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Surface Friction of Polyelectrolyte Gels

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Summary: The friction between two chemically cross-linked polyelectrolyte gels carrying the same sign of charges has been investigated in pure water as well as in salt solutions using a rheometer. It is found that the friction was largely dependent on the charge densities of the gel surface and the ionic strength of the aqueous solution. The chemical structures of the polyelectrolyte gels also play an important role. The friction is described in terms of the hydrodynamic lubrication of the solvent layer between the two gel surfaces, which is formed due to the electrostatic repulsion of the two gel surfaces. The thickness of the solvent layer has been estimated using the Poisson-Boltzmann equation supposing that the ionic osmotic pressure is balanced by the normal pressure applied on the gel. The friction values have been calculated by considering the shear flow of solvent in gel region using the Debye-Binkman equation. For strongly charged polyelectrolyte gels swollen in pure water, the theoretical analysis shows that the friction coefficient almost has no dependence on the water content of the gel, which well agrees with the experimental observations.

Keywords: electrostatic interaction; friction; gel; polyelectrolyte

1. Introduction

In earlier papers[1-5], the sliding friction of various kinds of hydrogels has been studied and it was found that the frictional behaviors of the hydrogels do not conform to Amontons' law $F = \mu W$, which commonly describes the friction of solids. The frictional force and its dependence on the load are quite different depending on the chemical structures of the gels, surface properties of the opposing substrates, and the measurement condition. The gel friction is explained in terms of interfacial interaction, either attractive or repulsive, between the polymer chain and the solid surface. According to this model, friction is ascribed to the viscous flow of solvent at the interface in the repulsive case. In the attractive case, the force to detach the adsorbing chain from the substrate appears as friction. Surface adhesion between glass particles and gels measured by AFM showed a good correlation with the friction, which supports the repulsion-adsorption model proposed by authors.

According to the above consideration, low friction can be realized when two repulsive surfaces slide against each other, since under this condition, it is favorable for low molecular weight solvent to exist between the interface gap and to serve as a lubricating layer. Therefore, the stronger the repulsion between the two surfaces and the more solvent that exists at the interface, the lower the friction. In order to obtain a thicker solvent layer, which

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leads to lower friction, surfaces with strong electrostatic repulsion are expected to be effective. In this paper, the effect of electrostatic repulsion on friction has been investigated experimentally and theoretically. The theoretical values are compared with the experimental observations, and the essential feature of the mechanism proposed is confirmed.

2. Experimental Results

The effect of interface interaction on the gel friction can be very clearly observed from the frictional behavior between two gels carrying charges. When two polyelectrolyte gels carrying opposite charges, for example, PAMPS gel and PDMAPAA-Q gel, were slid over each other, the adhesion between the two gel surface was so high that the gels were broken in the measurement. The strong adhesion should apparently be attributed to the electrostatic attraction between the polyanions and polycations of the gels.

On the other hand, the friction between two polyelectrolyte gels carrying the same sign of charges was extremely low. Fig.1 shows the network charge density dependence of the friction for two pieces of PAMPS gels undergoing relative rotation. Modulation of charge density of the gel has been made by varying the amount of cross-linking agent in the

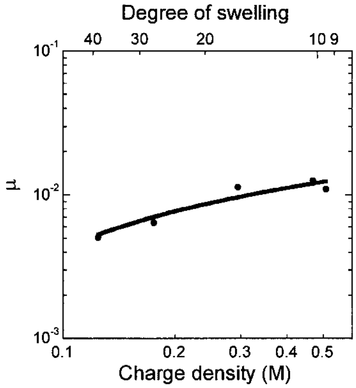

Figure 1. Charge density and degree of swelling dependencies of friction coefficient between two PAMPS gels in water. Sample radius R=7.5mm; angular velocity $\omega = 0.05 rad/s$. Initial normal force W=3N.

