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# Friction coefficient in gelatin and polyacrylamide gels

**Yu. B. Mel'nichenko, V. V. Klepko, T. A. Lobko, and V. V. Shilov***

The Institute of Macromolecular Chemistry, Academy of Sciences, Ukrainian SSR, SU-252160 Kiev, USSR

## Summary

The slow neutron transmission technique is used to measure the friction coefficient f of gel macromolecules moving against a solvent. It is shown that in the range of concentrations C = 3 - 30 %, f of gelatin gels is linearly dependent on C. The values of the monomer friction coefficient of gelatin and the friction coefficient at infinite dilution are determined. It is demonstrated that the friction coefficient of polyacrylamide gels varies as the viscosity of a solvent in a wide temperature range, however at temperatures below ~ 25°C the deviation from proportionality is observed.

## Introduction

The rate at which polymer gels absorb or expel a solvent is governed by the collective diffusion coefficient $D_c$ which varies with the concentration of a polymer in the gel. The coefficient $D_c$ is related to the frictional resistance of the polymer moving against the solvent (or vice versa):

$$D_c = M_{os}/f, \tag{1}$$

where $M_{os}$ is the longitudinal osmotic modulus; f is the total friction of a polymer against a solvent per unit volume. The latter may be described as

$$f = \frac{\xi N_A C}{M}, \tag{2}$$

where $\xi$ is the frictional resistance (force per unit volume) per a monomer unit; $N_A$ is the Avogadro number; C is the concentration of a polymer in g/cm$^3$; M is the molecular weight of a monomer.

Recently, it has been shown that the Flory description of the free energy of the gel (1) provides a valid description of $M_{os}(C)$, and to define $D_c$ in Eq. (1), it is necessary to know only the concentration dependence of the friction coefficient f (2). However, the data on the function f(C) in different systems are scarce which is associated with the problem of a direct experimental measurement of the friction coefficient. Therefore, to interpret swelling experiments, various trial forms for f(C) are usually used.

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*To whom offprint requests should be sent

The object of the present work is to demonstrate the scope of applying the slow neutron transmission technique to macroscopic measurements of the friction coefficient in various polymer gels and to investigate its concentration and temperature dependences in gelatin and polyacrylamide (PAA) hydrogels.

## Experimental

The friction coefficient can be determined by fixing the polymer network and measuring the solvent flow rate through it for a given pressure applied to the liquid alone. To determine f, a special cell was designed (Fig. 1). From the examination of Fig. 1 we obtain

$$f = \frac{\rho g H S}{h\dot{V}}, \qquad (3)$$

where $\rho$ is the solvent density; g is the acceleration of gravity; H is the height of the solvent column above the reservoir level; h and S are the length and cross-sectional area of the gel, respectively; $\dot{V}$ is the volume flow rate.

The value of $\dot{V}$ in Eq. (3) can be determined by the slow neutron transmission technique from the variation of neutron transmission of the reservoir as a function of time. The transmission is inversely proportional to the concentration of a protonated solvent which flows through the gel to the reservoir filled with its deuterated analogue. And as is shown in (3)

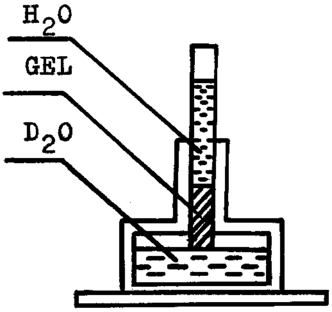

Fig. 1. Cell for friction coefficient measurements. A solvent flows through a fixed polymer network. The neutron beam is incident on the reservoir perpendicularly to the figure plane

$$\dot{V} = \frac{m}{t} \cdot \frac{G \ln\left[P(t)/P_0\right]}{1 - G\ln\left[P(t)/P_0\right]} \equiv \frac{K}{t}, \qquad (4)$$

where m is an initial weight of the deuterated solvent in the reservoir; t is the time; $P = I/I_0$ is the neutron transmission ($I$, $I_0$ are the intensities of the incident and transmitted neutron beams); G, $P_0$ are the experimental constants determined by calibration measurements.

