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Immobilization of polymers on cellulose acetate membranes

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Abstract

Using models of dead-end filtration theory, the kinetics of forming dynamic layers of sulfate lignin (SL) and sodium carboxymethylcellulose (Na-CMC) onto CA membranes during cross-flow filtration of dilute solutions of polymers was studied. It was found for both polymers (compact SL and linear Na-CMC), that the polymer layer with the least hydraulic resistance, which yields a small reduction in membrane water permeability (10–20%), but a significant increase in salt rejection, is formed, if the process kinetics corresponds to *J–V* linear dependence predicted by the model of 'blocking a pore by a single particle'. The results obtained may be used to define the optimum conditions for immobilizing the available catalytic active polymers on regular semipermeable membranes during the membrane filtration process.

1. Introduction

The main problem in making membranes for catalytic applications is simultaneously ensuring their catalytic activity, permeability and selectivity.

One of the methods to obtain catalytic membranes is by the immobilization of appropriate polymers on regular semipermeable membranes under dynamic conditions.

It is known that dynamic immobilization of solutes on membranes changes both their surface properties and porosity [1,2]. A decrease in effective pore size caused by adsorption and deposition of a polymer onto/in membrane pores may be the dominating factor of changes in hydraulic permeability and selectivity [3–5]. For example, the deposition of compact polymers inside large pores results in a decrease of membrane hydraulic permeability by 50–95% and above [5].

In this study the conditions of immobilization of polymers on semipermeable membranes during cross-flow filtration to obtain the composite structure with the least hydraulic resistance and high salt rejection are discovered. Two kinds of polymers with carboxylic functional groups were used as models: sulfate lignin (SL), a compact polymer, and sodium carboxymethylcellulose (Na-CMC), a linear polymer. Ultrafiltration and low-selective reverse osmosis cellulose acetate (CA) membranes of various pore size and density, but with an equal ability to adsorb the polymers were employed for the study.

2. Methods

It was earlier shown that the kinetics of cross-flow membrane filtration of colloids [1] as well as compact polymer dilute solutions [5] may be characterized by models of dead-end filtration theory. The theory [6] distinguishes between three

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Table 1
Characteristics of deposits according to the filtration theory [6]

Deposit type	Equations describing the process kinetics at straight-linear dependencies between variables	Characteristics of the process formation
Intrapore deposits		
Type 1	$J=J_0-k_1V$	(1) Blocking a pore by a single particle
Type 2	$1/J=1/J_0+k_2\tau$	(2) Intermediate deposit (transition from type 1 to 3)
Type 3	$\tau/V=1/J_0+(k_3/2)\tau$	(3) Gradual overlapping a pore section by the great number of particles
External	$\tau/V=1/J_0+(k_4/2)V$	(4) Cake formation on external surface of a porous partition

types of intrapore deposits and a deposit on the external surface of a porous partition.

Characteristics of the deposits according to filtration theory are given in Table 1.

On experimental data of cross-flow filtration kinetics interpreted in terms of Eqs. (1)–(4) (found in Table 1), the deposit type may be detected and water permeability decline (q_{pm}/q_m) caused by each type of deposit may be defined.

Such a method gives us the possibility to reveal the main factors determining the permeability of the membranes with an additional polymer layer and to find conditions leading to the formation of the layer with the least hydraulic resistance.

3. Experimental procedure

The experiments were performed in a continuous cross-flow pressure unit, including thin channel cells with a membrane area of 30 cm (length) × 0.3 cm (wide), or 15 cm (length) × 0.5 cm (wide), and a height of 1 mm [5].

CA ultrafiltration (UF) membranes of the UAM series were used with a nominal pore size (D_n) from 3 nm to 45 nm and CA low-selective reverse osmosis (RO) membranes of MHA-60, MHA-70 and MHA-80 types, manufactured by 'NPO Polimersintez', Russia.

