

In I more density is clearly accumulated at the top of the molecule as evidenced by the contour lines lying above the corresponding lines in II. Distribution II concentrates more density below the oxygen in the vicinity of the hydrogens (and the binding region). It should be noted that the angle between the maximum density lobes in this plane for distribution II will be less than 180° even though the lone-pair orbitals are sp hybrids. The angle will lie between 150 and 160° as compared to distribution I where it is approximately 120° .

The concept of a binding region together with a knowledge of $\Delta\rho$ for various density distributions allows one to conclude that an acceptable density distribution for the water molecule must possess the following properties: the lone-pair orbitals must be close to sp hybrids, the oxygen orbitals which overlap with the hydrogens must be close to pure 2p orbitals, and the angle between these p orbitals must be considerably less than the bond angle, *i.e.*, the bonds must be bent. Only a density distribution with these characteristics can concentrate charge in the binding regions.¹⁶

These same requirements for the density function will hold for the ammonia molecule in which the binding region will be approximately pyramidal in shape and enclosed within the pyramidal geometry of the molecule. In this case, the lone pair must necessarily be close to a pure 2s orbital and the bonds, again bent, close to pure 2p orbitals from the nitrogen. These features of the density distributions for the water and ammonia molecules have been pointed out before,^{17,18} but this was accomplished by attempting a detailed force calculation for these molecules using Slater orbitals. This work has been criticized by Alexander and Salem¹⁹ on the grounds that simple Slater functions

(16) The SCF LCAO-MO calculations for the water molecules by H. Shull and F. O. Ellison, *J. Chem Phys.*, **23**, 2348 (1955), when transformed into equivalent orbitals have these very properties: lone pairs, 53% 2p character; bonding orbitals, almost 100% 2p from oxygen; and an orbital angle of 69° .

(17) R. F. W. Bader and G. A. Jones, *Can. J. Chem.*, **41**, 586 (1963).

(18) R. F. W. Bader and G. A. Jones, *J. Chem. Phys.*, **38**, 2791 (1963).

do not give an adequate enough description of the density for regions close to the nuclei. The present approach to the problem is meant to meet this objection in two ways. The use of SCF orbitals for the oxygen removes the objection regarding the inadequacy of the Slater orbitals. More important, a knowledge of the sign and magnitude of $\Delta\rho$ throughout the binding region excludes certain ranges of values for the parameters governing the degree of hybridization, etc., and does this regardless of the precise forms chosen for the orbitals. Thus it was found that the general forms of the plots of $\Delta\rho$ for the distributions exhibit only minor variations in magnitude if Slater rather than the SCF orbitals are employed, or if the orbital exponents are varied.

Full advantage has not been taken of the rigorous electrostatic approach to chemical binding. The knowledge that a chemical bond is the result of the accumulation of negative charge density in the binding region to the extent necessary to balance the nuclear forces of repulsion is a simple concept often overlooked. The electrostatic approach focuses attention on the three-dimensional electron density distribution in a molecule. Very few plots of ρ or $\Delta\rho$ have been given in the literature, and the effects of hybridization on the density are not at all as they are frequently pictured. The statement of Mulliken²⁰ that a little hybridization goes a long way is clearly brought to light by a $\Delta\rho$ plot. For example, in the present case, extreme rehybridization of the oxygen lone-pair density on the formation of the water molecule results in a large unfavorable shift in the density distribution. The electrostatic concept clearly demonstrates the important bonding role the lone-pair density plays in this molecule. Such results are difficult to appreciate on purely energetic grounds.

Acknowledgments.—We are indebted to Dr. G. A. Sefton for discussions regarding the binding regions in polyatomic molecules.

(19) L. Salem and M. Alexander, *ibid.*, **39**, 2994 (1963).

(20) R. S. Mulliken, *ibid.*, **19**, 900 (1951).

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Electrophoresis of a Polyelectrolyte in Solutions of High Ionic Strength

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Electrophoretic mobilities of poly(sodium acrylate) of different degrees of neutralization were determined in 0.1 *N* NaCl solution. It was found that the mobility is independent of molecular weight and equal to the mobility of segment. This result is in good agreement with the theories of Hermans-Fujita, Overbeek-Stigter, and Hermans. It may be concluded that the polyion coil is free draining in electrophoresis at high ionic strength, in remarkable contrast to the behavior of the polyion in viscous motion.

