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Electroviscosity of polyelectrolyte solutions

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Abstract

A theoretical expression for the electroviscous effect in polyelectrolyte solutions, caused by the distortion of counterion-distribution and counterion flow around a polyion under a velocity gradient of solvent flow, was obtained to elucidate the characteristic behaviour of the viscosity of highly charged polyelectrolyte solutions observed at low salt concentration. The derivation of the theory was performed on the basis of the Navier–Stokes–Onsager equation, Poisson equation, and diffusion equations for low molecular ions by the use of a cell model (free-volume model) for a polyion. Energy dissipation was obtained without directly solving these equations. It was found that the derived expression of viscosity explained the experimental results satisfactorily, and that the streaming potential effect caused by the counterion flow played an essential role in the increase in viscosity of polyelectrolyte solutions at finite polymer concentration and low salt concentration ranges.

Keywords: Polyelectrolytes; Electroviscosity; Free volume model, Navier–Stokes–Onsager equation; Poisson equation

1. Introduction

The characteristic behavior of the viscosity of polyelectrolyte solutions, especially the remarkable increase in viscosity and its strong dependence on added salt concentration (C_s), have been explained in terms of the spatial expansion of polymer chains resulting from electrostatic repulsion forces between charged segments. The significant viscosity rule that the specific viscosity increment due to charges, $\Delta\eta_{sp}$, is proportional to the inverse root of added salt concentration, $C_s^{-1/2}$ [1], has been theoretically examined on the basis of polymer expansion [2].

This $C_s^{-1/2}$-rule, however, is established only when C_s is more than about 10^{-2} mol/l. When C_s is below 10^{-3} mol/l, a different feature of $\Delta\eta_{sp}$ takes place; $\Delta\eta_{sp}/C_p$ increases tremendously with decreasing polymer concentration C_p (number concentration of polyion charges in molar), and a further decrease in C_p brings about a sudden decrease of $\Delta\eta_{sp}/C_p$ after a dominant peak (Fig. 1 shows our experimental data). It seems quite difficult to explain this behavior by the means of polymer extension, that is, polymer extension cannot become unlimittedly large and the excluded volume effect alone cannot simply explain the very sharp decrease of $\Delta\eta_{sp}$ accompanied by a decrease of C_p at low C_s. Further, it is unnatural to interpret the considerable dependence of $\Delta\eta_{sp}$ on counterion size, which has been widely observed, due to the difference in degree of ionization slightly dependent on ion size. Therefore, it is required to find a different mechanism which enables to explain the above characteristic properties of viscosity.

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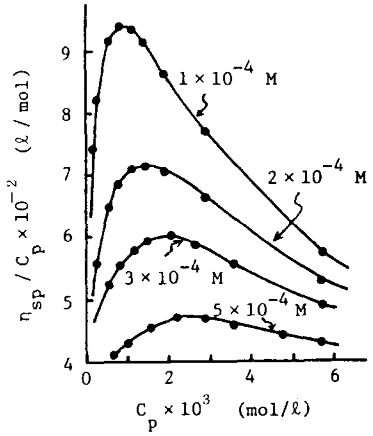

Fig. 1. Experimentally obtained values of η_{sp}/C_p of Na-polyvinyl sulphate solutions plotted versus C_p at various salt concentrations (C_s).

In this paper it will be shown that the electroviscous effect largely contributes to the viscosity increase of macroion solutions, and the theory derived here can explain well the above experimental results quantitatively. The electroviscosity of macroion solutions, which is caused by the energy dissipation due to the friction between counterions and solvent laminar flow, was first derived by Smoluchowski [3] and next by Booth [4] for spherical colloids many years ago. These theories, however, have presented very little contribution to the total energy dissipation. This is thought to be due to the fact that most of the counterions accumulate in the vicinity of the polyions where the solvent velocity must be almost zero, that is, in their model of infinite dilution of macroion solutions, the counterion concentration is so dilute that there is no room for the streaming potential to arise in a macroscopical range; it arises only in the vicinity of macroions.

In this paper, a cell model of polyions [5,6] is adopted to take into consideration the counterion contribution in the outer domain of the polyion. It is concluded that the counterions outside of polyions largely contribute to the energy dissipation which is accompanied by a strong streaming potential field in a wide region around the polyion in practically dilute polyion and salt concentrations.