SL studied (MW average 6×10^3) was separated from sulfate black liquor and was characterized in our laboratory [5]. The SL powder was dissolved in 0.05 M or 0.1 M NaOH and then dosed to the salt (NaCl or Na_2SO_4) solution to be filtered.

The Na-CMC used was a commercial product of 75/400 type (MW 9×10^4). The Na-CMC solutions were prepared by dissolving weighed amounts of the solid in NaCl or Na_2SO_4 aqueous solutions.

The concentration ranges of the salts (0.015–0.1 M) and the polymers (20–200 mg/l), as well as the pH range (6–9) ensured that both polymers dissolved in the filtered solutions.

The general methodology of obtaining data on changes in membrane transport characteristics due to the immobilization of the polymers onto the membranes was the same as described earlier [5]. Each membrane was treated with a polymer-free salt solution at the operating pressure (P) and cross-flow velocity (v) to obtain stable permeate flux J_m (or water permeability q_m) and salt rejection R_m. These J_m (q_m) and R_m values were accepted as initial ones. Then the test was carried out under the same conditions using the salt solution with the polymer additive up to stabilization. The transport membrane characteristics were measured as a function of time, polymer and salt concentrations, pH, pressure (in the range of 0.5–5 MPa), and cross-flow velocity (in the range of 0.1–1 m/s).

4. Results

(1) During cross-flow filtration on the membranes of Na_2SO_4 or NaCl aqueous solutions in the presence of SL or Na-CMC additives under

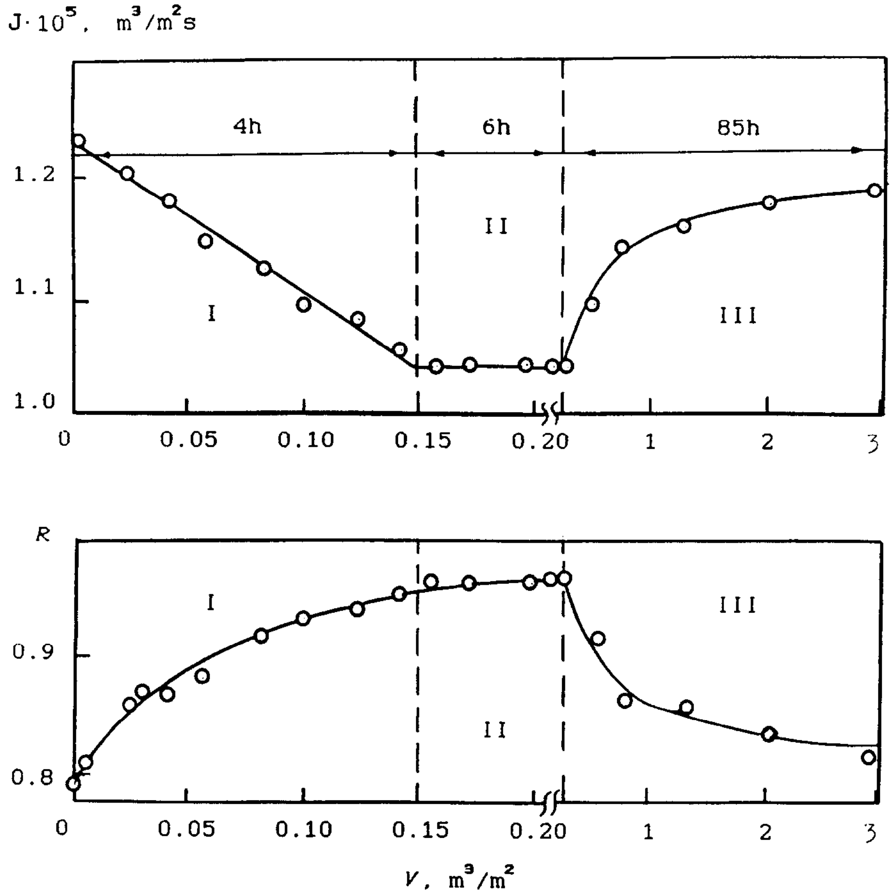

Fig. 1. Changes in permeate flux (a) and salt rejection (b) of MHA-80 membranes during formation (I), functioning (II) and destruction (III) of a SL polymer layer vs. cumulative permeate volume. Conditions: $P = 5$ MPa, $v = 1$ m/s, $C_s = 0.035$ M Na_2SO_4, pH = 7, $C_p = 50$ mg/l (I,II) and $C_p = 0$ (III).

