

Since we lack a priori information on the values of averaged parameters characterizing the micrononuniformity of the porous medium a and ℓ , even the calculations with Eq. (14) are very approximate. Nevertheless, by varying the parameters of the model within the broadest possible range for actual conditions, we come to the conclusion that for low-permeability inclusions with the above-indicated characteristics, the time of propagation of a recondensation wave may be considerably shorter than the duration of capillary impregnation.

The present investigation is the first stage of a larger study of the mechanism of mass transfer in a porous medium. Several questions pertinent to the study went unanswered. For example, it is still unclear how the period of recondensation in a single unit T_{cp} relates to the duration of the condensation process. These and other unanswered questions will be the subject of a future investigation.

NOTATION

v , rate of convective motion; L , characteristic size of zone in which the main change in the potential of the motive force for mass flow takes place; r , pore radius; μ , dynamic viscosity; Δp , characteristic pressure gradient; c , vapor concentration based on the concentration at the stationary meniscus; τ , time; ℓ , length of the constant-radius section of a capillary of variable cross section; D , coefficient of molecular diffusion; t , dimensionless time; x , linear coordinate made dimensionless with respect to the length ℓ ; T , dimensionless characteristic time of mass-transfer processes; χ , relative partial pressure of saturated vapor; β , ratio of the density of the liquid condensate to the partial density of the vapor at its critical concentration in the narrow pore.

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EFFECT OF TEMPERATURE ON RHEOLOGICAL CHARACTERISTICS OF WATER SOLUBLE POLYMER COMPLEXES

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Results are presented from a study of the effect of temperature on rheological characteristics of aqueous solutions of polymers and polycomplexes based thereon.

The rheological characteristics of water-soluble polymer materials depend significantly on temperature, which to a great extent controls the effectiveness of their use in various technological processes [1, 2]. This is related to change in the molecular characteristics of individual polymers [3]. Still more complex and practically unstudied is the behavior of polyelectrolyte complexes (PEC's), despite their primary significance in living nature and their ever wider employment in technology.

The dimensions of macromolecular complexes in a solution are determined not only by entropy factors, but also by polymer-solvent and polymer-polymer energy interactions [4]. Supramolecular formations in dilute polymer solutions have various densities and degrees of organization dependent on their chemical nature. Change in temperature and the changes pro-

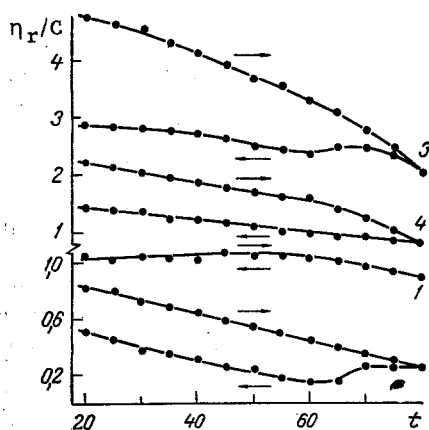


Fig. 1

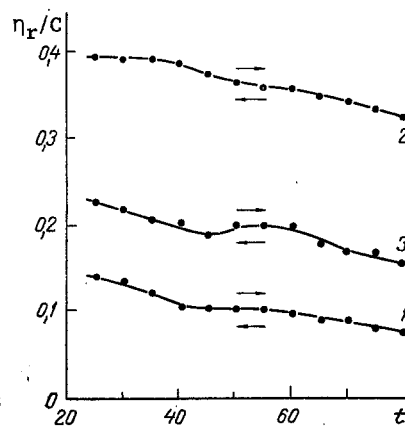


Fig. 2

Fig. 1. Reduce viscosity η_r/C vs. temperature for SPS (curve 1), ASM (curve 2), freshly prepared ASM polycomplex solution CMA:SPS = 3:7 (3) and same solution after repetitive thermal processing for 72 hr (4).

Fig. 2. Reduced viscosity η_r/C vs. temperature for solutions of PVPD (curve 1), PEI (curve 2), and PVPD:PEI = 1:1 polycomplex (curve 3).

duced in molecular characteristics of polymers in solution thereby have an especially well expressed effect on viscosity of dilute solutions [5].