2. Cell model and expression of energy dissipation

Let us imagine a coiled polyion situated in the solvent with velocity vector $U = (U_x, U_y, U_z)$ relative to the polyion (Fig. 2). Here we define z-plane, y-plane, and x-plane as the planes perpendicular to z-axis, y-axis, and x-axis, respectively. (The z-plane in this definition is xy-plane, for example.) Let us assume that the solvent flow is a laminar flow brought about by two hypothetical plates in parallel sliding in opposite x-directions at $z = L$ and $z = -L$. We also imagine a cubic cell, V of volume $(2L)^3$ around the polyion at the center of V, and assume that the cell holds overall neutrality and is connected with the adjacent cells similar to this V in x- and y-directions [5,6]. The surfaces of the cell perpendicular to the x-, y- and z-axis are defined by S_x, S_y, and S_z, respectively, and the cell surfaces facing to S_x, S_y, and S_z are denoted by S_x', S_y' and S_z', respectively.

Now, let us express U_x, the x-component of U, in the following form:

$$U_x = U_x^0 + u_x \tag{1}$$

where U_x^0 is the solvent velocity in x-direction in the absence of polyion charges, and u_x is the x-component of $u = (u_x, u_y, u_z)$ which represents the deviation of the solvent velocity (vector) from that in the absence of the polyion charges.

Our purpose is to derive the expression of energy dissipation due to this u, under the same

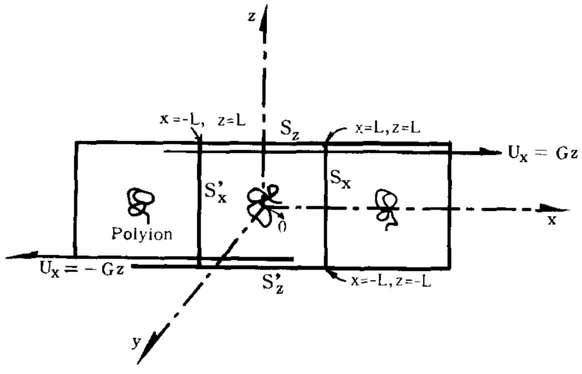

Fig. 2. Cubic cell model for a coiled polyion in a solvent flow (flow in x-direction with shear rate U_x/L).

boundary condition for U_x as that for U_x^0. Let U_x be given by

$$U_x(S_z) = U_x^0(S_z) = GL, \text{ and } U_x(S_z') = U_x^0(S_z') = -GL \qquad (2)$$

then, one of the boundary conditions for u_x is given by

$$u_x(S_z) = 0 \quad \text{and} \quad u_x(S_z') = 0 \qquad (3)$$

Now, if the increment of hydrodynamical stress in the x-direction on an arbitrary z-plane due to the polyion charges is denoted by τ_{xz}, τ_{xz} is hydrodynamically given by

$$\tau_{xz} = \eta\left(\frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x}\right) \qquad (4)$$

where η is the viscosity of solvent. By using τ_{xz} and considering eq. (2), we can express W_{el} by the following equation:

$$W_{\mathrm{el}} = 2\int^{S_z} U_x(S_z)\tau_{xz}(S_z)\,\mathrm{d}S_z = 2GL\int^{S_z}\tau_{xz}(S_z)\,\mathrm{d}S_z \qquad (5)$$

where $\tau_{xz}(S_z)$ represents the stress τ_{xz} on S_z, and $\mathrm{d}S_z$ is the surface element of S_z.

3. The relation between W_{el} and electric fields

The surface integral of eq. (5) can be related with the electric fields in the solvent by the use of Navier–Stokes–Onsager equation and the equation of incompressibility condition of solvent. The latter equation for the flow deviation $\boldsymbol{u}$ is written by

$$\nabla \cdot \boldsymbol{U} = 0 \qquad (6)$$

The Navier–Stokes–Onsager equation for u_x is written by

$$\eta\nabla^2 u_x + \eta\frac{\partial}{\partial x}(\nabla \cdot \boldsymbol{U}) - \frac{\partial p}{\partial x} = -\rho E_x \qquad (7)$$

where ∇^2 is

$$\nabla^2 \equiv (\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)$$

p is the hydrodynamic pressure, ρ is the spatial charge density formed by the distributed low molecular ions and segmental charges on the polyion, and E_x is the x-component of the electric field, $\boldsymbol{E} = (E_x, E_y, E_z)$, existing in solution. The second term on the left-hand side of eq. (7), $\partial\nabla\cdot\boldsymbol{U}/\partial x$, is zero as shown in eq. (6). This term, however, is added for our later convenience.

The charge density ρ in eq. (7) is related to the electric field $\boldsymbol{E}$ by the Poisson equation;

$$\nabla \cdot \boldsymbol{E} = (4\pi/D)\rho \qquad (8)$$

where D is the dielectric constant of solvent.