the outlined conditions, permeate flux gradually decreased and salt rejection increased up to the attainment of dynamic equilibrium and the stabilization of J_{pm} and R_{pm} values. The new membrane transport characteristics slowly approached the initial ones when the process filtration proceeded in the absence of the polymer additive (Fig. 1). Thus, the formation of SL or Na-CMC layer onto the membranes used is a reversible process.

(2) The kinetics of cross-flow filtration on the membranes of SL or Na-CMC solutions and, consequently, the kinetics of formation of the polymer layers onto the membranes during the first stage of the process correlates the filtration models based on the build-up of a pore deposit.

In the case when using RO membranes (MHA-60, MHA-70, MHA-80) or UF membranes with relatively small pore size ($D_n = 3$–20 nm), especially decreasing after compression, permeate flux varies with time (or permeate volume) in a manner consistent with the model of 'blocking a pore by a single particle', i.e. Eq. (1) (Fig. 1 and Fig. 2). As it was shown earlier for compact polymers and sorptive membranes [5], this may take place if sizes (equivalent diameters) of membrane pores and macrosolutes are close, so that the macrosolute is able to enter the pore or to cause partial occlusion of the pore entrance. It may be supposed that the possibility of pore blocking by the linear polymer, such as Na-CMC, on the model

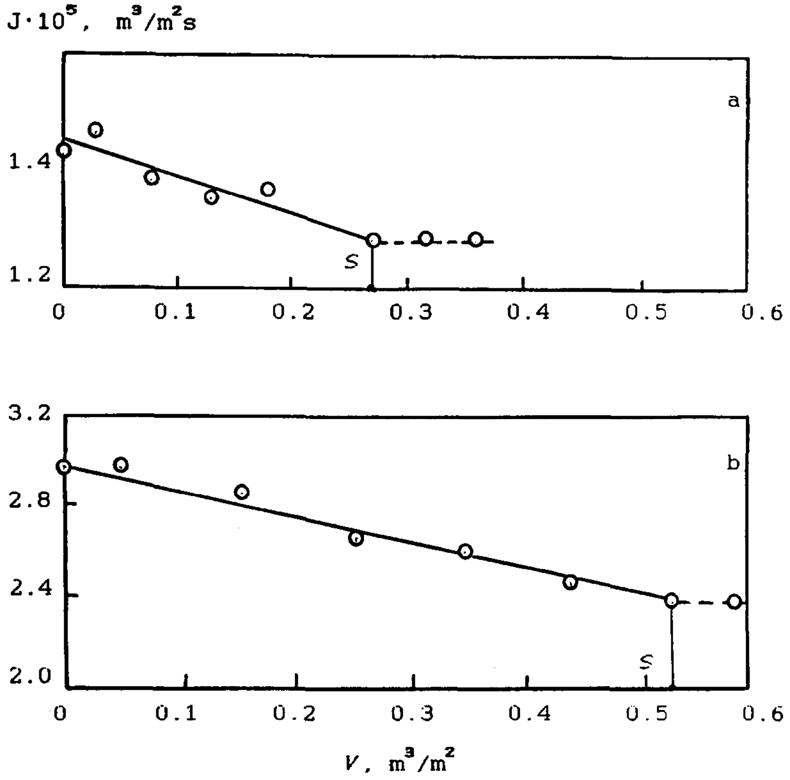

Fig. 2. Examples of membrane filtration kinetics of Na-CMC solutions through MHA-80 (a) and UAM-200 (b) membranes in terms of Eq. (1). S — stabilization points in kinetics. Conditions: $P=5$ MPa, $v=1$ m/s, $C_p=50$ mg/l, $C_s=0.04$ M Na_2SO_4, pH = 7.

of type 1 is defined by the size of the molecule small axis.