Introduction

Various transport phenomena such as viscosity, sedimentation, diffusion, and electrophoresis are fundamental for clarifying the hydrodynamic behavior of a polyion coil in solution. Among these, the electrophoresis is unique in the feature that the polyion and the counterions move in opposite directions, while the polyion moves together with the counterions in viscosity, sedimentation, and diffusion.

Theories of the electrophoresis of the linear polyelectrolytes have been presented by Hermans and Fujita,¹ Overbeek and Stigter,² and Hermans.³ These theories differ in mathematical development but yield essentially the same results; this arises from the fact that they all use the same model, *i.e.*, the partially

(1) J. J. Hermans and H. Fujita, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **B68**, 182 (1955).

(2) J. Th. G. Overbeek and D. Stigter, *Rec. trav. chim.*, **75**, 543 (1956).

(3) J. J. Hermans, *J. Polymer Sci.*, **18**, 529 (1955).

draining sphere introduced by Debye and Bueche⁴ in their theory on viscosity and sedimentation of non-ionic polymers, and also the same assumption that the electrostatic potential in the polymer coil is so small that the Debye-Hückel approximation is valid. Moreover, the relaxation effect of ionic atmosphere was neglected in all their theories.

The resulting theoretical equations for the electrophoretic mobility U of polyions are all expressed in terms of two characteristic parameters σ and β . The parameter σ , the shielding ratio originally defined by Debye and Bueche,⁴ is related to the radius of polymer sphere R , the number of segments contained in a unit volume of the sphere ν , the frictional coefficient of segment f , and the viscosity coefficient of the solvent η_0 , by the relationship

$$\sigma^2 = \nu f R^2 / \eta_0 \quad (1)$$

The parameter β is the ratio of R to the radius of the ionic atmosphere around the polyion $1/\kappa$. Thus

$$\beta = \kappa R \quad (2)$$

where κ is

$$\kappa^2 = \frac{4\pi N_0 e^2 \Sigma C_i}{10^3 D k T}$$

and C_i is the molar concentration of the i th ion in the solvent.

According to Hermans and Fujita,¹ the mobility U in solutions of high ionic strength is given by

$$U = \frac{e_s}{f} \left(1 + \frac{\sigma^2}{3\beta^2} \frac{2 + \sigma/\beta}{1 + \sigma/\beta} \right) \quad (3)$$

where e_s is the charge of a segment. Except for polymers of extremely low molecular weight, the second term (the correction term) in the parentheses of eq. 3 is small compared with unity if β is high enough. Thus for solutions of high ionic strength eq. 3 reduces to

$$U = e_s / f \quad (4)$$

and hence U must be equal to the mobility of a segment and independent of the molecular weight of the polyion. This conclusion implies that the polyion behaves like a free-draining coil in electrophoresis at high ionic strength, in sharp contrast to the behavior of the polyion in viscous motion.⁵

It was reported⁶⁻¹³ that the theories of Hermans-Fujita, Overbeek-Stigter, and Hermans, at least qualitatively, accounted well for experimental results. However, there are still few studies which deal with the important electrophoretic behavior of the polyion at high ionic strength as explained above. The purpose of the present study is to examine whether the electro-

phoretic mobility of a polyion at high ionic strength is really independent of molecular weight and can be compared to that of the segment. For this purpose it would be best to carry out experiments in a Θ solvent. However, since the electric resistance of the Θ solvent is too low to establish an electrical field in the solution strong enough for measurements, an aqueous NaCl solution of 0.100 N was used as the solvent. It is clear from a previous work that this NaCl concentration is high enough to allow the second term in the parentheses of eq. 3 to be neglected.¹¹

Experimental

Material.—Poly(sodium acrylate) used in this study was kindly supplied from Toa Gosei Co., Ltd. The samples, three times purified by precipitation from aqueous solution with methanol, were fractionated at 25° by using a methanol-water mixture (1:1) in the presence of 0.4 N NaOH. Each fraction was further purified in a similar manner and dried under vacuum at 50°. Several samples of different molecular weights were selected for the subsequent physical measurements. Sample no. 6 was used without fractionation.

Molecular weights of these samples were estimated from intrinsic viscosity in 2 N NaOH at 25° using the equation¹⁴ $[\eta] = 6.52 \times 10^{-3} \bar{P}_n^{0.64}$, where \bar{P}_n is the number-average degree of polymerization. The chosen samples cover the molecular weight range of 3.2×10^4 – 120×10^4 in sodium form. The results are shown below.