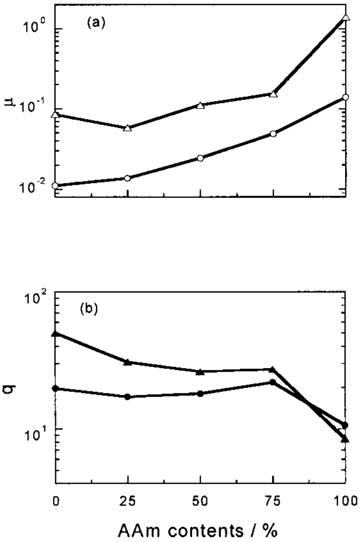

Figure 2. Dependencies of the friction coefficient (open symbols) and the degree of swelling (solid symbols) on the copolymer composition. The frictions are the values between poly(AAm-co-NaAMPS) gel and PNaAMPS gel (○,●) or poly(AAm-co-DMAPAA-Q) gel and PDMAPAA-Q gel (□,▲) in water. Sample radius R=7.5mm; angular velocity $\omega = 0.01 rad/s$. Initial normal force W=3N.

process of gel synthesis, which gives rise to gels of different swelling ability. Since the polyelectrolyte gels used in this work fully dissociate in water, carrying one charge for each monomer unit, the charge density, c, (in units of mol/L) equals the polymer network concentration. Therefore, $c = 1000 / qM_w$, where Mw is the formula molecular weight of the monomer. As shown in Fig.1, the friction increases modestly with the increase in charge density. That is, the frictional force does not sensitively change with the degree of swelling. Two opposite effects on the frictional force can be considered by examining the increase in charge density: One is the enhanced repulsion between the two gel surfaces, which favors the formation of a thicker solvent layer between the surfaces and decreases the viscous friction. The other is the increased network density, which increases the hydrodynamic resistance of the water in the polymer network and leads to an increase in the frictional force of the gel. Higher water content would lead to a small friction force since the fraction of polymer network which is non-flow decreases with an increase in the water content. Therefore, a higher charge density would bring a thicker liquid layer, which leads to a lower friction but gives rise to an increase of non-flow network density, which increases the friction. These two opposite effects on the friction explain why the friction is not sensitive to the network charge density.

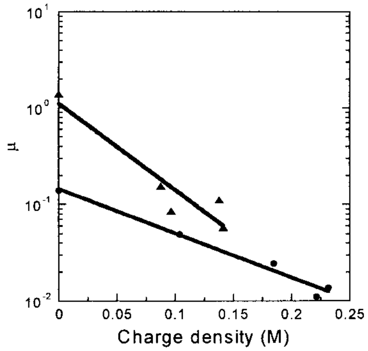

Figure 3. Relationship between the friction coefficient and the gel charge concentration calculated from Fig.2. (●) poly(AAm-co-NaAMPS) gels; (▲) poly(AAm-co-DMAPAA-Q) gels.

The effect of charge density was also studied by sliding copolymer gels containing different numbers of ionic monomers on homopolymer gels. Fig.2 shows the friction force when poly(AAm-co-NaAMPS) gels with various composition were allowed to slide on a

PNaAMPS gel. The friction between two homopolyelectrolyte gels of PNaAMPS showed the lowest values. With an increase of AAm composition, i.e., a decrease of negative charge density, the friction increases and PAAm homopolymer gel showed the highest friction. Similar results were obtained if the poly(AAm-co-DMAPAA-Q) gels were allowed to slide on the PDMAPAA-Q gel. Taking into account the change in the swelling ratio brought on by changing the copolymer composition, the charge density of the gel was calculated and the relation between the friction coefficient and the charge density of the copolymer gels is plotted as shown in Fig.3. The figure clearly shows that the coefficient of friction decreases with an increase in the charge density. So far, we can not explain why the poly(AAm-co-DMAPAA-Q) gel on PDMAPAA-Q gel shows a higher friction than the poly(AAm-co-NaAMPS) gel on PNaAMPS gel. It could be related to the stronger interaction between AAm and DMAPAA-Q.

