Appendix

The general expression for the flow behavior of solutions is $\beta = f(\tau)$, where β = rate of shear, and $f(\tau)$ is some function of the shear stress τ. The problem of viscometry is the determination of the form of this function from experimental measurements. In the case of Newtonian fluids, the function becomes τ/η, where η is the viscosity.

For a concentric cylinder viscometer

$$\beta = r \frac{d\omega}{dr} = f(\tau)$$

where ω is the angular velocity at a distance r from the axis of rotation. Integration of this equation between the limits of r_1 and r_2, the radii of the inner and outer cylinders, respectively, gives

$$\int_{r_1}^{r_2} \frac{f(\tau)}{r} \, dr = \omega_0$$

where ω_0 is the angular velocity of the outer cylinder. Since the viscous torque $M = 2\pi L \tau r^2$ = constant, where L is the length of the inner cup, we have $-d\tau/dr = 2\tau/r$ and $\tau_2 = k\tau_1$, where $k = (r_1/r_2)^2$. The integral now becomes

$$\omega_0 = \frac{1}{2} \int_{k\tau_1}^{\tau} \frac{f(\tau)}{\tau} \, d\tau$$

Differentiation of this equation with respect to τ_1 gives

$$\frac{d\omega_0}{d\tau_1} = \frac{1}{2\tau_1} [f(\tau_1) - f(k\tau_1)]$$

This expression contains the solution for the desired function.

An additional differentiation and expansion of $f(k\tau_1) = f(\tau_1 + h)$ in a Taylor's series, neglecting derivatives higher than the second, allows an ap-proximate solution of $f(\tau_1)$ from the two differential equations. If the difference in radii is a small fraction of the average radius, one obtains

$$f(\tau_1) = \frac{2}{1+k} \left(\frac{2k\omega_0}{1-k} + \tau_1 \frac{d\omega_0}{d\tau_1} \right)$$

The general relation for relative viscosity is

$$\frac{f(\tau_1)_{\text{solvent}}}{f(\tau_1)_{\text{soln.}}} = \eta/\eta_0$$

If the solvent is Newtonian, then

$$f(\tau_1)_{\text{solvent}} = \frac{2\omega_0}{1-k}$$

and

$$\eta/\eta_0 = \frac{\left(\frac{\omega_0}{\tau_1} \right)_{\text{solvent}} (1+k)}{2k \left(\frac{\omega_0}{\tau_1} \right)_{\text{soln}} + (1-k) \left(\frac{d\omega_0}{d\tau_1} \right)_{\text{soln}}}$$

A plot of β versus V^2 (voltage squared) for solvent and solution enables the terms to be evaluated. The term $d\omega_0/d\tau_1$ is found at any point by graphical differentiation.

It is clear that the error committed in neglecting the non-equality of the two radii will be greater the more pronounced the curvature of the β versus V^2 plot, and in the direction of higher apparent relative viscosities. In the present work, for solutions only slightly shear dependent, and for $k = 0.823$, the correction amounted to about 5%.

On the Bjerrum Relation and the Formation of Ion Pairs

BY STUART A. RICE[1]

The Bjerrum relation for the ratio of the ionization constants of a dibasic acid or general bolaform electrolyte is derived from a consideration of the Grand Partition Function. The derivation emphasizes the physical processes occurring and enables the relationship between the depression of the secondary ionization constant of a dibasic acid and the formation of ion-pairs to be studied. The interrelation between ion association in solutions of polyelectrolytes and the properties of bolaform electrolytes is briefly discussed.

I. Introduction

It is well known that the primary (K_1) and secondary (K_2) dissociation constants of a dibasic acid usually differ by more than a factor of four. If the ionization processes at the two acid groups were independent K_1/K_2 would be exactly four, since both the un-ionized and doubly ionized species have symmetry numbers of two and the singly ionized intermediate has a symmetry number of unity. A theoretical explanation of the deviation of K_1/K_2 from the value 4 was given by Bjerrum[2] in terms of the electrostatic forces operative within the molecule. Subsequent refinement of this model by Kirkwood and Westheimer[3] has shown that the concepts originally introduced are adequate to account quantitatively for the observations.