The materials chosen for study were ionogenic polymers: sodium salts of sulfopolystyrol (PSP), with molecular mass equal to $1.8 \cdot 10^4$, and sulfodextran (SD), molecular mass = $5 \cdot 10^5$, amidized styrol copolymer with maleic acid (ASM), molecular mass = $3.0 \cdot 10^5$, a statistical copolymer of acrylic acid with polypropionbetane (CACPB), molecular mass = $5.0 \cdot 10^5$, polyethylenes (PEI), molecular mass = $7.4 \cdot 10^4$, nonionogenic polyvinylpyrrolidone, molecular mass = $1.2 \cdot 10^4$, and polycomplexes based on these compounds.

The viscosity of the solution studied was measured in an Ostwald capillary viscosimeter with capillary diameter 0.56 mm: solvent (distilled water) escape time at 25°C was 95.4 sec. The solutions were temperature stabilized for 15 min.

The hydrodynamic studies were performed in a capillary rheometer developed at Kiev State University for study of hydrodynamic parameters of the flow of dilute polymer solutions in narrow tubes in the Reynolds number range $5 \cdot 10^2 - 5 \cdot 10^4$, calculated for water at 20°C, with maximum pressure head of 3.5 atm: measurement cell volume was 55 cm³.

The effect of temperature on hydrodynamic activity was studied over the range 20-80°C. Measurements were performed in the following manner: a series of solutions was prepared, each of which was heated to a specific temperature under static conditions, and the reduction in friction of each solution was measured in a thermally stabilized cell. To obtain the dependence $\Delta\lambda/\lambda = f(t)$ upon cooling each of the solutions studied was heated to a temperature of 80°C and cooled to a specified temperature under static conditions, whereupon the hydrodynamic resistance reduction was measured.

In studying the temperature dependence of relative viscosity η_r/C of the SPS polyelectrolyte in the range 20-80°C it was established that with increase in temperature η_r/C decreases somewhat, with the dependence obtained being completely reversible (Fig. 1, curve 1). The insignificant monotonic fall in viscosity and the reversibility of the process indicate the stability of the SPS macromolecule conformations in water solution.

Upon heating of the CMA polyampholyte solution values of η_r/C decreased (Fig. 1, curve 2), the process not being reversible, with the final reduced viscosity value being lower than the initial one. The observed hysteresis can be explained as the effect of temperature increase on mobility of segments within the compact CMA macromolecules in the solution, which leads to the possibility of better orientation relative to each other and formation of a denser intermolecular packing [6].

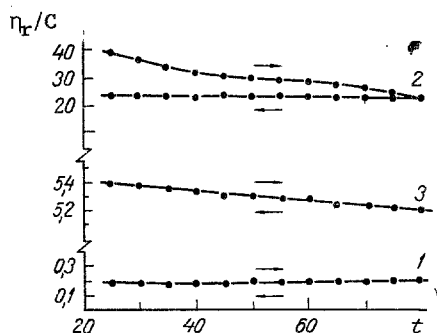


Fig. 3

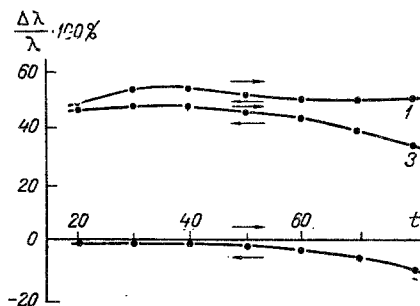


Fig. 4

Fig. 3. Reduced viscosity η_r/C vs. temperature of SAKPB (curve 1), SD (curve 2), and polycomplex SAKPB:SD = 6:4 (curve 3).

Fig. 4. Effect of temperature on hydrodynamic activity of 0.025% solutions of SAKPB (curve 1), SD (curve 2), and polycomplex SAKPB:SD = 6:4 (curve 3) for shear stress $\tau = 2.27 \cdot 10^2$ N/m.

In Fig. 1 curve 3 shows the temperature dependence of reduced viscosity of a ASM-SPS polyelectrolyte complex (PEC) with component ratio of 3:7, where maximum output of the polycomplex with a loose structure is observed [7]. Heating has a greater effect on the freshly prepared complex, as shown in the significant difference in the values of the initial and final reduced viscosity. Apparently the process of rapid interaction between components due to electrostatic forces leads to a distortion of the conformation of the polycomplex macromolecules. Upon heating a gradual ordering of the internal structure of the polycomplex into more stable conformations occurs, strengthening of which is also achieved by secondary binding forces, for example, hydrophobic interactions [3].