Sample no.	1	2	3	4	5	6
Mol. wt. $\times 10^{-4}$	3.2	11.5	30.0	32.9	46.5	120

The samples thus obtained are completely neutralized; *i.e.*, $\alpha = 1$. Partially neutralized samples were prepared by converting the fully neutralized samples into the acid form with a mixed bed ion-exchange resin (Amberlite IR 120 and IR 400), followed by partial neutralization with the addition of calculated amounts of NaOH in the presence of 0.1 N NaCl.

The polymer solutions were not dialyzed before electrophoresis because the difference of small ion concentrations between the solution and solvent phases due to the Donnan effect can be neglected when the ionic strength is as high as 0.1 N . The neglect of dialysis is particularly immaterial when the limiting mobility at zero polymer concentration is concerned.

Electrophoresis.—Electrophoretic mobilities of poly(sodium acrylate) in 0.1 N NaCl were determined at $25 \pm 0.01^\circ$, with the schlieren optical system of a Beckman SPINCO Model H electrophoresis apparatus. The cell used was a standard 11-ml. cell. The electric current was 1 mA. The heat generated by this electric current was 0.15×10^{-2} w./ml. at maximum, and any convection current was not observed.^{11,12}

The distance h traveled by the maximum refractive index gradient was measured on a photographic plate with a micro-comparator. The migrating velocity h/t was determined by plotting the distance h against time t on a graph paper. An example of h vs. t is shown in Fig. 1. The values of h/t for ascending and descending boundaries were determined at three or four polymer concentrations and extrapolated to zero polymer concentration.^{11,12} The extrapolated values of h/t for the two moving boundaries agreed well as demonstrated in Fig. 2.

The electrophoretic mobility U (cm.²/sec. v.) was calculated from the limiting electrophoretic velocity by means of the equation

$$U = \frac{K A h}{i t} \quad (5)$$

where h/t is the velocity of the moving boundary at zero polymer concentration (cm./sec.), A is the cross-sectional area of the cell (0.761 cm.²), K is the specific conductance of 0.100 N NaCl used as the solvent (1.0674×10^{-2} ohm⁻¹ cm.⁻¹), and i is the electric current used (1.00×10^{-3} amp.). The value of A was determined from the weight of mercury filled in the cell, and K was obtained from a table.

(14) A. Takahashi, T. Hayashi, and I. Kagawa, *Kogyo Kagaku Zasshi*, **64**, 1637 (1961).

(4) P. Debye and A. M. Bueche, *J. Chem. Phys.*, **16**, 573 (1948).

(5) A. Takahashi and M. Nagasawa, *J. Am. Chem. Soc.*, **86**, 543 (1964).

(6) J. J. Hermans, "The Structure of Electrolyte Solutions," John Wiley and Sons, Inc., New York, N. Y., 1959, Chapter 21.

(7) S. A. Rice and M. Nagasawa, "Polyelectrolyte Solutions," Academic Press, Inc., New York, N. Y., 1961.

(8) W. H. Cook, R. C. Rose, and J. R. Colvin, *Biochim. Biophys. Acta*, **8**, 595 (1952).

(9) E. B. Fitzgerald and R. M. Fuoss, *J. Polymer Sci.*, **14**, 329 (1954).

(10) D. A. I. Goring and E. G. Young, *Can. J. Chem.*, **33**, 480 (1955).

(11) M. Nagasawa, A. Soda, and I. Kagawa, *J. Polymer Sci.*, **31**, 439 (1958).

(12) P. J. Napjus and J. J. Hermans, *J. Colloid Sci.*, **14**, 252 (1959).

(13) B. van Geelen, Thesis, Utrecht, 1958.

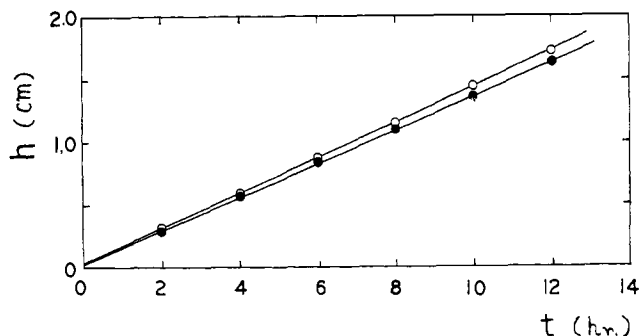


Fig. 1.—Linear relationship between migrating distance and time (sample no. 6, concn. 0.0674 g./dl., $\alpha = 1$): upper, ascending boundary; lower, descending boundary.