In the case of using UF membranes with a larger pore size (up to $D_n=45$ nm), membrane filtration of both SL and Na-CMC solutions yields a deposit of type 2, i.e. a decrease of the permeate flow corresponds to Eq. (2) (Fig. 3a).

The formation of pore deposits onto highly permeable membranes can be followed by the second stage, namely cake formation on the external surface of the membranes (Fig. 3b). However, the contribution of such external polymer layers to flux decline, in comparison with that of pore deposits, for both SL and Na-CMC under accepted operating parameters is small (see Fig. 3b).

(3) Permeate flux decline caused by immobilization of the polymers onto/in membrane pores was characterized by membrane relative permeability q_{mp}/q_m. Dependencies of relative permeability on initial membrane permeability q_m over the accepted ranges of physico-chemical and hydrodynamic parameters for both the polymer solutions are shown in Fig. 4.

A significant alteration of q_{mp}/q_m with increasing initial membrane permeability at $q_m > 0.6 \times 10^{-11}$ $m^3/m^2 \cdot s \cdot Pa$ observed for SL solutions (Fig. 4a), is connected with the change in membrane filtration kinetics (i.e. a pore deposit type) from type 1 to type 2. As was earlier recognized [5], such behavior is typical for compact polymers.

Contrary to SL, the linear polymer, Na-CMC, does not yield an essential alteration of q_{mp}/q_m with q_m (Fig. 4b), although the kinetics of crossflow filtration on the membranes for Na-CMC solutions changes from type 1 to type 2 at a q_m of approximately 0.6×10^{-11} $m^3/m^2 \cdot s \cdot Pa$ as well. This result may be explained by the different formation mechanisms of SL and Na-CMC deposits. The linear polymer builds up a pore deposit by