Now, let us multiply both sides of eq. (7) by z and then integrate with respect to x, y, and z over the whole cell V. At first, the volume integral of the left-hand side of eq. (7) multiplied by z, which is denoted by Q, can be transformed into the surface integrals on the cell as shown in the following equation;

$$Q = \delta\int^{S_x} z\tau_{xx}\,\mathrm{d}S_x + \delta\int^{S_y} z\tau_{xy}(S_y)\,\mathrm{d}S_y + 2L\int^{S_z}\tau_{xz}(S_z)\,\mathrm{d}S_z - \delta\eta\int^{S_x} u_z\,\mathrm{d}S_x - \delta\eta\int^{S_z} u_x\,\mathrm{d}S_z \qquad (9)$$

where δ is the operator to take the difference between the values on the two facing surfaces on the cell, that is

$$\delta\int^{S_k} \equiv \int^{S_k} - \int^{S_k'} \qquad (k = x, y, z) \qquad (10)$$

(The δ-opperation in the third term just gives twice of S_z integration.) τ_{xx} and τ_{xy}, are stresses in the x-direction on the x- and y-plane, respectively, defined by the following equation (τ_{xz} has been already given in eq. 4).

$$\tau_{xx} = 2\eta\frac{\partial u_x}{\partial x} - p, \qquad \tau_{xy} = \eta\left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}\right) \qquad (11)$$

On the other hand, Q in eq. (9) is equal to the integral of the right-hand side of eq. (7) multiplied by z. Substituting eq. (8) into ρ on the right-hand side of eq. (7), we have:

$$Q = \frac{-D}{4\pi}\int zE_x\nabla\cdot\boldsymbol{E}\,\mathrm{d}V \qquad (12)$$

Now, Q in eq. (9) can be simplified by considering the nature of the cells and the condition of dilute polyion solution in the following way;

At first, in eq. (9), the last term on the right-hand side is zero, since $u_x(S_z) = 0$ and $u_x(S_z') = 0$ from eq. (3). Next, under the consideration that the hydrodynamic state in V is identical with that in the adjacent cells in x-direction, $\tau_{xx}(S_x)$ is the same as τ_{xx} on the right yz-surface of the left adjacent cell of V. This means that $\tau_{xx}(S_x)$ is equal to $\tau_{xx}(S_x')$ at the same z. Thus the first integral in eq. (9) vanishes.

By the same reasoning, $u_z(S_x) = u_z(S_x')$. Hence, the first and the fourth integrals in eq. (9) vanish. In the same way, and the second integral in eq. (9) also vanishes. Thus, only the third term remains, and comparing with eq. (5), we have

$$Q = G^{-1} W_{\mathrm{el}} \tag{13}$$

In obtaining eq. (13), the relation $\tau_{xz}(S_z) = \tau_{xz}(S_z')$ due to the symmetry of the planes S_z and S_z' has been taken into the consideration.

Comparing eq. (13) with eq. (12), we have

$$W_{\mathrm{el}} = \frac{-DG}{4\pi} \int z E_x \boldsymbol{\nabla} \cdot \boldsymbol{E} \, \mathrm{d}V \tag{14}$$

Next, let us perform the integration of Q in eq. (14). It is known that the volume integral of $E_x \boldsymbol{\nabla} \cdot \boldsymbol{E}$ over V can be transformed into the surface integrals indicating the Maxwell tensors in the x-direction. However, the volume integration of $z E_x \boldsymbol{\nabla} \cdot \boldsymbol{E}$ has a term inconvertible to the surface integral. This can be recognized immediately by the following identical equation;

$$z E_x \boldsymbol{\nabla} \cdot \boldsymbol{E} = \frac{\partial}{\partial x} \left\{ z \left(E_x^2 - \tfrac{1}{2} \boldsymbol{E}^2 \right) \right\} + \frac{\partial}{\partial y} z E_x E_y + \frac{\partial}{\partial z} z E_x E_z - E_x E_z \tag{15}$$

The last term on the right-hand side of this equation is left to be a term inconvertible to a surface integral on volume integration.

In performing the volume integration of eq. (15), the first term gives the difference of the braced terms between on S_x and on S_x', and from the identity principle of the adjacent cells, this integration becomes zero. The integral of the second term is the surface integral of $2LE_xE_z$ on S_z. Although E_x is not zero (due to the occurence of the streaming potential field as described later), since E_z is zero because of the neutrality of the whole cell V, this integral vanishes. By the same reason, since $E_y = 0$, the integration of the third term on S_y also vanishes. Finally, we obtain the following equation from eq. (13).

$$W_{\mathrm{el}} = \frac{DG}{4\pi} \int^{V} E_x E_z \, \mathrm{d}V \tag{16}$$

4. Diffusion equations for low moleqular ions and derivation of W_{el}

It was found in eq. (16) that in order to obtain W_{el}, it is required to perform the volume integration of the right-hand side. As shown in the following, this integral can be obtained directly from the following fundamental equations for low molecular ions without difficulty as a function of activities of these ions in V.