3. Theoretical Analysis

According to the repulsion-adsorption model, the low friction between two polyelectrolyte gels carrying the same charge is a hydrodynamic mechanism, in which the strong electrostatic repulsion plays an important role in forming a solvent layer between the two gel surfaces. Here we estimate the thickness of the solvent layer under a certain load. When the load is not very high, the electrostatic repulsion prevails and the van der Waals interaction between the two surfaces can be neglected. Supposing that the polyions are homogeneously distributed in the bulk gel as well as on the gel surface, we have an average surface charge density. For a homopolymer gel carrying one charge for each monomer unit, the number surface charge density, σ (in units of m^{-2}), is

$$\sigma = (1000cN_A)^{2/3} = (\frac{10^6 N_A}{qM_W})^{2/3} \qquad (1)$$

Here, c is the bulk charge density of the gel or the monomeric concentration (in units of mol/L) and N_A is the Avogadro's number.

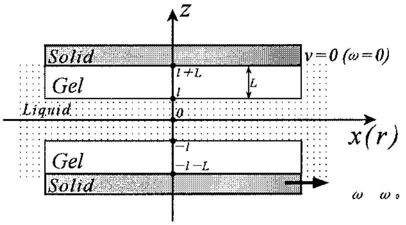

Figure 4. The geometry of two polyelectrolyte gel surfaces of the same kind approaching with each other in water. Due to the electrostatic repulsion, a water layer $2l$ in thickness is formed under a normal pressure P. One of the gels is doing translation motion in a velocity of v_0.

We denote the solvent layer thickness between two gel surfaces as $2l$, and the gel sample thickness as L, and we choose the origin of the coordinate system at the middle point between two gel surfaces with the x-axis parallel to and the z-axis vertical to the gel surfaces(Fig.4). Here, $L >> l$. Thus, the electrical potential distribution between the two gel surfaces, $\psi(x)$, given by the Poisson-Boltzmann equation is expressed as

$$\frac{d^2\psi}{dz^2} = -\frac{en_0}{\varepsilon}\exp(-e\psi/kT) \qquad -l < z < l \qquad (2)$$

where ε is the dielectric constant of water, n_0 is the density of counter-ions at a position where $\psi = 0$, e is the charge of an elementary electron, k is the Boltzmann constant, and T is the absolute temperature. For simplicity, we only consider the case of monovalent ions. On the gel surface,

$$(\frac{d\psi}{dz})_{z=\pm l} = \mp\frac{e\sigma}{\varepsilon}, \qquad (3)$$

On the symmetric plane,

$$(\frac{d\psi}{dz})_{z=0} = 0 \qquad (4)$$

From electrical neutrality,

$$\sigma = n_0\int_0^l \exp(-e\psi/kT)dz \qquad (5)$$

By choosing $\psi_{z=0} = 0$, we have

$$e\psi/kT = 2\ln\cos(\sqrt{n_0 r_0/2}z) \qquad (6)$$

where n_0 is a function of the surface number charge density given by

$$\sigma = \sqrt{2n_0/r_0}\tan(l\sqrt{n_0 r_0/2}) \qquad (7)$$

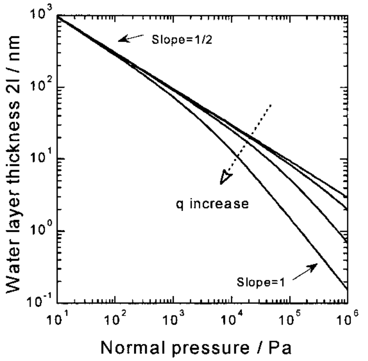

Figure 5. Normal pressure dependence of the solvent layer thickness 2l for charged gels with various degree of swelling. Following the direction of the arrow in the figure, q=1, 100, 1000, 10000. Parameters used in the calculation: $\varepsilon = 78\varepsilon_0$, $T = 300K$, $M_w = 229$ (Mw of NaAMPS).