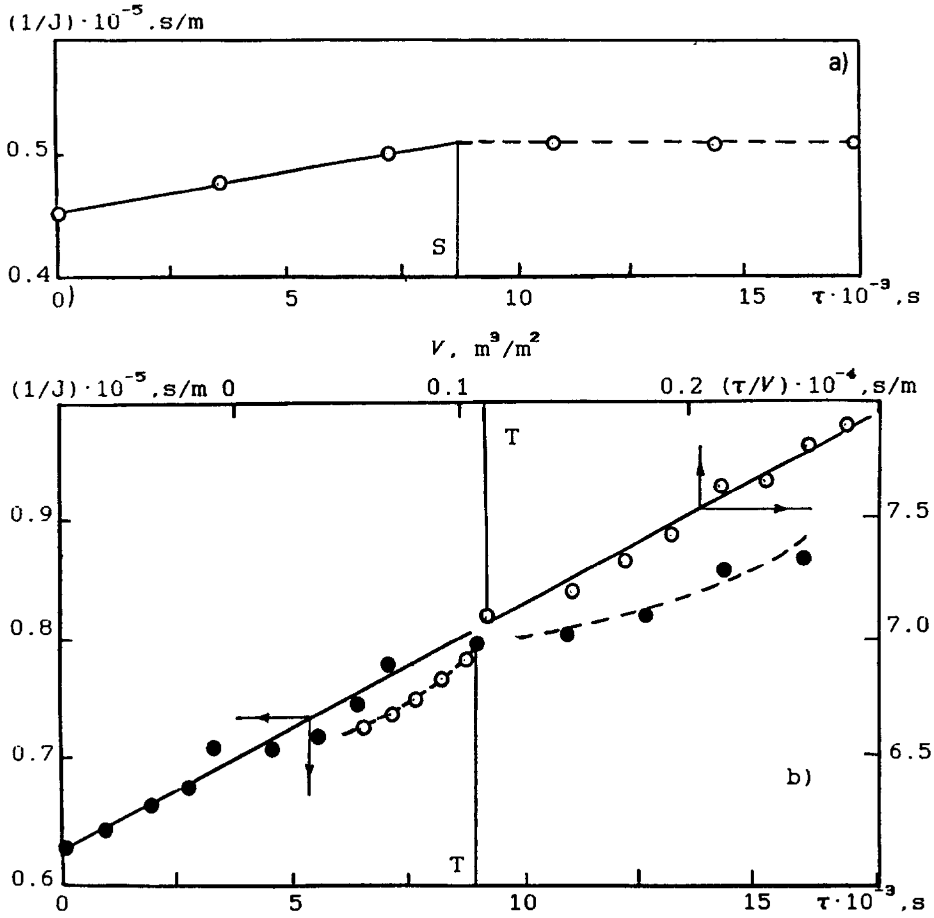

Fig. 3. Examples of membrane filtration kinetics of Na-CMC solutions through UAM-300 (a) and UAM-450 (b) membranes in terms of Eqs. (2) and (4). S —stabilization point in kinetics, T —turning point in kinetics. Conditions: (a) $P = 1$ MPa, $v = 1$ m/s, $C_p = 50$ mg/l, $C_s = 0.01$ M NaCl, pH = 6.5; (b) $P = 1$ MPa, $v = 0.1$ m/s, $C_p = 100$ mg/l, $C_s = 0.01$ M NaCl, pH = 6.

absorbing macromolecules in the membrane pores probably by the model of 'a snake in a pore' and does not allow the formation of a dense deposit in large pores of highly permeable membranes such as compact polymers [5].

Thus, the compact polymer, SL, forms a dynamic layer with the least hydraulic resistance if the membrane filtration kinetics corresponds to J–V linear dependence. Under these conditions the composite 'membrane-immobilized polymer' is characterized by the highest relative water permeability, which is mainly in the range of 0.8–0.9 for various physico-chemical (pH, concentrations) and hydrodynamic (P, v) parameters studied (see Fig. 4a).

The linear polymer, Na-CMC, forms the dynamic layer with small hydraulic resistance onto the membranes characterized by a wider range of initial permeability (i.e. of pore size), when the process kinetics corresponds to both J–V and $1/J - \tau$ linear dependencies. Under these conditions relative water permeability of the membranes with immobilized Na-CMC makes up on average 0.8–0.9 at various operating parameters as well (see Fig. 4b).

Alterations in salt rejection due to the formation of the polymer layers onto the membranes were controlled by Na^+-ion concentration, and salt permeability coefficients before (a_m) and after formation of the polymer layer (a_{mp}) were