In recent years, interest in this problem has been reawakened from two diverse points of view. Fuoss and co-workers[4-7] have extensively studied the properties of a class of compounds known as bolaform electrolytes. (It will be recalled that a bolaform electrolyte is one in which the charges are

(1) Junior Fellow, Society of Fellows, Harvard University.

(2) N. Bjerrum, Z. physik. Chem., **106**, 219 (1923).

(3) J. G. Kirkwood and F. H. Westheimer, J. Chem. Phys., **6**, 506 (1938).

(4) R. M. Fuoss and D. Edelson, THIS JOURNAL, **73**, 269 (1951).

(5) R. M. Fuoss and V. H. Chu, ibid., **73**, 949 (1951).

(6) H. Eisenberg and R. M. Fuoss, ibid., **75**, 2914 (1953).

(7) O. V. Brody and R. M. Fuoss, J. Phys. Chem., **60**, 156 (1956).

separated from one another by a chain of atoms.) It is interesting to note that these compounds exhibit ion-pair formation between the bolaform ion (bolion) and its counterions, even in solvents such as water.[4-7] Further interest derives from the observation that the counterions to a polyelectrolyte in solution are intimately associated with it. It has been suggested that this intimate association is due to the formation of ion-pairs at specific groups along the polymer chain.[8,9] Thus, the two types of ion-pair formation in bolaform electrolytes and in polyelectrolytes are postulated to be closely related.

The original calculations of Bjerrum and of Kirkwood and Westheimer are not well adapted to the discussion of the mechanism of ion-pair formation and its extension to more complex systems. In this brief communication we shall show that the Bjerrum relation (or its subsequent modification) may be derived easily in a manner which emphasizes the physical processes leading to ion-pair formation and the subsequent deviation of K_1/K_2 from the value four. The relation of the considerations presented here to the general problem of ion association in polyelectrolytes will be briefly discussed.

II. Some General Considerations

We consider a volume v containing N bolions, with the total number of dissociable groups $2N$. Let the solution also contain, in addition to the counterions to the bolions, additional electrolyte consisting of L_j ions of charge q_j where $\Sigma L_j q_j = 0$. We shall deal mostly with 1:1 electrolytes, though no restriction will be made limiting the development to this case. Each of the $2N$ dissociable groups may be occupied by a charged group or a bolion–counterion pair. We shall assume, as implied, that the sites at which ion-pair formation occurs are the charged groups.

It is convenient to divide the free energy of the solution into three parts. The first portion, F_1, is the electrostatic free energy arising from the interactions between charged groups on the same bolion. The remainder of the electrical free energy, F_2, results from the interaction between all charged species in solution, regarding each as a structureless particle. Finally, the last portion of the free energy, F_3, is the chemical free energy associated with the state of ion-pair formation and is computed from a reference state in which the bolion is in its completely ion-paired form. This choice of reference state emphasizes the calculation of the dissociation constant rather than the association constant. Obviously the choice of the completely dissociated state would have been equally suitable. With the convention adopted above, and letting α be the degree of dissociation of the bolion, we note that the total free energy of the solution may be written

$$F = F_1(\alpha) + F_2(\{a_i\}) + F_3(\alpha) \qquad (1)$$

with a_i the activity of species i. Of the contributions to F_2, we may distinguish between F_{21} which is the electrical free energy of the free counterions which may bind to a bolion and form ion

(8) F. E. Harris and S. A. Rice, *J. Phys. Chem.*, **58**, 725, 733 (1954).
(9) S. A. Rice and F. E. Harris, *J. Chem. Phys.*, **24**, 326, 336 (1956).

pairs and F_{22} which contains the remainder of free energy of interaction between all ions in the solution treated as structureless particles. To compute F_1 we shall regard ion-pairs as uncharged.

