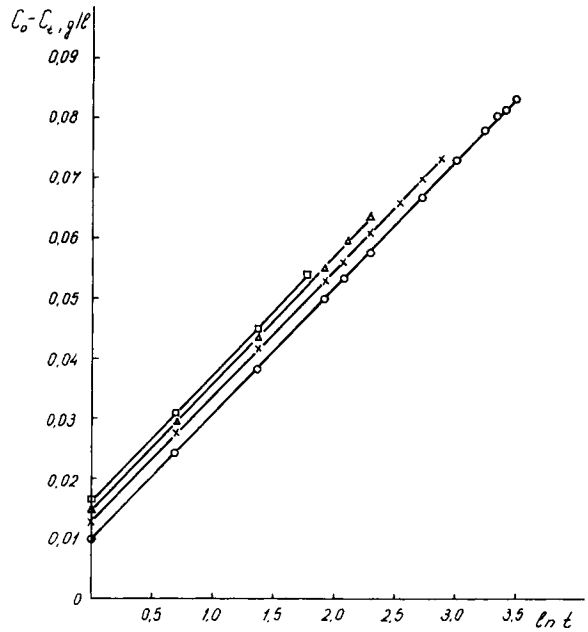

Figure 4 Quantity of L-1 adsorbed on bleached sulfite pulp of soft wood at $C_0 = 0.200$ g/liter in regard to ln t at temperatures of: (○) 0°C, (×) 20°C, (△) 40°C, and (□) 60°C.

The coefficient of heterogeneity (α) depends on temperature as follows[9]:

$$\alpha = \frac{B}{R.T} - \alpha_0, \qquad (3)$$

where B is a coefficient characterizing the energetic inhomogeneity of the surface, α_0 is a coefficient of the entropy heterogeneity of the surface, which is associated with the number and accessibility of the active centers on which the adsorption process takes place, and RT is experimental temperature.

The values of the coefficient α within the temperature range investigated (0–60°C) are determined from the slopes of the straight lines in Figures 2–4. Obviously, α depends on the pulp type and is practically independent of temperature. This indicates that during L-1 adsorption on cellulose, α denotes the entropy inhomogeneity of the absorbent surface ($\alpha = \alpha_0$), which is determined by the different accessibility of active centers for adsorption of the polymer molecules. The mean values of the coefficient α for the three kinds of cellulose at $C_0 = 0.200$ g/liter within the temperature interval investigated are presented in Table 1.

The values of coefficient α permit calculation of

Table I Kinetic Characteristics of the Adsorption Process of L-1 on Bleached Pulp at Temperatures of 0–60°C and C_0 = 0.200 g/liter

Bleached Pulp	α (liter/g)	E (kJ/mol)	A_0 (g/liter/min)	V_0 (g/liter/min) 0°C	20°C	40°C	60°C
Sulfate, hard wood	40.40	4.47	0.205	0.0300	0.0333	0.0365	0.0408
Sulfate, soft wood	43.64	4.34	0.180	0.0247	0.0280	0.0326	0.0378
Sulfite, soft wood	46.70	4.00	0.205	0.0351	0.0388	0.0450	0.0498

the current process speed (V_t) at a given moment (t) on the basis of the following equation:

$$V = \frac{1}{\alpha t} \tag{4}$$

According to the logarithmic form of eq. (2),

$$\ln V = \ln V_0 - \alpha(C_0 - C_t) \tag{5}$$

there should be a linear dependence between ln V and the corresponding quantity of adsorbed L-1 ($C_0 - C_t$). This dependence is confirmed by the data obtained on the three kinds of cellulose and is presented graphically in Figure 5 for bleached sulfate pulp of soft wood at C_0 = 0.200 g/liter within the temperature interval investigated.