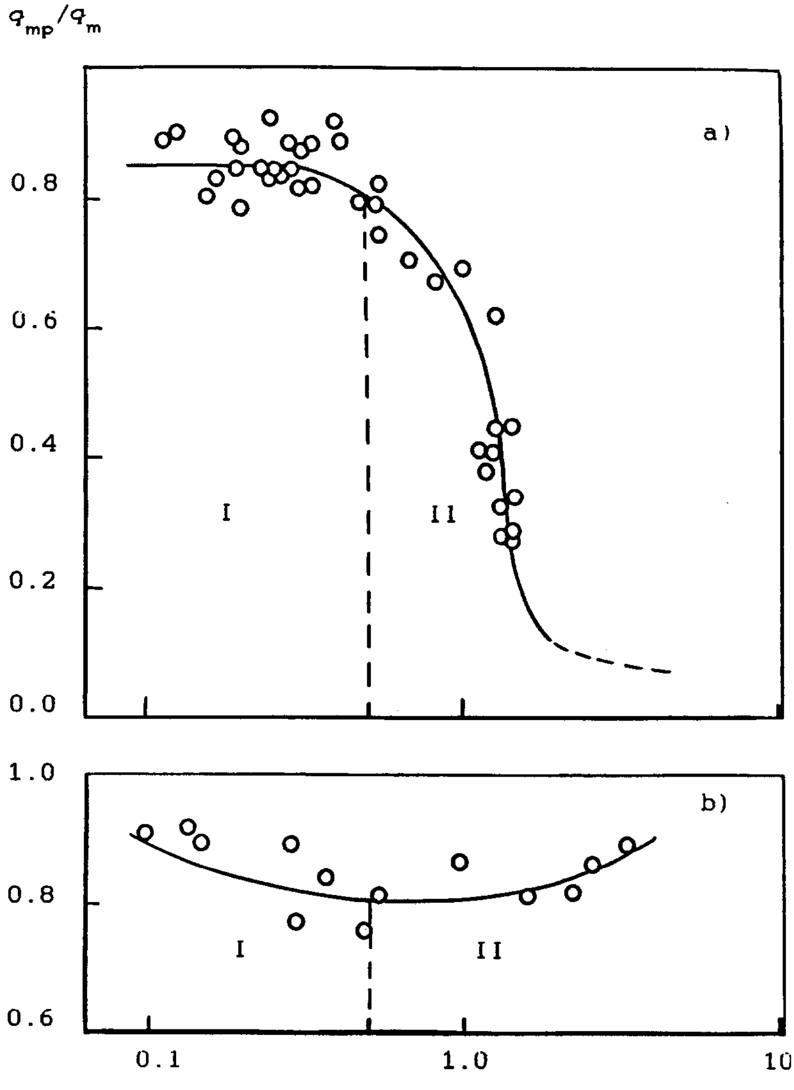

Fig. 4. Relative water permeability of a composite 'membrane-adsorbed polymer' as a function of initial permeability for SL (a) and Na-CMC (b) solutions. Conditions: $C_p = 50$–200 mg/l, $C_s = 0.035$–0.07 M, pH = 6–7.5, $P = 1$–5 MPa, $v = 0.1$–1 m/s. Region I —kinetics of type 1: region II — kinetics of type 2.

compared. Correlations between these characteristics for compact (SL) and linear (Na-CMC) polymers at various parameters are shown in Fig. 5.

The results given in Fig. 4 and Fig. 5 indicate that both SL and Na-CMC are able to form the immobilized layer onto CA membranes, which yields markedly enhanced rejection and, simultaneously, high water permeability, provided that the process kinetics corresponds to the model of 'blocking a pore by a single particle', i.e. as described by Eq. (1). In this case the passage of salt through the composite 'membrane-immobilized polymer' is half the initial one (Fig. 5, region I), and relative water permeability of the composite averages between 0.8 and 0.9 (Fig. 4, region I). If the kinetics of the polymer layer formation corresponds to another pore deposit