here $r_0 = e^2/\varepsilon kT$ is a constant with a dimension of length. The repulsive osmotic pressure, Π, between two approaching charged surfaces is determined by the microion charge density at the symmetry plane of z=0, where the electrostatic attraction on the micro-ions is zero since $(\frac{d\psi}{dz})_{z=0} = 0$, so we have

$$\Pi = n_0 kT \qquad (8)$$

In the equilibrium state, this osmotic pressure is counterbalanced by the applied pressure, P, that is, $P = \Pi$. Thus, the solvent layer thickness under a normal pressure P is obtained

$$2l = 2\sqrt{2kT/\mathrm{P}r_0}\arctan(\sigma\sqrt{kTr_0/2P}) \qquad (9)$$

When σ is very small and P is high so that $\sigma\sqrt{kTr_0/2P} << 1$ is satisfied, $\arctan(\sigma\sqrt{kTr_0/2P}) \approx \sigma\sqrt{kTr_0/2P}$. Accordingly, $2l \propto P^{-1}$. This inverse relation between the solvent layer thickness and the pressure agrees with our previous result derived for the repulsive case from the scaling rules. When σ is very large and P is not too high so that $\sigma\sqrt{kTr_0/2P} >> 1$, $\arctan(\sigma\sqrt{kTr_0/2P}) \approx \pi/2$. Accordingly, $2l \propto P^{-1/2}$. This indicates that highly charged surfaces are able to sustain more pressure.

Fig.5 shows the theoretically calculated relations between the solvent layer thickness and the normal pressure P at various degrees of swelling of the gel. At a high surface charge density, which corresponds to a low degree of swelling, the repulsion distance 2l is not sensitive to the pressure when the pressure is not very high. Notice that the experimental investigation in Fig.5 was performed at $q = 10-30$ and $P \approx 10^4\,Pa$. Under these conditions, the solvent layer thickness $2l$ is not sensitive to the gel surface charge density and it has a value of 30nm.

When the two gel surfaces intermediated by a water layer of thickness $2l$ are allowed to undergo relative motion, the shear flow of the water layer exerts shear forces on the two gel surfaces and gives rise to friction. Since the gel consists of an elastic polymer network and viscous water, the latter can flow under the shear stress, and we cannot simply use a non-slippery boundary condition on the two gel surfaces. Instead, the velocity profiles in the gel regions should be taken into consideration. The flow of solvent in a polymer network is successfully expressed by the Debye-Brinkman equation, where the effect of the polymer network is represented by a distributed body force $-\eta v/K_{gel}$ [6]. Here η and $\sqrt{K_{gel}}$ are the viscosity of solvent and the permeability of the gel, respectively. Using the Debye-Brinkman model, the shear stress at the gel surface is

$$f = -\eta\left(\frac{dv}{dz}\right)_{z=\pm l} = \frac{\eta v_0}{2(l+\sqrt{K_{gel}})} \tag{10}$$

This result indicates that the shear flow can penetrate into the gel with a thickness of $\sqrt{K_{gel}}$, or the equivalent non-slippery boundary of a gel surface is located at a depth of $\sqrt{K_{gel}}$ from the gel surface.

Equation 10 indicates that the friction is inversely proportion to $l+\sqrt{K_{gel}}$. $\sqrt{K_{gel}} \cong \xi$ decreases with an increase in the polymer network density. On the other hand, as has been shown, l increases with an increase of the polymer network density. So the dependence of the parameter ξ / l on the degree of swelling as well as on the pressure is very important in determining the friction behavior. When q is not too large, $\xi / l << 1$ and the effect of ξ can be neglected. For very high q, ξ becomes important and should be taken into consideration.