By minimizing the free energy of the solution with respect to the degree of dissociation at constant external salt activity, the equilibrium counterion activity may be obtained. Performing the indicated differentiation, one obtains

$$\left(\frac{\partial F_1}{\partial \alpha}\right)_{\{a_i\}} + 2N\mu_{C^-} + 2N(\mu^\circ_{B^+} - \mu^\circ_{B^+C^-}) = 0 \quad (2)$$

where we have used the fact that the various contributions to the free energy may be written as

$$F_1 = F_1(\alpha)$$
$$F_2 = F_{21} + F_{22} = 2N\alpha\mu_{C^-} + N\mu_{BB} + \sum_j L_j\mu_j$$
$$F_3 = 2N\alpha(\mu^\circ_{B^+} - \mu^\circ_{B^-C^-})$$
$$\sum_i N_i\, d\mu_i = 0 \qquad (3)$$

and where μ_i is the chemical potential of species i. We use the notation μ_{BB} to refer to the chemical potential of the bolion and μ_B^+ to refer to the chemical potential of the group at which ion pairs form. Use of the relations

$$\mu_i = \mu^\circ_i + kT \ln a_i$$
$$- kT \ln K^\circ_s = \mu^\circ_{B^+} + \mu^\circ_{C^-} - \mu^\circ_{B^+C^-} \quad (4)$$

enables us to write, after substitution of (4) into (2)

$$\left(\frac{\partial F_1}{\partial \alpha}\right)_{\{a_i\}} + 2NkT \ln a_{C^-} - 2NkT \ln K^\circ_s = 0 \quad (5)$$

III. The Electrical Free Energy

In this section we consider the calculation of the electrostatic free energy of the electrolyte solution under discussion. If a model is used which represents the bolion as having two discrete charges and occupying a spherically symmetric region of space from which other bolions are partially excluded, but into which the small ions and counterions may penetrate, it is possible to solve the Poisson–Boltzmann equation with only the Debye–Hückel approximations.[10] That is, the equation is linearized, and the potential of the bolion represented as spherically symmetric. Though this model makes the approximation of representing the mass distribution as continuous and spherically symmetric, this is far less serious than would be the approximation of replacing the discrete charges by a homogeneous charge distribution. In dilute solution, where the average distance between ions is very large relative to the separation of the charges within one bolion, the approximation of spherical symmetry ought to be quite good. In fact, as the solution approaches the state of infinite dilution all effects due to the separation of the charges within the bolion must disappear and the properties of the solution become independent of both the sizes of the ions and their charge distributions. The model described above also accounts for the removal of counterions from the solution by the formation of ion pairs with bolions. As might have been anticipated, it is found that the screened coulomb potential is a valid first approximation to the potential of mean force between two charges in the solution. In general, due to the partial ex-

(10) F. E. Harris and S. A. Rice, in press.

clusion of other bolions from the region between the charges of any one bolion, the screening constant for the interaction of the fixed groups on the bolion differs from that in the bulk of the solution. This effect is very large for polyelectrolyte solutions where the region occupied by any one polyion contains a very large number of charges constrained by the polymer backbone to remain close together. However, due to the small number of charges on a bolion, and to the fact that the region between charges is, in reality, readily accessible to all the small ions and to most of the charge due to others of its kind, the difference in screening constants will be small. To a good approximation, we may therefore neglect the difference and treat all charge–charge interactions with one screening constant. These considerations enable us to write for the electrical free energy of the solution, the expression

$$F_{elec} = \frac{N}{2} \sum_{i \neq j} \frac{q^2 e^{-\kappa |\vec{r}_{ij}|}}{D' |\vec{r}_{ij}|} - \frac{\kappa}{3D} \sum_i L_i q_i^2 - \frac{2N\alpha q^2 \kappa}{3D} - \frac{4N\alpha^2 q^2 \kappa}{3D}$$

$$\kappa^2 = \frac{4\pi}{DvkT}(\Sigma L_i q_i^2 + 2N\alpha q^2 + 4N\alpha^2 q^2) \quad (6)$$