Now, let $f_i(x, y, z)$ and $\boldsymbol{v}_i(x, y, z)$ be the number density, and the velocity vector of the ith low molecular ions at x, y, z, whose components are (v_{ix}, v_{iy}, v_{iz}), respectively, then, [*1*] the Poisson equation, eq. (8), [*2*] the equation of continuity for the ith low molecular ions, and [*3*] the force balance equation for the ith ions are written by the following equations:

$$[1] \quad \boldsymbol{\nabla} \cdot \boldsymbol{E} = (4\pi/D) \left(\sum_i \nu_i e_0 f_i - e_0 f_{\mathrm{s}} \right) \tag{17}$$

$$[2] \quad \boldsymbol{\nabla} \cdot f_i \boldsymbol{v}_i = 0 \tag{18}$$

$$[3] \quad \xi_i (v_i - \boldsymbol{U}) = e_0 \nu_i E - kT \nabla \ln f_i \tag{19}$$

where f_{s} is the segment density (which is dominant only in the polymer domain $|\boldsymbol{x}| \leqq a$), ξ_i and ν_i are friction constant and valence of the ith small ions, kT is the Boltzmann factor, and e_0 is the elementary charge, respectively. Equation (18) is deformed into

$$\boldsymbol{\nabla} \cdot x f_i \boldsymbol{v}_i = f_i (v_{ix} - U_x) + f_i U_x \tag{20}$$

$$\boldsymbol{\nabla} \cdot x z f_i \boldsymbol{v}_i = \sum\nolimits^{0} z f_i (v_{ix} - U_x) + \sum\nolimits^{0} z f_i U_x \tag{21}$$

where Σ^0 is an operator expressing the following summation for an arbitrary function of x and z, $g(x, z)$, (including suffixes x and z).

$$\sum^0 g(x, z) \equiv g(x, z) + g(z, x)$$

Substituting the expression for $(v_{ix} - U_x)$ in eq. (19) into that in eq. (21) and summing up with respect to i, we have

$$\sum_i \xi_i \boldsymbol{\nabla} \cdot xzf_i \boldsymbol{v}_i = \sum^0 z\{(D/4\pi)E_x \boldsymbol{\nabla} \cdot \boldsymbol{E} + e_0 E_x f_s\}$$

$$- \sum^0 z\{kT(\partial f_i/\partial x) + f_i \xi_i U_x\} \tag{22}$$

Let us integrate the both sides of eq. (22) with respect to x, y, and z over the cell V. We can perform the integration of the first term of the right-hand side by refering to the identical equation, eq. (15), and its conjugate equation for (x, z). In this integration, the term concerning E_x^2 appearing in the form $\partial zE_x^2/\partial x$ in eq. (22) becomes zero due to the identy on S_x and S_x'. Next, the integrals of other differential terms concerning E_y and E_z in eq. (15) are transformable into the surface integrals on the cell V, and become zero, since E_y and E_z are zero on the cell surfaces. The term, $z\ \partial f_i/\partial x$ in eq. (22) is rewritten as;

$$\sum^0 z\ \partial f_i/\partial x = 2z\ \partial f_i/\partial x + (x\ \partial f_i/\partial z - z\ \partial f_i/\partial x) \tag{23}$$

The volume integral of the first term on the right-hand side of this equation is expressed by the difference of f_i between on S_x and S_x'. This difference should be zero due to the identity of the adjacent cells. Next, the integral of the second term (in brackets) becomes zero in the process of the integration with respect to x and z on an arbitrary y-plane in the cell V.

On the other hand, the volume integral on the left-hand side of eq. (22) can be transformed into surface integrals on the cell surfaces. Since it is obvious that there is no average ion-flow passing through S_y and S_z in perpendicular directions, that is, $v_{iy}(S_y) = 0$ and $v_{iz}(S_z) = 0$, the integral on the left-hand side of eq. (22) includes only v_{ix} on S_x. Thus we have

$$2L\int^{S_x} z\sum_i \xi_i f_i{}^* v_{ix}^*\ \mathrm{d}S_x$$

$$= \frac{D}{2\pi}\int^V E_x E_z\ \mathrm{d}V + \int^V \sum^0 \sum_i z\xi_i f_i U_x\ \mathrm{d}V \tag{24}$$

where $f_i{}^*$, and v_{ix}^* are defined by $f_i{}^* = f_i(S_x)$ and $v_{ix}^* = v_{ix}(S_x)$, respectively. The integral of $zE_x f_s$ in eq. (22) is neglected since it is a/L times smaller than the quantity of the left-hand side. This is proved in the following way. Equation (20) is integrated into

$$L\int^{S_x} \sum_i \xi_i f_i{}^* v_{ix}^*\ \mathrm{d}S_x$$

$$= \int^V e_0 E_x f_s\ \mathrm{d}V + \int^V \sum_i \xi_i f_i U_x\ \mathrm{d}V$$

This equation demonstrates that the integral of $E_x f_s$ multiplied by L has the same order value as the left-hand side of eq. (24), and it is obviously L/a times larger than the integral of $zE_x f_s$ over V, since f_s contributes only in polymer domain $|\boldsymbol{x}| \leqq a$.