The readjustment of the internal structure of the ASM-SPS polyelectrolyte complex during initial thermal processing is not final. Upon repeated heating of the PEC further ordering occurs and a hysteresis loop is observed again, although the difference between initial and final η_r/C values in this case is three times as small (Fig. 1, curve 4). A similar pattern is observed for the isomolar ASM-SPS series as a whole, which indicates the generality of the processes occurring with temperature change in polycomplexes of the given type.

For reversible dissociating polycomplexes formed primarily due to hydrogen bonds hysteresis phenomena are not characteristic. Using the example of a PVPD-PEI system we have shown that polymer compositions are quite sensitive to temperature change (Fig. 2). For a solution of individual PVPD there is a sharp decrease in viscosity (Fig. 2, curve 1), which is apparently related to transition of the PVPD macromolecules into a more compact state due to hydrophobic interaction [3]. Near the hydrophobic lateral hydrocarbon radicals the water has a high entropy structure possessing a higher free energy [3].

Due to the stabilizing action of the hydrophobic portions of the PVPD macromolecules their disruption of water structure occurs less intensely than in the volume of the solution, as a result of which upon increase in temperature from 45 to 65°C conditions are created for manifestation of hydrophobic interactions. The latter prove to have a stabilizing action on the structure of the PVPD macromolecules, and the drop in viscosity is retarded. At temperatures above 65°C disruption of the hydrophobic bonds occurs because of thermal motion.

Water solutions of PEI behave differently (Fig. 2, curve 2). In the interval 25-40°C the reduced viscosity of a water solution of PEI changes weakly. Obviously the stabilizing action of hydrogen bonds formed in the solution between individual PEI macromolecules has an effect. Upon heating above 40°C, due to destruction of the physical lattice created by hydrogen bonds and as a consequence of disruption of the cluster structure of the water, an attenuation of the hydrogen bonds occurs, which manifests itself in a reduction of viscosity [8].

As for the PVPD-PEI polycomplex, increase in temperature to 45°C leads to a drop in viscosity. The latter is apparently related to disaggregation of polycomplex particles. In the interval 45-60°C there is an insignificant increase in viscosity which we relate to crumbling of complex particles due to breaking of a portion of the hydrogen bonds participating in polycomplex to 80°C thermal destruction of the hydrogen bonds occurs and the viscosity falls again.

Our position on crumbling of PVPD-PEO polycomplex particles due to breaking of a portion of the hydrogen bonds is supported by data obtained by the turbidity spectrum method. The polycomplex particles have their maximum size (of the order of 100 nm) at a temperature of 55°C, and upon further thermal processing the particle size decreases by a factor of several times. A similar pattern is observed upon introduction of urea into the system, which compound destroys hydrogen bonds chemically and thus crumbles and then destroys (depending on the quantity of additive) the polycomplex particles.

In studying the effect of temperature on the complex SAKPB-SD, formed due to salt bonds and stabilized by hydrophobic interactions, it was established that hysteresis is absent, and the decrease in reduced viscosity with increase in temperature is quite insignificant (Fig. 3, curve 1).

It is obvious that the polyelectrolyte complex SAKPB:SD exists in solution in the form of rigid supramolecular formations which undergo no readjustment under the action of external factors. The character of the behavior of the individual components forming the polycomplex is different under the same conditions. The monotonic and reversible change of η_r/C with t for SAKPB solutions (Fig. 3, curve 3) indicates the stability of its macromolecular structure. Meanwhile SD solutions show hysteresis (Fig. 3, curve 2). When temperature acts on SD solutions compacting of the SD macromolecules occurs due to increasing segmental mobility and the viscosity of sulfodextran solutions falls.

Thus, in various temperature regimes the rheological characteristics of polymers are determined by their chemical nature. Polymer systems formed by hydrogen bonds have a labile structure subject to readjustment under the influence of external factors. Polyelectrolyte complexes additionally stabilized by hydrophobic interactions are more stable with respect to temperature.

The varying behavior of polymer materials with temperature change must be considered when they are used under shear stress conditions.