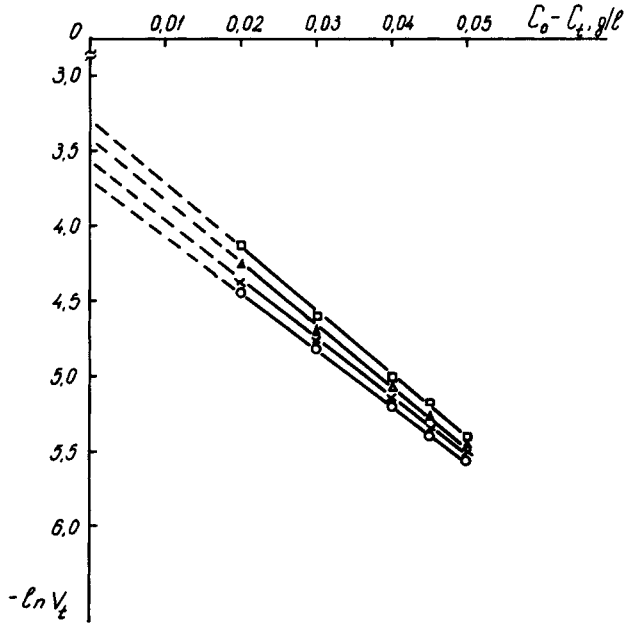

Figure 5 ln V_t in regard to the amount of L-1 adsorbed on bleached sulfate pulp of soft wood at C_0 = 0.200 g/liter and temperatures of: (○) 0°C, (×) 20°C, (△) 40°C, and (□) 60°C.

The initial process speed (V_0) is determined on the basis of eq. (5), and the values found are given in Table I. From the straight lines in Figure 5 and the data in Table I, it is evident that with rising temperature the initial speed of the process increases, whereas an increase in quantity of the adsorbed L-1 leads to a drop of the adsorption speed.

On the basis of data concerning the process speed at C_0 = 0.200 g/liter and temperatures of 0–60°C, the dependencies ln $V = f(1/T)$ are plotted for the three kinds of cellulose. They are presented in Figures 6–8 according to the Arrhenius equation:

$$V = Ae^{-E/RT} \tag{6}$$

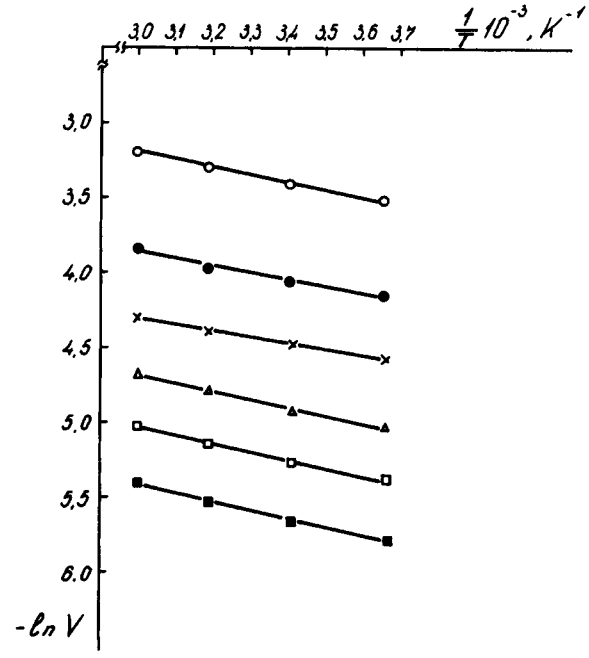

Figure 6 Temperature dependence of ln V for bleached sulfate pulp of hard wood at C_0 = 0.200 g/liter and adsorbed L-1 amounting to: (○) $C_0 - C_t \to 0$, (●) $C_0 - C_t$ = 0.020 g/liter, (×) $C_0 - C_t$ = 0.030 g/liter, (△) $C_0 - C_t$ = 0.040 g/liter, (□) $C_0 - C_t$ = 0.050 g/liter, and (■) $C_0 - C_t$ = 0.060 g/liter.