In this work we investigated the friction coefficient in gelatin and PAA hydrogels. For the gels $H_2O$ was used as a solvent, and the reservoir was filled with $D_2O$. Due to a considerable difference of bulk neutron cross-sections of hydrogen and deuterium, an absolute error of $H_2O$ concentration measurements did not exceed $\Delta C = 3.6\times10^{-4}$ for a 1-cm inside thickness of the reservoir and an exposure time of 5 min. A schematic arrangement of the experimental unit and a procedure are described in (4). A two-stage thermostatting system enabled the temperature of the cell to be controlled within several mK. The temperature gradient along the cell height was checked by a 16-junction copper-constantan thermocouple and did not exceed $10^{-2}$ K. The values of the parameters in Eq. (3) were $H = 20$ cm; $S = 1.77$ cm$^2$; $h = 1.5$ cm.

To prepare gels, gelatin of a photographic grade was used. The viscosity of a 10% solution in water at 40°C was $2\times10^{-2}$N m$^{-2}$s, its isoelectric point was 4.7, pH of aqueous solutions was 6.2. The "dry" gelatin was first swollen in an appropriate amount of water (taking into account that the gelatin itself contained 11 % residual water) for 2 h. Then the mixture was warmed up to 45 °C and stirred thoroughly until dissolution was complete. The gelatin concentration C in g/cm$^3$ was calculated by assuming the additivity of gelatin and solvent volumes, taking the gelatin density as 1.465 g/cm$^3$. The solution was poured into a glass tube and quenched to 16 °C at which the gel aged for 12 h. Such quenching temperature and ageing time provided the realization and completion of the initial gelation stage when the amount of renaturated helices grows rapidly (5). The next gelation stage is much slower, thus the gels can be treated as quasi-equilibrium systems during the time of investigation which did not exceed several hours.

PAA gels were prepared from Reanal premixed reagents using a standard procedure (6). Acrylamide (0.25 or 0.5 g), the linear constituent; N,N'-methylene-bis-acrylamide (0.0133 g), the tetrafunctional crosslinking constituent; ammonium persulfate (4 mg), the initiator, and tetra-methylethylene diamine (TEMED) (16 $\mu$l), the accelerator were dissolved in distilled, degassed water at 25 °C to a final volume of 10 ml to get 2.5 % and 5 % solutions, respectively. The solutions were then transferred to glass tubes where gelation occurred within five minutes. The gels were left in the tubes for an hour, then placed in a large amount of distilled water to wash away residual acrylamide, bis-acrylamide, ammonium persulfate and TEMED.

## Results and Discussion

The kinetic functions of K(Eq.(4)) for several investigated gels at 16 °C are given in Fig. 2. The initial portions of these curves correspond to the unsteady flow. The moment $t = 0$ corresponds to the moment at which $H_2O$ was poured to the gel-containing tube. After attaining the steady flow, the function K(t) becomes linear. Several special measurements have demonstrated that the dependence remains linear for several days. The slope of the linear portions is the $H_2O$ volume flow rate $\dot{V}$ which was determined by a least squares fit. Similar plots were obtained for PAA gels at different temperatures.

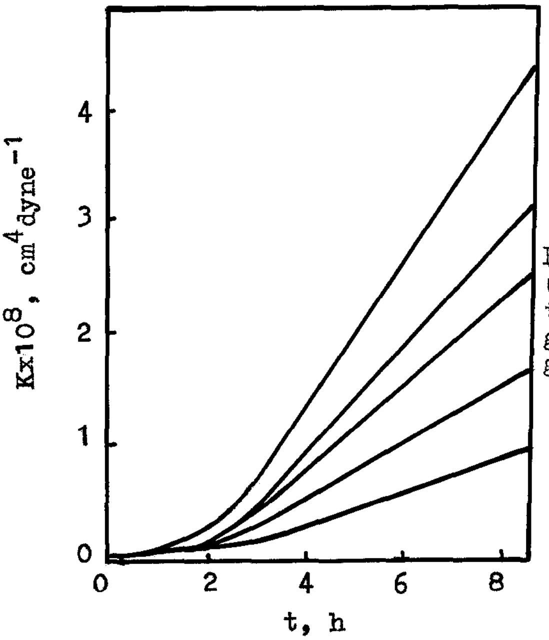

Fig.2. The variation of K (Eq. (4) ) as a function of time for gelatin gels at gelation concentrations, $g/cm^3$;

1-0.0269; 2-0.0543; 3-0.1153; 4-0.1394; 5-0.2917.