where D' (which may differ from D) is the effective dielectric constant for the interaction of two groups on the same ion when *separated* by a distance $|\vec{r}_{ij}|$. Note that, aside from the first term representing the self energy of the bolions, the expression for the electrostatic free energy is exactly that which might have been deduced from the Debye–Hückel theory of ordinary electrolytes. Thus the second term in eq. 6 is the electrostatic free energy of the added electrolyte, the third is that of the counterions, and the last is due to the bolions interacting as structureless particles. The first term corresponds to F_1 and the last three to F_2. Of the three terms comprising F_2, the electrostatic free energy of the counterions may be also visualized as the electrical free energy change on building ion atmospheres about each of the charged groups on a bolion. We now turn to a further specification of the term F_1.

The Self Energy of the Bolions.—The sum in eq. 6 is to be carried out over all charged groups within the same molecule. In this section we shall develop a practical method of evaluating the sum and obtaining the degree of dissociation. We shall use the method of the Grand Partition Function since it is especially simple and elegant in the case under consideration. Moreover, the use of a Grand Partition Function[11] enables us to calculate the degree of dissociation, the extent of charge fluctuation, etc., by simple differentiation.

It will be seen that due to the manner in which the free energy of the solution has been subdivided, the quantity to be calculated in this section is the electrical free energy due to the self interactions of N *independent* particles. Now consider each of the $2N$ ionizable groups in the solution, each of which may be in one of two states, ionized or ion paired. With each group let us associate a state

(11) See, for example, G. S. Rushbrooke, "Introduction to Statistical Mechanics," Oxford University Press, New York, N. Y., 1949.

variable η_i $i = 1, 1', 2, 2', \ldots, N, N'$, where we temporarily regard the ions as distinguishable. The η_i may have two values, 0 and 1, $\eta_i = 0$ referring to an ion paired group and $\eta_i = 1$ to an ionized group. The total electrostatic energy may therefore be written

$$E = \sum_{i=1}^{N} \frac{\eta_i \eta_i' q^2 e^{-\kappa |\vec{r}_{1i}|}}{D_1' |\vec{r}_{1i}|} = \sum_{i=1}^{N} \chi_i \eta_i \eta_i' \quad (7)$$

which states that the total energy is the sum of the energy of all the bolions. Equation 7 is equivalent to the statement of the independence of the ions made above. We next introduce a semi-grand partition function $\Xi(\lambda, T)$ defined by the relation

$$\Xi(\lambda, T) = \sum_{\{\eta_i\}} e^{-E/kT} \lambda^{\Sigma \eta_i + \eta_i'} \quad (8)$$

where λ plays the role of an absolute activity whose value is determined by the total charge due to the bolions and where the summation is to be carried out over all possible values of the η_i. Introducing (7) into (8) we immediately obtain

$$\Xi(\lambda, T) = \left(\sum_{\{\eta_i \eta_i'\}} e^{-\chi \eta_i \eta_i'/kT} \lambda^{\eta_i + \eta_i'} \right)^N \quad (9)$$

which may be evaluated by inspection, yielding the relation

$$\ln \Xi(\lambda, T) = N \ln (1 + 2\lambda + \lambda^2 e^{-\chi/kT}) \quad (10)$$

In eq. 9 and 10 it has been assumed that the charge separation is the same in all bolions. When the number of atoms in the chain that separates the charges is small, this is a very good approximation. As the chain length between charges increases, the distribution of charge separations broadens. In that instance, it is easiest to assume that, for the purpose of calculating the electrostatic energy, all bolions have their charges separated by the average charge separation. This should be a quite adequate approximation for our purposes (see Appendix I.)