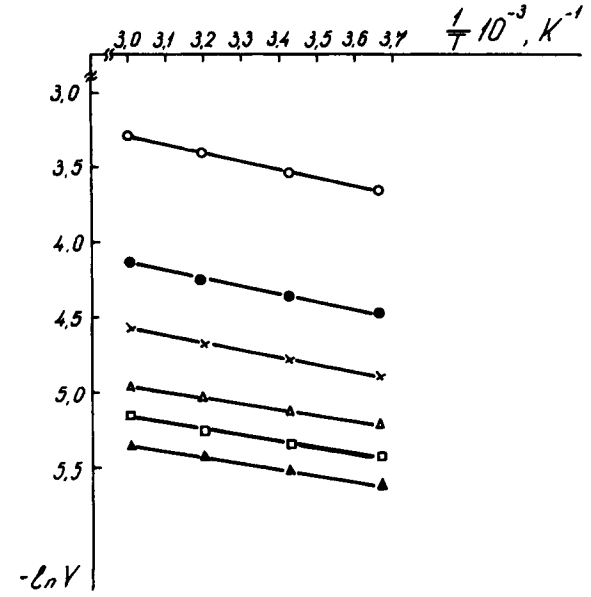

Figure 7 Temperature dependence of ln V for bleached sulfate pulp (soft wood) at C_0 = 0.200 g/liter and an adsorbed amount of L-1 of: (○) $C_0 - C_t \rightarrow 0$, (●) $C_0 - C_t$ = 0.020 g/liter, (×) $C_0 - C_t$ = 0.030 g/liter, (△) $C_0 - C_t$ = 0.040 g/liter, (□) $C_0 - C_t$ = 0.045 g/liter, and (▲) $C_0 - C_t$ = 0.050 g/liter.

From the slopes of the straight lines obtained, the activation energy (E) at $C_0 - C_t$ = const. is obtained as well as the values of E at the initial moment (E_0) when $C_0 - C_t \rightarrow 0$. It is found that the activation energy does not substantially change with increasing quantity of adsorbed L-1 and it practically constant ($E = E_0 \approx$ const.). The activation energies for the pulps under investigation are close in value, the lowest value being found for bleached sulfite pulp of soft wood. Since E is independent of the adsorbed quantity, the decisive role in decreasing the process speed should belong to the preexponential factor. The low activation energy values indicate that the adsorption process is materialized at the expense of relatively weak electrostatic interactions. From the segment of the straight lines in Figures 6–8, the preexponential factor (A_0 and A) is determined. It is a quantitative characteristic of the number of active adsorption centers and steric effects due to steric hindrance. It is established that with all three kinds of cellulose, the preexponential factor decreases with advancing adsorption process (Fig. 9). This is obviously associated with occupation of part of the active centers on the surface of cellulose fibers by polymer molecules and the appearance of steric effects caused by these molecules

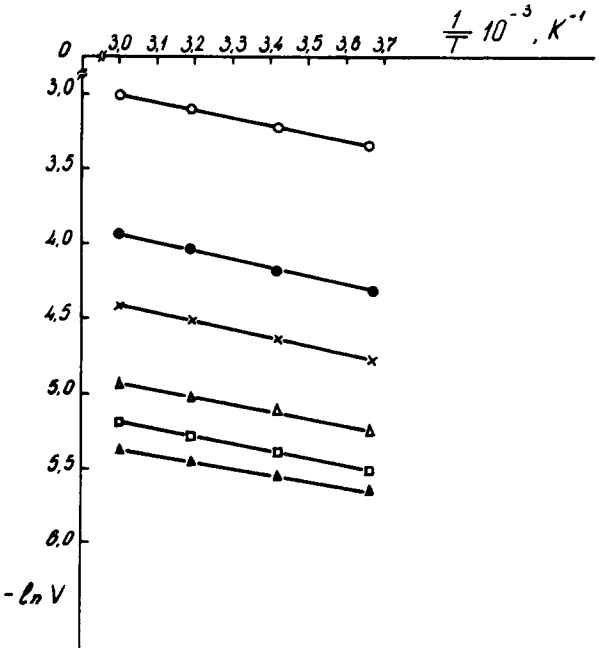

Figure 8 Temperature dependence of ln V for bleached sulfite pulp of soft wood at C_0 = 0.200 g/liter and an adsorbed quantity of L-1 of: (○) $C_0 - C_t \rightarrow 0$, (●) $C_0 - C_t$ = 0.020 g/liter, (×) $C_0 - C_t$ = 0.030 g/liter, (△) $C_0 - C_t$ = 0.040 g/liter, (□) $C_0 - C_t$ = 0.045 g/liter, and (▲) $C_0 - C_t$ = 0.050 g/liter.