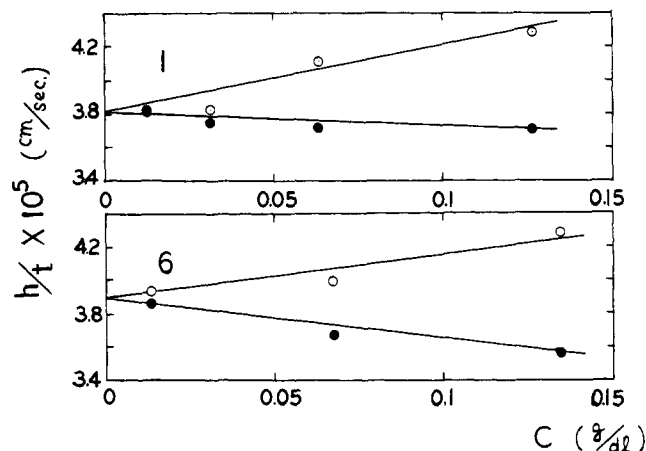


Fig. 2.—Concentration dependence of observed migrating velocities (samples no. 1 and 6, $\alpha = 1$): upper, ascending boundary; lower, descending boundary.

Error in the measurement of mobility due to current leakage was less than 0.1% when checked with the leakage tester of the apparatus.

Viscosity.—Intrinsic viscosities of poly(sodium acrylate) in 0.100 N NaCl were measured at $25 \pm 0.01^\circ$ with a capillary viscometer of the modified Ubbelohde type. The correction for kinetic energy was not more than 0.3%, and the constant k in the equation for the average rate of shear ($\gamma = k/\eta_{rel}$) was 250 sec.⁻¹.

Results

The observed electrophoretic mobilities of poly(sodium acrylate), fully and partially neutralized, are plotted against the viscosity-average molecular weight in Fig. 3. Although only the experiments for $\alpha = 1$ and 0.2 cover a range of molecular weight, it is clear from the figure that the electrophoretic mobility is independent of molecular weight, regardless of whether the sample is fully neutralized or partially neutralized. This may be contrasted to the fact that the intrinsic viscosity of a polymer varies with the molecular weight.

The mobility of the polyion as a function of the degree of neutralization is shown in Fig. 4. The same graph is obtained for other molecular weights. It is observed that the mobility at $\alpha = 1$ is as high as mobilities of small ions, and, moreover, the decrease in mobility is not proportional to the decrease in the charge density of polyion.¹³

Discussion

There are two routes to the understanding of the electrophoretic behavior of linear polyelectrolytes.

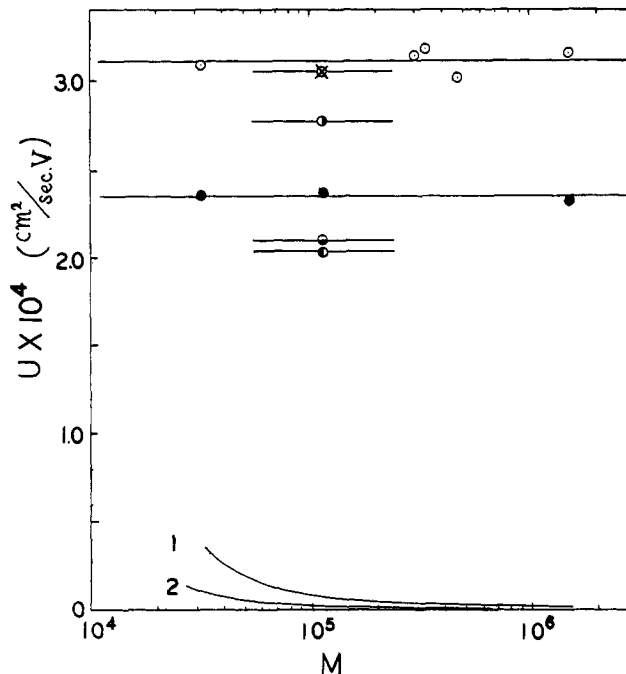


Fig. 3.—Molecular weight dependence of electrophoretic mobilities (cm.²/sec. v.) of the samples of different degrees of neutralization. Lines denoted by 1 and 2 are the calculated mobilities from Henry's theory (eq. 6) for the samples of $\alpha = 1$ and 0.2, respectively; degree of neutralization (α): \circ 1, \times 0.6, \bullet 0.4, \bullet 0.2, \circ 0.1, \bullet 0.05.