In the case of two gel surfaces rotating, the shear stress on the gel surfaces at a distance r from the axis is

$$f = -\eta r (\frac{d\omega}{dz})_{z=\pm l} = \frac{\eta r \omega_0}{2(l + \sqrt{K_{gel}})} \qquad (11)$$

So the total friction for a disk-shaped gel of radius R is

$$F = \int_0^R 2\pi r f dr = \frac{\pi \eta \omega_0 R^3}{3(l + \sqrt{K_{gel}})} \qquad (12)$$

From the above equation, we know that the friction per unit area is proportional to the angular velocity and the radius of the gel, since the average velocity increases with the radius. The friction coefficient is determined by

$$\mu = \frac{F}{\pi R^2 P} \qquad (13)$$

Fig.6 shows the simulation results for the dependence of friction coefficient on the water content for two like-charged gels undergoing relative rotation at a certain applied pressure. At a wide range of P, the friction is not sensitively dependent on the degree of swelling. This is due to the cancellation of the opposite effects of the degree of swelling on the solvent layer thickness and on the gel permeability, K_{gel}, as discussed previously. Fig.6 explains well why the observed friction in Fig.1 is not sensitively dependent on the degree of swelling.

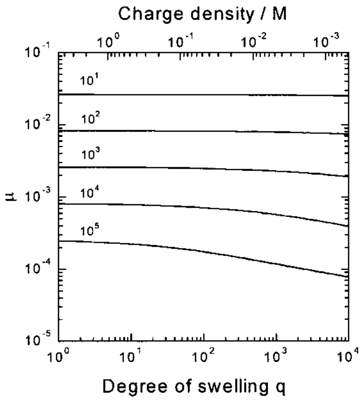

Figure 6. Dependencies of the friction coefficients on the degree of swelling and on the charge density for two charged gels undergoing relative rotation. Numbers in the figure are normal pressure in Pa. Parameters used in the calculation: $\omega = 0.05 rad/s$, $R = 7.5mm$, $\eta = 10^{-3} Ns/m^2$ (bulk water viscosity).

Under the experimental condition of 10^4Pa, Fig.6 gives a friction coefficient in the order of 10^{-3}. This simulation value with no free parameter is about 1 order lower than that of the experimental observation in Fig.1. This discrepancy may be associated with the presence of so-called "associated water". The thermal movement of water molecules located adjacent to the macroions is locally restricted due to strong attractive interaction with macrocharges located nearby. This suggests that the water molecules located within a certain distance from the macroions hardly move out from the potential energy valley made by the charged network. On the other hand, free water existing far from the ionic "atmosphere" can easily migrate under external stimuli such as an electric field, hydrostatic pressure, or, in the present case, the shear force. From our previous research on the electric field induced contraction of PAMPS gels [7], which occurs due to the electro-osmotic migration of water in the gel, about 148 water molecules per sulfonate moiety are bound to the polymer chain strongly and not displaced by an electric field. This corresponds to water molecules absorbed around the macroions at a thickness of 3-4 times the radius of the macroions. Our previous experimental research also showed that the electro-osmotic migration velocity of water in the PAMPS gels is only 1/10 of that from theoretical estimation, in which the free water viscosity had been used also. Therefore, using the bulk viscosity value of water would largely underestimate the friction force. An effective viscosity of water should be taken into consideration in the future[8].

4. Conclusion

From the above experimental results, it is demonstrated that the friction is largely dependent on the electrostatic interaction between the two gel surfaces. The low friction between two polyelectrolyte gels carrying the same charge should be attributed to the surface electrostatic repulsion of charges fixed on the polymer network. As shown in Fig.1 and Fig.5, there is a disagreement in the absolute value of Friction coefficient between the theoretical model and the experimental observations. The theoretical prediction, however, demonstrates qualitatively the hydrodynamic nature of the friction between strongly repulsive gel surfaces.

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