Substituting the first term on the right-hand side of eq. (24) into eq. (16), we have the following concrete expression of W_{el}.

$$W_{\mathrm{el}} = -GL\int^{S_x} z\sum_i \xi_i f_i{}^* v_{ix}^*\ \mathrm{d}S_x$$

$$+ \tfrac{1}{2}G\int^V \sum_i \xi_i f_i \sum^0 zU_x\ \mathrm{d}V \tag{25}$$

For our later convenience, we rewrite eq. (25) as follows;

$$W_{\mathrm{el}} = -GL\int^{S_x} \sum_i z\xi_i f_i{}^* (v_{ix}^* - U_x{}^*)\ \mathrm{d}S_x + W_0 \tag{26}$$

where U_x^* is defined by $U_x^* = U_x(S_x)$, and W_0 is defined by

$$W_0 \equiv \tfrac{1}{2} G \sum_i \int^V \xi_i f_i \textstyle\sum^0 z U_x \, \mathrm{d}V - GL \int^{S_x} \sum_i \xi_i f_i^* z U_x^* \, \mathrm{d}S_x$$

The surface integral on S_x of this equation is transformed, on the based of the following equation derived from eq. (6);

$$\int^V \boldsymbol{\nabla} \cdot xz\boldsymbol{U} \, \mathrm{d}V = \int^V \textstyle\sum^0 z U_x \, \mathrm{d}V$$

into

$$W_0 = \tfrac{1}{2} G \sum_i \xi_i \int^V (f_i - \langle f_i^* \rangle)(zU_x + xU_z) \, \mathrm{d}V \tag{27}$$

where $\langle f_i^* \rangle$ is the average value of f_i^* on S_x.

5. Streaming potential field and the expression of electroviscosity

Applying eq. (19) for the cell surface S_x, and taking into the consideration that in the case of dilute polyion solutions, f_i near the cell surface S_x is not appreciably dependent on x, that is, $\partial f_i / \partial x$ on S_x may be neglected, we have the following relation;

$$\xi_i (v_{ix}^* - U_x^*) = \nu_i e_0 E_x^* \tag{28}$$

where E_x^* denotes E_x on S_x. Generally, E_x^*, U_x^* are functions of y and z on S_x.

Substituting eq. (28) into eq. (26), we have the relation;

$$W_{\mathrm{el}} = -2GL \int^{S_x} \sum_i e_0 \nu_i \langle f_i^* \rangle E_x^* z \, \mathrm{d}S_x + W_0 \tag{29}$$

The expression of E_x^* can be easily obtained from the condition that the macroscopic current is zero. This condition, having often been used in electrochemistry, is based on the energy-dissipation minimum principle in irreversible thermodynamics.

The macroscopic current in our present cell model may be expressed by the charge flow (brought about by low molecular ions) crossing the cell surface perpendicular to the direction of this charge flow. Therefore, the current I in the x-direction per unit area, at (y, z) on S_x is written by

$$I = \sum_i e_0 \nu_i \langle f_i^* \rangle v_{ix}^* \tag{30}$$

Substitution v_i^* of eq. (28) into the above equation, and applying the non current condition $I = 0$, we obtain the following expression for the streaming potential field E_x^* on S_x:

$$E_x^*(y, z) = \Big(-\sum_i \nu_i e_0 f_i^* \Big/ \sum_i \nu_i^2 e_0^2 \langle f_i^* \rangle \xi_i^{-1} \Big) \times U_x^*(y, z) \tag{31}$$

Substituting eq. (31) into eq. (29) yields

$$W_{\mathrm{el}} = -GL \int^{S_x} z \sum_i \nu_i e_0 \langle f_i^* \rangle E_x^* \, \mathrm{d}S_x + W_0 \tag{32}$$

In eq. (32), for simplicity, let us replace $f_i^*(y, z)$ by its average (over S_x), $\langle f_i^* \rangle$, which has been defined in eq. (27). In the absence of solvent flow, this quantity, $\langle f_i^* \rangle$, represents the ith ion activity, since there is no electric field present on the cell surface and no electric force is acting on the small ions. In the presence of solvent flow, $\langle f_i^* \rangle$ must have a shear rate (G)-dependent term in addition to the activity. However, if we restrict the present theory to the limiting case $G \to 0$, $\langle f_i^* \rangle$ in W_{el} may be regarded as the activity of the ith ions.