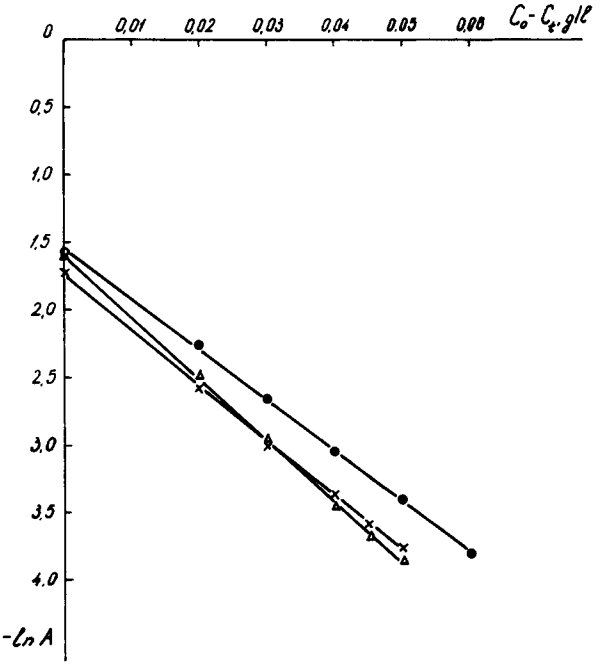

Figure 9 ln A in regard to the adsorbed amount of L-1 ($C_0 - C_t$) at C_0 = 0.200 g/liter on bleached pulp: (●) sulfate, hard wood; (×) sulfate, soft wood; and (△) sulfite, soft wood.

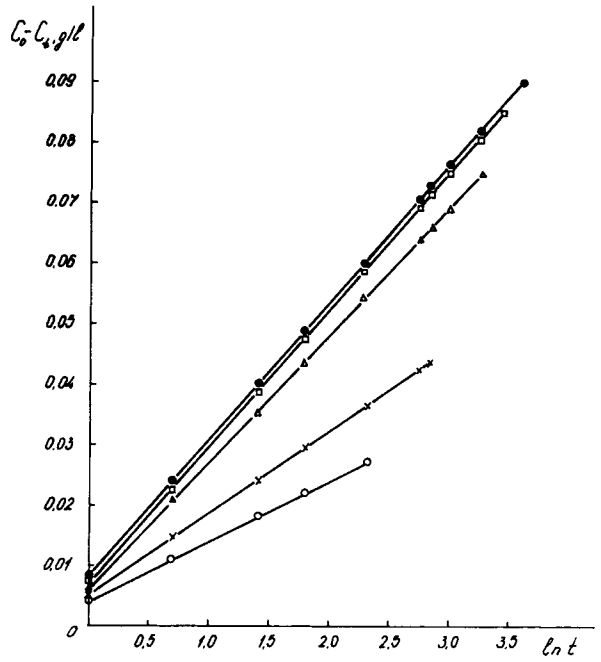

Figure 10 Quantity of adsorbed L-1 in regard to ln t on bleached sulfate pulp of soft wood at a temperature of 0°C and C_0 (g/liter) of: (○) 0.030, (×) 0.050, (△) 0.100, (□) 0.150, and (●) 0.200.

present in the adsorption layer. From the values obtained for the preexponential factor, it follows that the number of active centers and the steric hindrance due to secondary interactions of the adsorbed molecules in the adsorption layer exercise the strongest effect on the adsorption speed.

The influence of the initial concentration of the L-1 solutions on the speed of the adsorption process for the three kinds of pulp has been investigated at 0–20°C. These temperatures allow investigation of the process kinetics due to the low process speed. The kinetic curves obtained for the three kinds of pulp at concentration of 0.030–0.500 g/liter and temperatures of 0–20°C are similar to those given in Figure 1. They are linearized in coordinates $C_0 - C_t = f(\ln t)$, as is shown in Figure 10 for bleached sulfate pulp of soft wood. The kinetic characteristic of the sorption process under consideration is presented in Table II. Figure 10 and Table II show that adsorption equilibrium is attained more quickly with lower polymer concentrations in the solution (10–11 min at 0°C and C_0 = 0.30 g/liter; 33–40 min for C_0 = 0.200 g/liter). Concentrations above 0.200 g/liter have no effect on the speed of the sorption process because under these conditions saturation of

Table II Kinetic Characteristic of the Adsorption Process of L-1 on Bleached Pulps at Temperatures of 0 and 20°C and Concentrations of 0.030–0.500 g/liter