Returning to the definition of $\Xi(\lambda, T)$, it is possible to see that

$$\left(\frac{\partial \ln \Xi}{\partial \ln \lambda} \right)_T = 2\alpha N \quad (11)$$

using the fact that the most probable value of $\Sigma \eta_i + \eta_i'$ may be identified with $2\alpha N$, the total charge in solution residing on the bolions. The free energy F_1 may now be expressed as

$$F_1 = - kT \ln \Xi(\lambda, T) + 2\alpha NkT \ln \lambda \quad (12)$$

Standard procedures then enable us to obtain the relations

$$\alpha = \frac{\lambda + \lambda^2 e^{-\chi/kT}}{1 + 2\lambda + \lambda^2 e^{-\chi/kT}} \quad (13)$$

$$\frac{S_1(\alpha)}{2Nk} = \frac{1}{2} \ln (1 + 2\lambda + \lambda^2 e^{-\chi/kT}) -$$

$$\alpha \ln \lambda + \frac{\chi}{2kT} \frac{\lambda^2 e^{-\chi/kT}}{1 + 2\lambda + \lambda^2 e^{-\chi/kT}} \quad (14)$$

$$\frac{1}{2Nk} \left(\frac{\partial S_1(\alpha)}{\partial \alpha} \right) = - \ln \lambda + \frac{\chi}{kT} \frac{\lambda(1 + \lambda)e^{-\chi/kT}}{1 + 2\lambda e^{-\chi/kT} + \lambda^2 e^{-\chi/kT}}$$

$$(15)$$

where $S_1(\alpha) = -(\partial F_1(\alpha)/\partial T)$ is the entropy arising from the distribution and interaction of the charges. From eq. 13 it can be seen that when the interaction between charges on the same molecule

tends to zero, then $\exp(-\chi/kt)$ tends to unity, and the degree of neutralization is given by

$$\alpha = \frac{\lambda}{1 + \lambda} \qquad (16)$$

By substitution of (10) and (12) in (5) we thus find for the equilibrium condition (5) the relation

$$\ln a_{C^-} + \ln \lambda - \ln K^\circ_s = 0 \qquad (17)$$

We can now calculate the equilibrium counterion activity or, if this is known, the equilibrium degree of dissociation, presuming only that we know the intrinsic dissociation constant K_s. In dilute solution, to a sufficient approximation, the activity coefficient term appearing in eq. 17 may be neglected relative to the contributions from the other terms. At equilibrium then (in very dilute solutions)

$$\lambda = \frac{K^\circ_s}{C_C} \qquad (18)$$

The equilibrium constant for the secondary dissociation reaction may be written

$$K_2 = C_{C^-} \frac{K^\circ_s(2\alpha - 1) + \alpha C_C^-}{2K^\circ_s(1 - \alpha)} \qquad (19)$$

where we have put $K_1 = 2K^\circ_s$. Note that eq. 19 is defined for the hypothetical ideal solution, or for a solution sufficiently dilute that activity coefficients may be approximated by unity. Since K_2 must obviously be independent of concentration, it will have the same value in all real solutions, and the activity coefficients are just those factors which correct K_2 to this constant value. We may now find by substitution of (18) into (13) and (13) into (19) that

$$K_2 = \frac{K^\circ_s}{2} \exp\left(-\frac{\chi}{kT}\right) \qquad (20)$$

which is the Bjerrum relation. The value of the dielectric constant for intercharge interaction is given by the Kirkwood–Westheimer theory, but the functional form (20) remains unaltered.

IV. Discussion

The obvious cause of ion-pair formation is the net increase in energy when a singly ionized bolion becomes doubly ionized. If this increase in energy is larger than the gain in translational free energy for the freed counterion, then ion-pairing is relatively favored. The extent of ion-pair formation depends on the concentration through the entropic part of the free energy since the gain in translational energy per counterion is larger the more dilute the solution.

More insight into the forces responsible for ion-pair formation can be obtained from an examination of the entropy changes arising from the charge-charge interactions within one bolion. A schematic plot of eq. 14 (Fig. 1) shows two peaks, corresponding to the placement of charge on one site and then on the other. Note that this entropy is lower than that for a bolion with no interaction between the charges. The physical changes corresponding to the entropy changes shown in Fig. 1 may be visualized as follows. At small degrees of ionization there are predominantly uncharged and singly charged species in solution. Since these species differ, we may regard them as forming a mixture and there is a corresponding entropy of mix-