Also, we employ a similar assumption to put $U_x^* = Gz$ on S_x, under the assumption that polymer concentration is very low. If polymer concentration is low, since the cell surface S_x is far from the polyion, the solvent flow around S_x should be approximately expressed by an ideal lamella flow in homogeneous solvent. These approximations never affect the generality of the theory.

Thus, we obtain the following expression of W_{el};

$$W_{\mathrm{el}} = \tfrac{8}{3} G^2 L^5 \frac{\left(\sum_i \nu_i \langle f_i{}^* \rangle \right)^2}{\sum_i \nu_i^2 \langle f_i{}^* \rangle / \xi_i} + W_0 \tag{33}$$

In eq. (33), it should be noted that W_{el} is composed of the two factors; one is the energy dissipation due to the occurrence of streaming potential and the other is the energy dissipation, W_0, due to the direct hydrodynamic friction force between the low molecular ions statistically bound to the polyion and the solvent flow. (cf. The volume integration of $f_i - f_i{}^*$ in eq. (27) gives the amount of the bound ith low molecular ions.)

It is extremely important that W_0 does not become zero even when polymer concentration C_{p} tends to zero at constant salt concentration C_{s}. This is due to the fact that the bound low molecular ions, whose local concentration is $(f_i - f_i{}^*)$, are distributed around the polyion even when C_{p} tends to zero at fixed C_{s}. Even in the case of a so-called "salt-free solution", a very small amount of low molecular ions exists (resulting from the ionization of solvent) playing the role of salt on extreme dilution of polyions.

On the contrary, the streaming potential part of W_{el}, the first term in eq. (33), becomes zero when C_{p} tends to zero at constant C_{s}, since the numerator is inversely proportional to $V^{1/3}$, while the denominator is almost equal to C_{s} (which is kept constant).

The electroviscosity derived by Booth's theory is just the above W_0, since it assumes an infinite dilution of macroions and introduces no explicit macroscopical streaming potential arising.

Despite the fact that W_0 is non zero even at infinite dilution, the value of W_0 is not significant. This is thought to be qualitatively due to the fact that the counterion distribution whose concentration is $(f_i - f_i{}^*)$ accumulates mainly in the vicinity of the polyion, but in this region, solvent velocity is nearly zero because of the laminar flow and the condition $U = 0$ in the surface area of the macroion. This is the main reason why the electroviscous effect has been disregarded and believed to be an unimportant factor to the viscosity of macroion solutions.

In this paper, we focus our attention mainly to the first term in eq. (33) resulting from the streaming potential effect, and examine whether or not this term explains the various characteristic behaviors of viscosity of dilute polyelectrolyte solutions having been observed. It is important that although the streaming potential contribution vanishes on infinite dilution of polymer solution as mentioned above, in usual attainable low C_{p}, this term exhibits a quantitatively remarkable contribution to the viscosity.

By omitting W_0 in eq. (33), and recalling a hydrodynamic relation connecting the energy loss W_{el} and the viscosity increase

$$\Delta\eta = W_{\mathrm{el}} / G^2 V \tag{34}$$

we obtain the following equation for the electroviscosity increase,

$$\Delta\eta = \frac{1}{3} \frac{L^2 \left(\sum_i \nu_i \langle f_i{}^* \rangle \right)^2}{\sum_i \nu_i \langle f_i{}^* \rangle / \xi_i} \tag{35}$$

6. Expression of electroviscosity for uni–uni valent ion systems and the application of additivity rule for counterions

Let us apply eq. (35) to a uni–uni valent low molecular ion system. If we define a_+ and a_- as the counterion and byion activities in molar concentration scale (polyions are taken here to be negatively charged.) and consider that the relation between L and the number concentration of polyion charges C_{p}', is given by $C_{\mathrm{p}}' \simeq n/(2L)^3$ where n is the number of charges on a polyion, eq. (35) in our present case is written by

$$\Delta\eta = \frac{1}{12} \left(\frac{n}{C_{\mathrm{p}}'} \right)^{2/3} \frac{(a_- - a_+)(f_+^* - f_-^*)}{\{(a_+/\xi_+) + (a_-/\xi_-)\}} \tag{36}$$

where f_+^* and f_-^* denote the activities (in number concentration scale) of counterions whose friction constant is ξ_+ and byions whose friction constant is ξ_-, respectively.