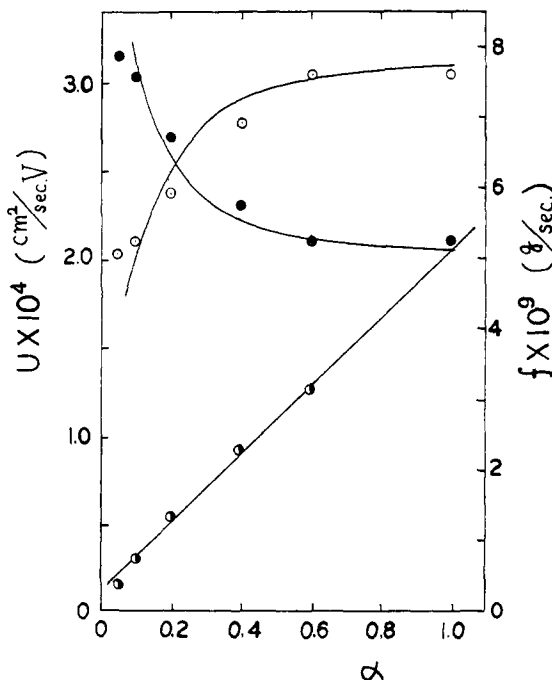


Fig. 4.—Dependence of electrophoretic mobility on the charge density of the polyion: \circ U_{obsd} , \circ $f_{monomer}$, \bullet $f_{segment}$ (see Table II). The full lines are calculated from eq. 11 assuming the prolated ellipsoid model for a segment.

One is the method^{15,16} in which a given polyion coil is *a priori* assumed to be nondraining for solvent and the well-known theory of Henry¹⁷ for colloidal particles is applied to the linear polyion. The other is the method^{11,12} in which the polyion is assumed to be made

(15) A. Katchalsky, N. Shavit, and H. Eisenberg, *J. Polymer Sci.*, **13**, 69 (1954).

(16) N. Ise, M. Hosono, and I. Sakurada, *Kobunshi Kagaku*, **14**, 624 (1957); **15**, 339 (1958).

(17) D. C. Henry, *Proc. Roy. Soc. (London)*, **A133**, 106 (1931).

of beads uniformly distributed in a sphere and the hydrodynamic resistance to determine electrophoretic mobility is caused by the interaction between the beads and the solvent penetrating through the sphere. The theories of Hermans-Fujita,¹ Overbeek-Stigter,² and Hermans³ as explained in the Introduction belong to the latter group.

According to Henry,¹⁷ the electrophoretic mobility of a rigid nondraining sphere is given by the equation

$$U = \frac{S_{\text{eff}}}{6\pi\eta_0 R(1 + \beta)} \quad (6)$$

if the ionic strength is high enough and the electric conductivity of the sphere is the same as that of the solvent. Here, S_{eff} is the effective charge uniformly distributed on the surface of the sphere of radius R , and η_0 is the viscosity coefficient of the solvent. This equation is also obtained as the limit of infinite σ in the theory of Hermans-Fujita. R may be estimated from intrinsic viscosity using various theories, in particular the following Flory-Fox equation¹⁸

$$[\eta] = \Phi \frac{\langle h^2 \rangle^{3/2}}{M} \quad (7)$$

where Φ is the so-called Flory constant, $\langle h^2 \rangle^{1/2}$ is the root mean square end-to-end distance of the polymer chain, and M is the molecular weight. Although there is an ambiguity in the numerical value of Φ ,⁷ it is not an important problem for the present purpose. We may use $\Phi = 2.1 \times 10^{21}$ and estimate R from $\langle h^2 \rangle^{1/2}$ with the assumption that

$$R^2 = \frac{5}{18} \langle h^2 \rangle$$

As far as the nondraining model is concerned, S_{eff} may be taken as the net charge appearing on the surface of the sphere, *i.e.*, the difference between the fixed charges on the polyion and the total charges of counter- and by-ions absorbed in the sphere. The concentrations of counter- and by-ions inside the sphere can be calculated from the Poisson-Boltzmann equation

$$\nabla^2 \psi = -\frac{4\pi e}{D} (n_c e^{-e\psi/kT} - n_c e^{e\psi/kT}) \quad (8)$$