					T = 0°C			T = 20°C		
			$\alpha = aC_0^b$			$V_0 = K_0C_0^n$			$V_0 = K_0C_0^n$	
Bleached Pulp	C_0 (g/liter)	α (liter/g)	a	b	V_0 (g/liter/min)	K_0	n	V_0 (g/liter/min)	K_0	n
Sulfate, hard wood	0.030	93.3			0.0071			0.0080		
	0.050	71.4			0.0129			0.0136		
	0.100	46.5	30.00	0.50	0.0218	0.0550	0.93	0.0224	0.0564	0.93
	0.150	41.2			0.0270			0.0273		
	0.200–0.500	40.4			0.0300			0.0330		
Sulfate, soft wood	0.030	100.0			0.0071			0.0080		
	0.050	75.6			0.0111			0.0123		
	0.100	53.5	33.78	0.50	0.0179	0.0388	0.75	0.0188	0.0428	0.75
	0.150	44.4			0.0224			0.0247		
	0.200–0.500	43.6			0.0247			0.0280		
Sulfite, soft wood	0.030	105.5			0.0074			0.0086		
	0.050	77.5			0.0120			0.0139		
	0.100	56.3	38.86	0.50	0.0192	0.0388	0.70	0.0213	0.0450	0.70
	0.150	48.6			0.0235			0.0273		
	0.200–0.500	46.7			0.0351			0.0388		

the cellulose fiber surfaces with polymer molecules is reached, and probably a possibility of net shaping around the molecules arises, which makes the adsorption process difficult.

The values of α given in Table II are determined from the slope of the straight lines obtained (Fig. 10). The data in Table II show that α decreases with increasing initial concentration of the L-1 solutions and does practically not change after adsorption saturation of the surface of cellulose fibers with polymer molecules (C_0 = 0.200 g/liter) is attained.

The equation that describes the concentration dependence of α for the process investigated can be written as

$$\alpha = aC_0^b \tag{7}$$

From the logarithmic form of eq. (7),

$$\ln \alpha = \ln a + b \ln C_0 \tag{8}$$

and the linear dependences presented in Figure 11, the coefficients of eq. (7) are found (Table II). The initial speed (V_0) is calculated on the basis of eq. (4) and (5) at different initial concentrations (C_0)

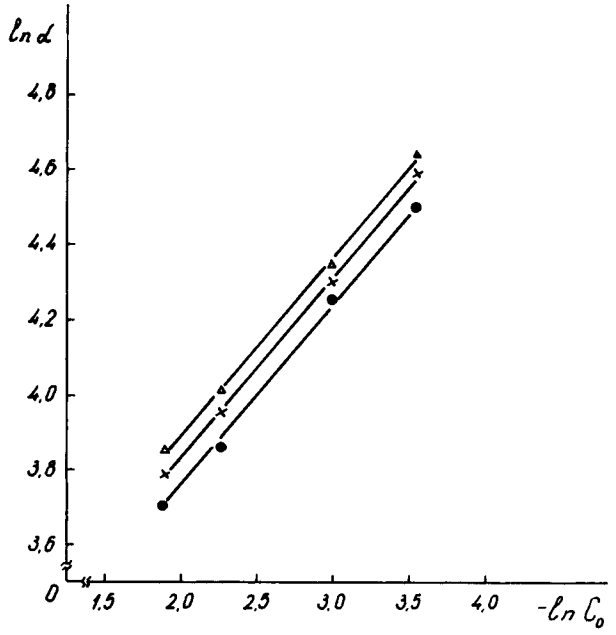

Figure 11 Coefficient α versus C_0 over the temperature range 0–60°C during L-1 adsorption on bleached pulp: (●) sulfate, hard wood; (×) sulfate, soft wood; and (△) sulfite, soft wood.