Now, let us put

$$a_+ = \gamma_p C_p + \gamma_s C_s \quad \text{and} \quad a_- = \gamma_s C_s \tag{37}$$

where γ_s indicates the activity coefficient of byions, and $n\gamma_p C_p$ denotes the apparent polyion charge, in other words, unbound counterions. In usual polyion systems in which only electrostatic interaction is involved, γ_s may be regarded as the mean activity coefficient of a simple salt solution having the same concentration as that of byions. If the amount of added salt solution is low (like in our present case), γ_s can be put to unity.

Considering the relation: (1) $f_+^* - f_-^* = \gamma_p C_p'$ (in number concentration scale), (2) $C_p' = 6 \times 10^{20}\ C_p$, and (3) the Robinson–Stokes rule, $\xi_+ = 6\pi\eta b_+$, where b_+ is the radius of a counterion, we obtain the following final expression for the electroviscous effect:

$$\frac{\Delta\eta_{sp}}{C_p} = \frac{B b_+ n^{2/3} \gamma_p^2 C_p^{1/3}}{\gamma_p C_p + \varepsilon C_s} \tag{38}$$

where $\Delta\eta_{sp}$ is the specific viscosity for the electroviscous effect defined by $\Delta\eta/\eta$, and the constants B and ε are defined by

$$B = N_A^{1/3}\pi/20 = 1.32 \times 10^7, \qquad \varepsilon = (\xi_+ + \xi_-)/\xi_- \tag{39}$$

where N_A is the Avogadro number.

Equation (38) is rewritten in the form;

$$C_p/\Delta\eta_{sp} = \left(B b_+ \gamma_p^2 n^{2/3}\right)^{-1} \left(\gamma_p C_p^{2/3} + \varepsilon C_p^{-1/3} C_s\right) \tag{40}$$

Let us apply the following additivity rule for counterions which has been widely examined theoretically and experimentally:

$\gamma_p =$ constant against C_s

If this rule is applied to eq. (40), eq. (40) predicts a linear dependence of $C_p/\Delta\eta_{sp}$ on C_s.

By the use of a further approximation that γ_p is almost independent of C_p, we can discuss also the C_p-dependence of $\Delta\eta_{sp}$ based on eq. (38). This assumption has been also examined over a wider range of C_p, although it is less precise than the C_s-independent nature of γ_p. (Theoretically C_p dependence is thought to be logarithmic.)

7. Comparison of theory with experimental results and discussion

There are three important check points to compare the present theory with experimental results, viz.: (1) whether or not the overall characteristic behavior of $\Delta\eta/C_p$, especially about the existence of its maxima, and the C_s-dependence of the maximum points of C_p can be well elucidated, (2) whether or not the experimental values of $\Delta\eta_{sp}$ coincide quantitatively with those from theory, and (3) whether or not the linear dependence of $C_p/\Delta\eta_{sp}$ on C_s predicted by eq. (40) is satisfied by the experimental results.

Concerning point (1), we can easily find that eq. (38) has a maximum with respect to C_p at $C_p = C_{pm}$ where C_{pm} is given by

$$C_{pm} = \varepsilon C_s / 2\gamma_p \tag{41}$$

Let us compare this result with the experiments in Fig. 1. We immediately find that if γ_p takes the value of 0.13, the experimental C_{pm} values almost coincide with eq. (41). A slight difference from theory is attributable to the assumption of constant γ_p at all C_p. Thus, the cause of the appearence of the maxima of $\Delta\eta_{sp}/C_p$ is attributable to the occurence of a streaming potential field created under solvent flow. This field disappears on extreme dilution of polyions because of the decrease of numerator values in eq. (31), and is also decreased at highly concentrated polymer solutions where the apparent polyion charge becomes almost zero because of the so small cell volume ($\gamma_p \to 0$).

Next, as regards point (2), we can examine whether or not the theory gives satisfactory numerical values for $\Delta\eta_{sp}/C_p$. Let us try to substitute the values for a datum in Fig. 1: $C_s = 10^{-4}$, (accordingly, $\gamma_p C_{pm} \cong C_s = 10^{-4}$), number of polyion charges, $n = 2 \times 10^3$, $\gamma_p = 0.13$, and $b_+ = 2 \times 10^{-8}$, for a hydrated Na^+ ion. Then, we obtain 215 for $\Delta\eta_{sp}/C_p$ at the maximum point. This should be 900 as from the experimental data. This

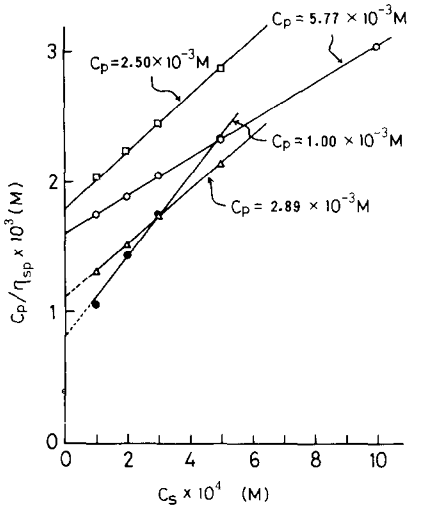

Fig. 3. Examination of eq. (40) by the use of data in Fig. 2 (The plots for $C_p = 2.5 \times 10^{-3}$ *M* are shifted upward +0.75 for ease of reading).