The plot of the friction coefficient calculated by Eq.3 for known $\bar{V}$ as a function of concentration is given in Fig.3. As can be seen in this figure, within experimental errors, f is linearly dependent on C over the whole range of concentrations. The solid line in the figure is described as

$$f = f(0) + \frac{\xi N_A C}{M}, \qquad (5)$$

with the parameters $f(0) = 2x10^8$ dyne s $cm^{-4}$, $\xi = 6.5x10^{-13}$ dyne s $cm^{-1}$. The value of the monomer friction coefficient of gelatin was calculated from the average of amino acids taken M = 100 (7). The parameter f(0) may be treated as the friction coefficient at infinite dilution.

The plot of f against temperature for PAA gels is given in Fig. 4. Taken f to be directly proportional to the viscosity of pure water (8), we thus can compute the variation of f with temperature from its value at 55 °C:

$$f(T) = f(55\ °C) \cdot \frac{\eta(T)}{\eta(55\ °C)}, \qquad (6)$$

where $\eta(T)$ is the viscosity of water. As can be seen in the figure, the experimental results for f(T) agree qualitatively with the above assumption over a rather wide temperature range. However, the data do significantly depart from the calculations as the temperature falls below ~ 25 °C. This suggests that f in general is not strictly proportional to the viscosity of a pure solvent.

From the above we see that the slow neutron transmis-

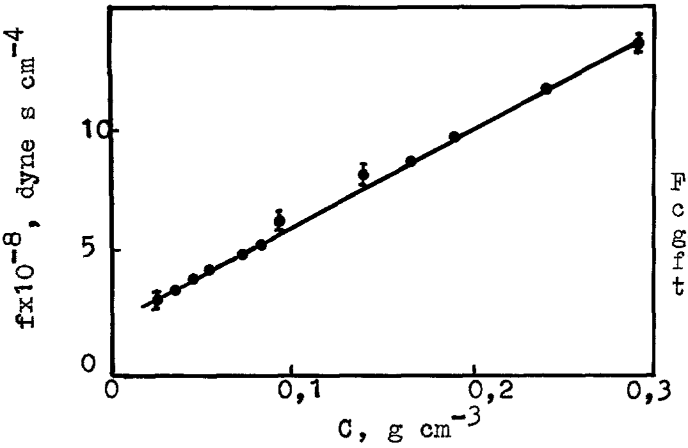

Fig.3. Friction coefficient in gelatin gels as a function of gelatin concentration.

T = 16 °C

sion technique can be used to provide detailed and accurate measurements of the friction coefficient in various polymer gels.

Within experimental errors, the function f(C) for gelatin gels appeared to be linear over a wide range of polymer concentrations. The values of the monomer friction coefficient $\xi$ of gelatin and the friction coefficient f(0) at infinite dilution were found. The temperature dependence of f for PAA gels is determined by that of the water viscosity over a rather wide temperature range. At present the

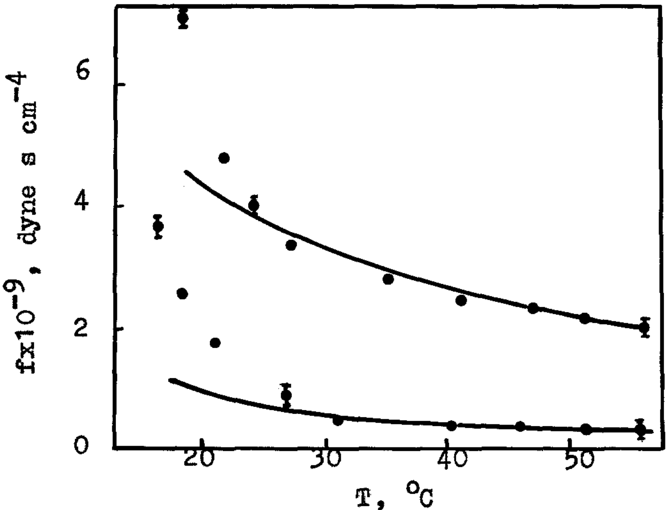

Fig.4. Friction coefficient in PAA gels as a function of temperature.

reasons for the discrepancy between the theory and experimental data observed at lower temperatures are not clear. One of the plausible explanations of the observed effect is anomalous growth of the solvent viscosity due to the cooperative behaviour displayed by water molecules with decreasing temperature (9).

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