where ψ is the electrostatic potential and n_c is the number concentration of both counter- and by-ions in the solvent. The resultant equation which gives S_{eff} is^{1,7,19}

$$S_{\text{eff}} = D \frac{E_D}{2\kappa} (1 + \beta) e^{-\beta} [(1 + \beta) e^{-\beta} - (1 - \beta) e^{\beta}] \quad (9)$$

where

$$E_D = -\frac{kT}{e} \ln \frac{1 + \sqrt{1 + \left(\frac{8\pi}{3} \frac{1}{Z} R^3 n_c\right)^2}}{\left(\frac{8\pi}{3} \frac{1}{Z} R^3 n_c\right)}$$

and Z is the number of fixed charges on the polyion. It has been shown⁷ that the net charge thus calculated

(18) P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904 (1951).

(19) M. Nagasawa and I. Kagawa, *Bull. Chem. Soc. Japan*, **30**, 961 (1957); M. Nagasawa, *J. Am. Chem. Soc.*, **83**, 300 (1961).

is distributed on the surface of the sphere, and the sphere is surrounded by the ionic atmosphere whose total charge is the same as the net charge of the sphere.

All the variables thus estimated for the present samples and the electrophoretic mobilities calculated from eq. 6 using these values are listed in Table I. It is observed that the calculated mobilities are much smaller than the observed values, and also that they decrease markedly with increasing molecular weight. This molecular weight dependence is clearly against our observed results. Although it is true that there are some ambiguities in the equations used for S_{eff} and R , the model of the nondraining solid sphere must essentially lead to calculated mobilities much smaller than that of the segment and also to their dependence on molecular weight.

TABLE I
ELECTROPHORETIC MOBILITIES OF THE POLYION CALCULATED FROM HENRY'S THEORY, ASSUMING A NONDRAINING SOLID SPHERE MODEL

Sample no.	$[\eta]$, dl/g.	$U_{\text{obsd}} \times 10^4$, cm. ² /sec. v.	$R \times 10^8$, cm.	$S_{\text{eff}} \times 10^8$, e.s.u.	$U_{\text{calcd}} \times 10^4$, cm. ² /sec. v.
[I] Degree of neutralization = 1					
1	0.61	3.09	110	2.51	0.32
2	2.32	3.05	270	3.14	0.076
3	4.02	3.14	440	5.06	0.044
4	4.17	3.18	460	5.44	0.044
5	5.22	3.02	550	6.15	0.034
6	9.3	3.16	920	10.6	0.020
		Average	3.11		
[II] Degree of neutralization = 0.2					
1	0.44	2.35	92	0.50	0.092
2	1.38	2.37	220	1.00	0.036
3
4
5
6	2.83	2.32	580	3.24	0.016
		Average	2.35		

These disagreements clearly stem from the assumption of a nondraining sphere for the linear polyion; in other words, from the fact that β increases faster than σ in the theory of Hermans-Fujita.

It was already reported^{6,7} that the theories of Hermans-Fujita, Overbeek-Stigter, and Hermans account for the electrophoretic behavior of the linear polyion, at least qualitatively. The present work also proves the predictions from these theories. When β is much larger than unity as in the present experiments, almost all counterions are inside the polymer coil, and the hydrodynamic perturbation arising from the electric force acting on fixed charges is canceled by the hydrodynamic perturbation from counterions so far as the assumption of continuous distribution of fixed charges inside the polyion sphere holds. Thus, (1) the polyion coil is free draining in electrophoresis at high ionic strength, and the mobility of the polyion must be independent of molecular weight. This prediction is supported by the experimental results shown in Fig. 3. (2) The mobility of the polyion must be equal to that of the segment, as expressed by eq. 4. If we assume that each segment consists of a monomer and the monomer is a sphere of radius a , we can calculate the frictional constant of the monomer (f) from the observed mobility using eq. 4 and then the radius a by application of the Stokes relationship

$$f = 6\pi\eta_0 a \quad (10)$$

The radius a obtained is 2.96 Å., which is reasonable compared to the actual size of the monomer.