The effect of temperature on hydrodynamic activity of a polymer additive was studied using the system SAKPB-SD at a shear stress $\tau = 2.27 \cdot 10^2 \text{ N/m}^2$ and optimal concentration $C = 0.025\%$, most sensitive to temperature change [9].

The SAKPB solution shows the ability to reduce friction resistance of a medium and maintain high hydrodynamic activity over the entire temperature interval studied (Fig. 4, curve 1). The compound SD itself is hydrodynamically inactive to 40°C, while with further temperature increase there is a negative effect - the friction resistance of the solution increases somewhat (Fig. 4, curve 2). The varying properties of polyelectrolytes are apparently related to unique features of the conformation state of their macromolecules in the hydrodynamic field.

The polycomplex SAKPB-SD also shows hydrodynamic activity, while with increase in temperature up to 40°C there is no decrease in the friction reduction effect (Fig. 4, curve 3). Further heating of solutions leads to degradation of hydrodynamic characteristics of the given polymer composition, which is apparently related to an increase in hydrophobic interactions and corresponding formation of rigid supramolecular formations in the polycomplex solution, which are not capable of effectively interacting with microvortices of the turbulent flow. It should be noted that in all the cases considered the dependence of hydrodynamic resistance reduction on temperature is completely reversible.

Comparing the data obtained on viscosity with results of studies in the shear regime, we conclude that under the experimental conditions the structure of the macromolecules studied and their polycomplexes in water solution change not only due to temperature. Under the action of shear stress at high temperatures additional readjustment of structures relaxing over time occurs, while ordered polymer systems stabilized by hydrophobic interactions do not undergo marked changes in macromolecule conformation in solution.

NOTATION

η_r/C , reduced viscosity; t , temperature, °C; $\Delta\lambda/\lambda$ hydrodynamic resistance reduction, %; τ , shear stress, N/m^2 .

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CONTROL OF GAS GENERATION USING A GAS-REGULATED HEAT PIPE

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The authors have performed an experimental and numerical investigation of the temperature field along the wall of a heat pipe, to provide a data base for the operation of gas generation control sensors for a gas-regulated heat pipe.

To solve some problems in material behavior it is important to know gas generation processes in a field of nuclear radiation. The specific conditions of operation of nuclear reactors (high temperature, corrosive medium, radiation, etc) limit the choice of the method of measuring gas generation inside the active zone in the immediate vicinity of the take-off points [1].

A method of control of gas generation was proposed in [2, 3], using a gas-regulated heat pipe (GRHP). The noncondensable fission products are stored in a gas reservoir, increasing the gas pressure, the result being displacement of the vapor-gas front and variation of the vapor temperature. Consequently, by varying the wall temperature of the GRHP in the transport zone we can evaluate the amount of gas in the reservoir.

However, to have a measured basis for operation of gas generation sensors using the GRHP we need to describe the temperature field along the GRHP mathematically as a function of the amount of noncondensable gas and the heater power.

Considering the internal space of the heat pipe as a channel through which there is isothermal mass transfer, and postulating the existence of an ideal vapor-gas boundary, we can describe the temperature field along the GRHP wall by a one-dimensional mathematical model, accounting for heat transfer at the wall and the location of the vapor-gas boundary.

We restrict ourselves to the case of low heat flux, when the vapor-gas boundary is located in the transport zone. Then the temperature distribution along the wall is described by the following system of equations:

$$\lambda\delta \frac{d^2T_w}{dx^2} = -q + \alpha_{c_v}(T_w - T_v), \quad 0 < x < L_1; \quad (1)$$

$$\lambda\delta \frac{d^2T_w}{dx^2} = \alpha_{c_v}(T_w - T_v) + \varepsilon\sigma(T_w^4 - T_{med}^4), \quad L_1 < x < L_1 + l; \quad (2)$$

$$\lambda\delta \frac{d^2T_w}{dx^2} = \varepsilon\sigma(T_{med}^4 - T_{med}^4), \quad L_1 + l < x < L_1 + L_2, \quad (3)$$

$$\lambda\delta \frac{d^2T_w}{dx^2} = \alpha_{c_\ell}(T_w - T_\ell), \quad L_1 + L_2 < x < L_1 + L_2 + L_3, \quad (4)$$