difference is, however, thought to be not so serious; for instance, if γ_p is chosen 0.2 instead of 0.13, the above value becomes to almost 440. Also the adoption of the Robinson–Stokes theorem for the friction constant of low molecular ions has some quantitative doubt; usually it has a tendency to estimate the friction constant too low. If b_+ is taken two times that from the Robinson–Stokes rule, the above $\Delta\eta_{sp}/C_p$ value matches the experimental result. Therefore, our theoretical result should be thought to be very satisfactory in view of the fact that no conventional adjusting parameter has been included in the above theory.

As regards point (3), i.e. $C_p/\Delta\eta_{sp}$ being linearly dependent on C_s, a surprising coincidence between experiment and theory is found. In Fig. 3, a plot of eq. (40) is shown. As predicted by our theory, a linear dependence of $C_p/\Delta\eta_{sp}$ on C_s is clearly observed. At $C_s = 0$ eq. (40) indicates that $C_p/\Delta\eta_{sp}$ increases as C_p increases, while the slope decreases as C_p increases.

From the above results, it is concluded that the characteristic nature of the viscosity of a polyion solution can be interpreted as being due to the effect of a streaming potential. The occurence of this streaming potential is essentially caused by the flow or distortion of the distribution of an excess amount of counterions, $\gamma_p C_p$, corresponding to the apparent polyion charges. As mentioned in Section 5, this streaming potential vanishes in extremely dilute polyion solution and W_0 in eq. (32) defined by eq. (27) becomes relatively important, although the value itself is very inappreciable. In order to evaluate the streaming potential effect theoretically, it is inevitable to introduce the cell model or some other suitable thermodynamical concept, such as the two-body distribution function, to clarify the contribution of $\gamma_p C_p$. Since there have been many theories which have succeeded to explain various experimental results based on the cell model, it is quite possible that a quasi-lattice formation really takes place even in dilute polyion solutions due to the strong intermolecular repulsive interaction which prohibits polymers to approach each other too closely.

In the theory of the viscosity of polymer solutions, the extension of the polyion chains has always been thought to play the most important role. We have neglected this in the present theory. We have concentrated our attention only to the electroviscous effect. At such low concentrations of salt-ions and polyions, however, it is unreasonable to assume polymers are still in the process of expansion when lowering the salt concentration, that is, it is possible that polymers already are in their maximum stretched state in the range of the present salt concentration. Also it seems quite difficult to demonstrate the experimental results of linear dependence of $C_p/\Delta\eta_{sp}$ on C_s shown in Fig. 3 and the dependence on the size of counterions. However, we cannot rule out the possibility that the degree of expansion of coiled polyions is sensitively influenced by the salt concentration when both C_p and C_s are extremely low. Hence, the polymer expansion at low salt conditions must be clarified in detail, since it has not yet been elucidated well.

The coiled polyion model was convenient for the hydrodynamic treatments in our present theory, since there was no singularity point in the spatial charge density and no solvent-impenetrable domain existed in the system, so that the volume integrations could be simply transformed into surface integrals on the cell surfaces.

The extension of this theory to rigid macroion systems is now our topic of ongoing research. This extention, however, evokes some problems as to how to define the boundary conditions of solvent velocity in relation to the osmosis resulting from small ions. However, a simpler mathematical way described below powerfully suggests the validity of the above eq. (38). It should also be kept in mind that it has been proved that the rotation velocity of a coiled polyion about its center of gravity is not affected by the polyion charges, so that there is no contribution from the changes of the rotation velocity. This can be demonstrated easily by the use of the energy dissipation minimum principle.

Finally, we would like to provide the reader with a simple way to derive eq. (29) of Section 5. Assuming that u_x, ρ, and E_x (streaming potential field in x-direction) near and on the cell surface S_x are independent of x and y, because S_x is far from the polyion at the center of the cell, the Navier–Stokes–Onsager equation is simply written by

$$\eta \frac{\partial^2 u_x}{\partial z^2} = \left(\sum_i e_0 \nu_i \langle f_i{}^* \rangle \right) E_x$$

Multiplying by z on the both sides and integrating with respect to z over S_x, we immediately obtain eq. (29) without W_0-term under the assumption that the stress in x-direction on S_z is almost constant everywhere on S_z.

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