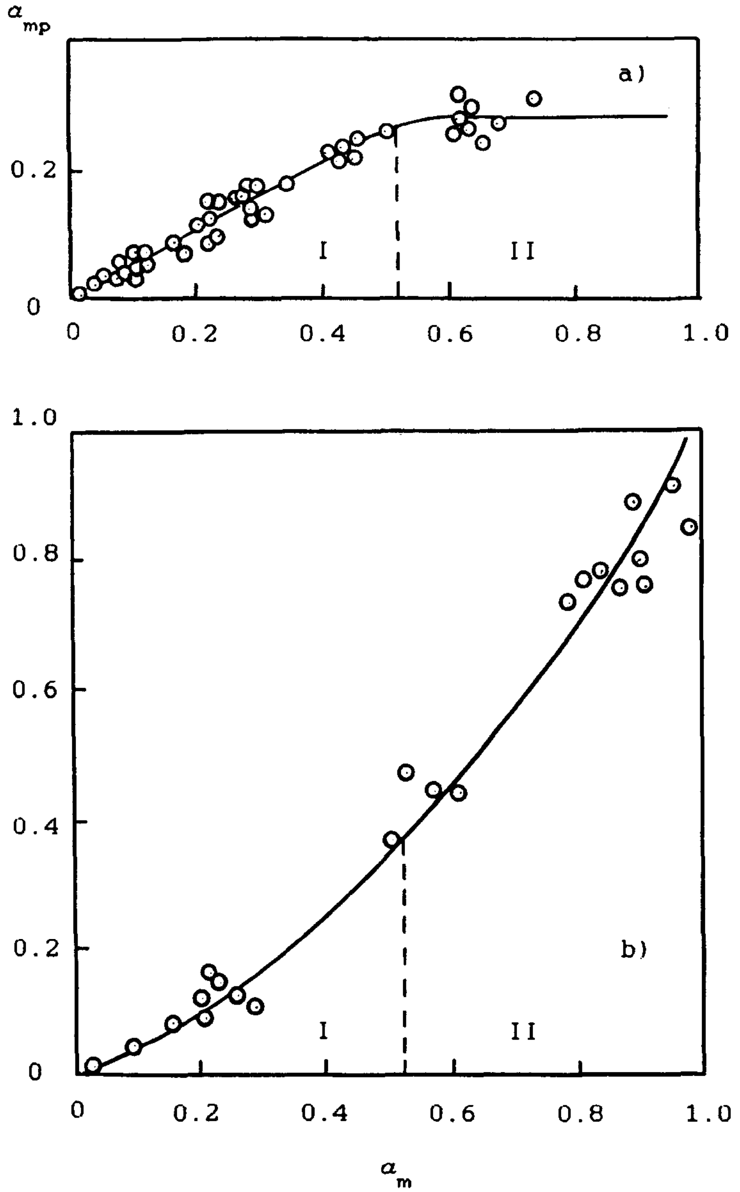

Fig. 5. Salt permeability coefficient of a composite 'membrane-adsorbed polymer' as a function of initial membrane salt permeability coefficient for SL (a) and Na-CMC (b) solutions. Conditions: see Fig.4. Region I — kinetics of type 1; region II —kinetics of type 2.

model, the compact polymer builds up the layer with lower water permeability (see Fig. 4a, region II), and the linear polymer slightly increases rejection (see Fig. 5b, region II). Thus the type of process kinetics is the determining factor in the formation of the reversible layer of the polymers with desirable transport characteristics onto the CA membranes. The other factors are of secondary importance.

5. Conclusion

The results of this work show that the formation of dynamic polymer layers on semipermeable membranes during cross-flow filtration and, consequently, the structure and transport characteristics of the composite 'membrane-immobilized polymer' may be controlled by kinetics of membrane filtration. The models of dead-end filtration theory are useful.

The reversible composite structure that yields high water permeability and salt rejection corresponds to kinetics of type 1, i.e. to J–V linear dependence predicted by the model of 'blocking a pore by a single particle'.

By forming reversible deposits of type 1 from appropriate polymers on regular semipermeable membranes, highly permeable catalytic membranes with accessible active centers and regulated selectivity may be obtained.

6. List of symbols

J	Observed flux, $m^3/m^2 \cdot s$
J_m	Initial membrane flux, $m^3/m^2 \cdot s$
V	Cumulative permeate volume per unit of membrane area, m^3/m^2
τ	Time, s
k_1,k_2,k_3,k_4	Kinetic coefficients characterizing deposit growth rate
P	Pressure, MPa
v	Cross-flow velocity, m/s
q_m	Initial water permeability of a membrane, $m^3/m^2 \cdot s \cdot Pa$
q_{mp}	Water permeability of the membrane with an immobilized polymer layer, $m^3/m^2 \cdot s \cdot Pa$
R	Salt rejection coefficient
a	Salt permeability coefficient $(=1-R)$
C_p	Polymer concentration, g/l
C_s	Salt concentration, mol/l

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