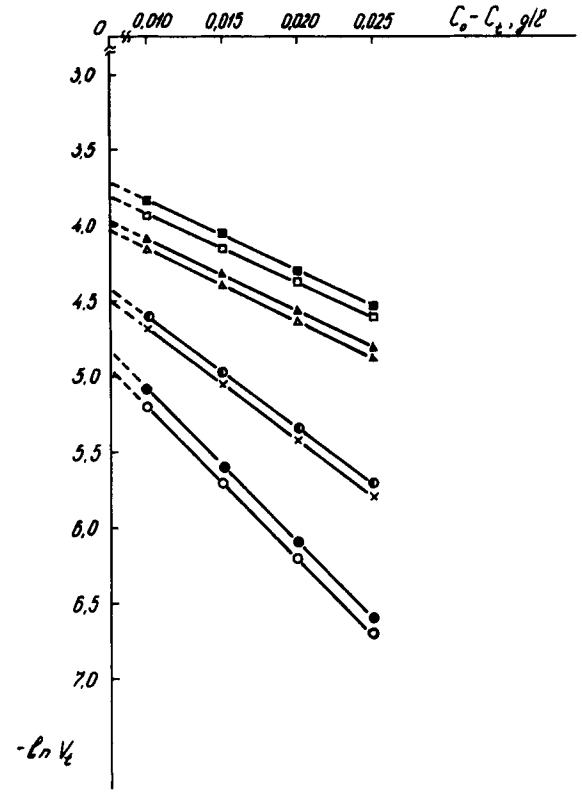

Figure 12 ln V_t for bleached sulfate pulp of soft wood in regard to the quantity of adsorbed L-1 ($C_0 - C_t$) at 0°C and C_0 (g/liter) of: (○) 0.030, (×) 0.050, (△) 0.100, (□) 0.150, at 20°C and C_0 (g/liter) of: (●) 0.030, (◐) 0.050, (▲) 0.100, (■) 0.150.

and temperatures of 0 and 20°C (Table II). Evidently, V_0 of the process increases with the initial concentrations of the L-1 solutions. This correlation is described by a power equation of the kind

$$V_0 = K_0 C_0^n \tag{9}$$

From the logarithmic form of eq. (9),

$$\ln V_0 = \ln K_0 + n \ln C_0 \tag{10}$$

and the linear dependence obtained (Fig. 12) for bleached sulfate pulp of soft wood, the process order (n) and the speed constant (K_0) are determined (Table II). From Table II it is obvious that n is independent of temperature but depends on the pulp type. The fractional numbers (smaller than 1) obtained for n show that after the first contact between the cellulose fibers and L-1, an adsorption process

of the Langmuir type takes place, for which the exponent n can have values from 0 to 1.0.

The investigations carried out and the results obtained lead to the following conclusions:

1. The kinetics of the adsorption process of L-1 on bleached pulps (sulfate pulp of hard wood and sulfate and sulfite pulp of soft wood) at temperatures of 0–60°C and a concentration interval of 0.030–0.500 g/liter are described by an Elovich–Tyomkin exponential kinetic equation.
2. The activation energy for all three kinds of cellulose is of the order of 4.14–4.42 kJ/mol and does not depend on the quantity of adsorbed L-1.
3. It is established that the effect of entropy factors due to steric hindrance is decisive for the change in current speed of the adsorption process.
4. It is established that for the adsorption process under consideration, the coefficient α is independent of temperature. An empirical equation is obtained for α depending on the initial concentration of L-1 solutions, whose coefficients are found.
5. The dependence of the initial process speed on the initial concentration of the L-1 solutions is described by an exponential kinetic equation, whose coefficients are determined.

REFERENCES

1. D. Horn and J. Melzer, *Water Interactions*, Pap.-Making Trans. Symp., Oxford, 1977; Vol. 1, London, 1978, pp. 135–148.
2. B. Alince, M. Inoke, and A. A. Robertson, *J. Appl. Polym. Sci.*, **23**(2), 539–548 (1979).
3. B. Alince, *J. Colloid Interf. Sci.*, **69**(3), 367–374 (1979).
4. B. Bianchin, G. Gervason, P. Vallette, and G. Sauret, Fibre–Water Interactions Pap.-Making Trans., Symp., Oxford, 1977, Vol. 1; London, 1978, pp. 151–160, Disscus. 161.
5. Westfelt Lors, *Cellul. Chem. Technol.*, **13**(6), 813–825 (1979).
6. A. K. Babko and A. T. Pilipenko, *Photometric Analyses, Methods of Determination of Nonmetals*, Chemia, 1974; Moscow, pp. 12–18.
7. M. Nedeltschewa, St. Mladenova, and E. Walschewa, *J. Appl. Polym. Sci.*, **31**, 1901–1912 (1986).
8. S. L. Kiperman, *Introduction to the Kinetics of Heterogeneous Catalytic Reactions*, Nauka, Moscow, 1964, (in Russian).
9. E. Valtcheva, *Reaction Kinetics Catalysis Lett.*, **5**(2), 85, (1978).

Received May 9, 1989
Accepted March 21, 1990