ing. Alternatively, the entropy change may be regarded as arising from the number of ways in which $2\alpha N$ charges may be placed on a total of $2N$ possible sites. In the case of a bolion with non-interacting charges, the entropy of mixing passes through a single maximum as α increases, just as for an ideal solution. This is due to the fact that it requires the same amount of energy to remove a charge for all values of α. In the presence of charge-charge interactions, this situation is modified. As α increases more and more bolions become singly ionized. In contrast to the previous case, to form a doubly ionized bolion requires that the energy of the solution be markedly increased. The concentration of doubly ionized ions remains low therefore, and the increase in charge as α increases is due predominantly to an increasing concentration of the singly ionized species. Now however, the solution contains a large number of singly ionized molecules and only a small number of doubly ionized or uncharged molecules. There is therefore a sharp decrease in the entropy of mixing as α approaches $1/2$ due to the increasing chemical homogeneity of the solution. When α exceeds $1/2$, there are once again a large number of energetically equivalent sites at which a charge can be placed. Doubly ionized species make their appearance and mix with the rest of the solution and the entropy goes through a second maximum as α tends to unity.

The difference between the entropy as a function of the degree of neutralization when there are charge–charge interactions and when there are no interactions indicates that a bolion with interactions will resist ionization more than one without interactions. The equilibrium constant for the secondary dissociation is accordingly lowered. If the bolaform electrolyte happens to be a dibasic acid, then as chemical neutralization is increased (by the addition of base, say) the bolion may bind the cation of the base to minimize its electrostatic free energy. In the case of the neutralization of a polyacid (or diprotic acid) in water, counterions are bound rather than protons because the proton concentration is dictated by the supplementary equilibrium governing the ion product of water. The proton concentration is therefore low. Only counterions are available to be bound to the polymer (or bolion) and thereby lower its free energy. For a strong bolaform electrolyte, this binding appears as a smaller dissociation constant, K_2.

Thus, there is a direct relation the mechanism of ion-pair formation and of the lowering of K_2. In the case of a polymer, the electrical interactions are very strong. As in the previous case, the macroion will resist having its charge built up by the expedient of binding counterions until the electrical free energy is minimized. The applicability of the site-bound ion-pair concept in treating the properties of bolaform electrolytes has been amply demonstrated, and the implication that the sites where ionization takes place and where ion-pair formation occurs are the same is also supported.[4-7]

It is interesting to speculate further on the relationship between ion-pair formation as observed in solutions of bolaform electrolytes, and the nature
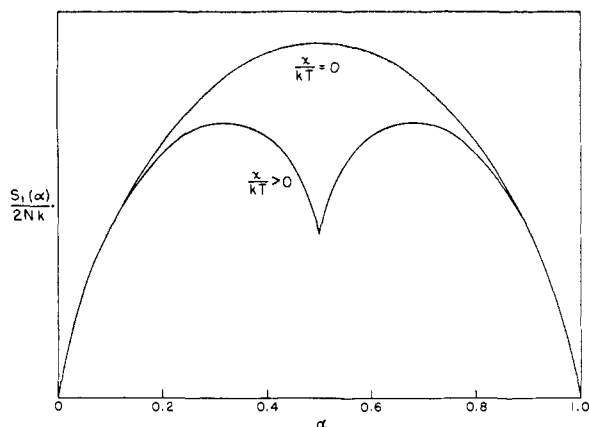
Fig. 1.—The entropic contribution to the electrostatic free energy, F_1.

of ion binding in solutions of polyelectrolytes. The ion-pair concept used in this paper differs in nature and purpose from that introduced by Bjerrum to extend the Debye–Hückel theory to higher concentrations.[12] The members of our ion pairs are much closer together than ion atmosphere dimensions, and exclude a negligible proportion of the configurations ordinarily considered in the Debye–Hückel theory. Introduction of this ion-pairing need not be as arbitrary as it seems, for it describes, to first order, the free energy contributions of the paired counterions and bolion charges. Application of the Poisson–Boltzmann equation to the modified system then enables the remainder of the electrostatic free energy to be calculated more accurately.[10] In addition, as we shall subsequently see, there is fragmentary evidence that the binding of counterions by polyelectrolytes may occur at specific sites.