In general, if the theory of Debye and Bueche⁴ is applied to intrinsic viscosity data, the size of a segment chosen to give best agreement between theory and experiments is found to be as small as one-tenth of its actual size. It is striking to see that a reasonable radius of segment, a , is obtained from the analysis of electrophoresis data using a theory based on the same model. (It has been reported that a similar result is also obtained for poly(sodium vinyl sulfate).¹¹) The reason may be considered as follows. The radius of the polymer sphere obtained from the theory of Debye and Bueche, and particularly its calculated molecular weight dependence, cannot be proper because the theory does not take into account the excluded volume effect. The improper molecular weight dependence leads to too small a radius of the segment. When the theories of Hermans-Fujita, Overbeek-Stigter, and Hermans are applied to electrophoresis, however, the mobility becomes independent of molecular weight and, therefore, such a weak point in the Debye-Bueche model becomes unimportant at the limit of high ionic strength, leading to a reasonable radius of the segment (*i.e.*, monomer). It is true that to take a monomer as a segment is merely an assumption, but this choice is not a serious problem at the limit of free drainage. Even if we take two or three monomers as a segment, the frictional coefficient of the segment simply becomes two or three times as high as $6\pi\eta_0 a$.

Since the hydrodynamic resistance of a monomer is independent of whether the monomer has a charge or not, the same frictional coefficient should be obtained for the monomer from experiments with samples of different degrees of neutralization. That is, at the limit of free drainage, the frictional coefficient of the polymer as a whole, F , should be independent of the degree of neutralization. Hence, the electrophoretic mobility should be proportional to the charge density of the polyion, because it follows from eq. 4 that

$$U = \alpha Ze/F = \alpha e/f_{\text{monomer}}$$

However, this prediction does not agree with our experimental results, which show that the frictional coefficient of the polymer, F , or the frictional coefficient of monomer, f_{monomer} , changes with the degree of neutralization (see Table II and Fig. 4).

This contradiction may be avoided if we assume that a segment consists of a sequence of monomers per an ionized fixed charge, and its shape is approximated by a prolated ellipsoid with a fixed diameter. The frictional constant of an ellipsoid, f , is given by Perrin's theory²⁰

(20) F. Perrin, *J. Phys. Radium*, (7) 7, 1 (1936)

$$f = f_0/Q \quad (11)$$

where $f_0 = 6\pi\eta_0 a$ and

$$Q = (p^{3/2}/\sqrt{1-p^2}) \ln [(1 + \sqrt{1-p^2})/p]$$

Here, p is the axial ratio and a is the fixed diameter of the ellipsoid which may be assumed to be equal to the Stokes radius of the monomer obtained when $\alpha = 1$.

TABLE II

ELECTROPHORETIC MOBILITIES AT DIFFERENT DEGREES OF NEUTRALIZATION FOR SAMPLE NO. 2^a

α	$[\eta]$, dl./g.	$U_{\text{obsd}} \times 10^4$, cm. ² /sec. v.	$f_{\text{monomer}} \times 10^8$, ^b g./sec.	$f_{\text{segment}} \times 10^8$, ^c g./sec.
1	2.32	3.05	5.25	5.25
0.6	2.05	3.05	3.15	5.25
0.4	2.03	2.78	2.30	5.75
0.2	1.38	2.37	1.35	6.75
0.1	0.77	2.10	0.76 ₁	7.61
0.05	..	2.03	0.39 ₅	7.90

^a Molecular weight equal to 11.5×10^4 . ^b The frictional coefficient of the monomer calculated from $U_{\text{obsd}} = \alpha e/f$. ^c The frictional coefficient of the segment, which is assumed to be a group of monomers per unit charge, calculated from $U_{\text{obsd}} = e/f$.

Then p is inversely proportional to the degree of neutralization α . The values of f calculated from eq. 11 with these assumptions are shown by a full line in Fig. 4. In the same figure, the experimental frictional coefficients of the segment (f_{segment}) calculated from $U = e/f_{\text{segment}}$ are shown for comparison. It is observed that the calculated values are in good agreement with experimental ones. The other two full lines in Fig. 4 are calculated from f in eq. 11 for comparison with the experimental mobility U and the frictional coefficient per monomer (f_{monomer}) using the relationship $f_{\text{monomer}} = \alpha f$. In all cases, the agreement between calculated results and experimental ones is quite good. Although there is little logical reasoning in this definition of a segment, it is likely that the theories of Hermans-Fujita, Overbeek-Stigter, and Hermans hold for partially neutralized polyions, too.

Thus, it may be concluded that the linear polyion behaves like a free-draining coil in electrophoresis experiments at high ionic strength, in sharp contrast to the fact that the polyion coil is essentially non-draining in viscous flow, particularly at high ionic strength.

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