The elegant experiments of Wall,[13-15] et al., leave little doubt that the counterions of a polyion are intimately associated with it. However, these experiments do not distinguish between counterions bound as ion-pairs and counterions that are merely trapped in the region where $|e\psi/kT| > 1$. There are two pieces of evidence that tend to support the former point of view. Howard and Jordan[16] studied the sedimentation of polymethacrylic acid as a function of the degree of neutralization of the polymer and the ionic strength of the medium. Kraut[17] has succeeded in interpreting their data on the basis that the sedimenting polyion has a net charge much smaller than the stoichiometric degree of neutralization. The net charge needed to fit the data is in quantitative agreement with the transference and diffusion measurements of Wall, et al.[13-15] Since the rate with which the bound ions exchange with those in solution is large,[15] the experiments of Howard and Jordan largely elim-

inate the possibility that counterions external to the polymer coil are dragged along with it. A second set of experiments is far more clear cut. Strauss and co-workers[18] found that it was possible to change the sign of the charge on polyvinylpyridinium bromide and several related polyelectrolytes if the bromide ion concentration was made sufficiently large. That is, the polyion starts out positive, then becomes negative, and moves to the opposite electrode as the bromide ion concentration increases. These results cannot be interpreted on the basis of electrostatic dragging of counterions in the region when $|e\psi/kT| > 1$, since once the polyion had no net charge there would be no incentive for the counterions to further cluster in the vicinity of the polymer. It is probable, therefore, that the binding observed by Strauss and co-workers is occurring at specific sites. Moreover, these experiments indicate that there are other forces (i.e., ion-dipole) than those commonly considered which may play a significant role in determining the thermodynamic and configurational properties of polyelectrolytes.

Finally we note that an immediate implication of the proposed site binding is that the extent of ion-pair formation should be essentially independent of the electric field strength applied, for example, in an electrophoresis experiment. In contrast, if the ion association were due to electrostatic dragging in the region where $|e\psi/kT| > 1$, the amount of ion pair formation should decrease continuously with increasing electric field strength. It should be noted that these statements are meant to be applied only in the region of low field strengths. At very high field strengths, where a Wien effect may occur, both types of ion-binding will respond in the same way, i.e., decrease with increasing field strength. However, by the time fields sufficiently strong are reached, the amount of $|e\psi/kT|$ binding, assuming both exist in the absence of any field, should be negligibly small, and only the site bound counterions would give the Wien effect.

Recent experiments by Wall[19] have shown that the binding of sodium ion to polyacrylic acid is independent of the applied field strength above a minimum value. The associated counterions may therefore be classed as loosely or strongly bound. The amount of non-specific loosely bound counterion association is of the order of 8% of the total amount of binding when the degree of neutralization is approximately unity. Theoretical considerations previously cited[10] indicate that in addition to the site bound ions there will be a number of loosely bound ions within the volume occupied by the macroion. The loosely bound counterions found in Wall's experiments may be identified with these. It should be noted that all of Wall's experiments are carried out at low field strengths (0.1 to 1.5 volts per cm.), and therefore are in agreement with the implications of the proposed model.

Bailey, Patterson and Fuoss[20] have examined the

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(13) F. T. Wall and R. H. Doremus, THIS JOURNAL, **76**, 1557 (1954).

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(18) U. P. Strauss, N. Gershfeld and H. Spiera, THIS JOURNAL, **76**, 5909 (1954).

(19) F. T. Wall, H. Terayama and S. Techakumpuch, J. Polymer Sci., **20**, 477 (1956).

(20) F. E. Bailey, A. Patterson and R. M. Fuoss, THIS JOURNAL, **74**, 1845 (1952).

Wien effect in a strong polyelectrolyte, finding an increase in conductivity of the order of 13% when the field was 10,000 volts per cm., with larger increases at still larger field strengths. The order of magnitude of the observed Wien effect was comparable to that observed in solution of tribenzylammonium picrate in a solvent of very low dielectric constant. Since the site bound ion pairs proposed ought to be similar to ion-pairs formed by salts in media of very low dielectric constant, the observed similarity of Wien effects is not unexpected. Further, Bailey, *et al.*, noted that though the Wien effect was reproducible, even when the pulses followed one another at very short intervals, the total conductivity of the polyelectrolyte solution did not reattain its equilibrium value after the high voltage pulse for a period of time much longer than either the pulse length or the interval between pulses. If the Wien effect observed is due only to the site bound counterions, as suggested, then a possible explanation of this anomaly might be as follows. Due to the fact that the loosely bound counterions can be removed by very low fields, they will be much further from the polyion after a high voltage pulse than the site bound ions that have also been affected. There will therefore be a relatively longer relaxation time for the return of the loosely bound counterions than for the strongly bound counterions. That is, loosely bound counterions will be found mostly outside the polyion and will have to diffuse to and into it, whereas strongly bound counterions, though in many cases removed from their charge sites, will remain largely within the domain occupied by the polyion. Since it is postulated that the Wien effect derives only from the strongly bound counterions, whereas the low field conductivity depends upon the numbers of both kind, the relaxation time for the recovery of low field conductivity should be longer than that for the Wien effect. This is in the observed direction.

The experiments cited do not completely preclude all other explanations of ion association in polyelectrolytes, but they are in complete agreement with the simple hypothesis of site-bound pairs.

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Appendix I

The Effect of Chain Flexibility and the Calculation of Charge Fluctuations.—Throughout the text we have assumed that the bolion is a rigid molecule, *i.e.*, there is no change of configuration due to changes in charge state or ionic strength. If such a change in configuration does occur, the free energy F_1 consists of both the self-energy of the ion, as previously calculated, and the free energy change on expansion. Under these conditions, eq. 17 is modified to read

$$\ln a_{C^-} + \ln \lambda - \ln K^\circ_a + \left(\frac{\partial F_{\exp}}{\partial \alpha}\right) = 0 \quad (A\text{-}1)$$

As an example, we shall calculate $(\partial F_{\exp}/\partial \alpha)$ for a randomly coiled chain with allowance for the finite contour length of the molecule. The probability density that an uncharged chain will assume an end-to-end distance h_1 is given by the relation

$$W(h_1)dh_1 = \text{const. exp}$$

$$\left\{ - \frac{h_m}{h_0{}^2} \int_0^{h_1} L^{-1}\left(\frac{h}{h_m}\right) dh \right\} 4\pi h_1{}^2 dh_1 \quad (A\text{-}2)$$

where h_m is the contour length of the molecule, h_0 its unperturbed length, and $L^{-1}(x)$ is the inverse Langevin function.[21] We shall approximate $L^{-1}(x)$ by an expression employed by Kuhn and Grun,[22] namely

$$L^{-1}(x) = 3x\left(1 + \frac{0.6x^2}{1 - x^2}\right) \quad (A\text{-}3)$$

If the bolion chain contains ν charges on each end, the free energy of expansion will be[23]

$$F_{\exp} = \frac{3kT}{2}\left[0.4\left(\frac{h_1}{h_0}\right)^2 - 1 - 0.6\left(\frac{h_m}{h_0}\right)^2 \ln\left(1 - \left(\frac{h_1}{h_m}\right)^2\right)\right] - 3kT\ln\frac{h_1}{h_0} + \frac{\alpha^2\nu^2 q^2}{D}\left[\frac{e^{-\kappa h_1}}{h_1} - \frac{e^{-\kappa h_0}}{h_0}\right] \quad (A\text{-}4)$$

leading to the result

$$\left(\frac{\partial F_{\exp}}{\partial \alpha}\right) = 3kT\left[0.4\frac{h_1}{h_0{}^2} + 0.6\left(\frac{h_m}{h_0}\right)^2 \frac{(h_1/h_m{}^2)}{1 - (h_1/h_m)^2} - \frac{h_0}{h_1}\right]\frac{\partial h_1}{\partial \alpha} + \frac{2\alpha\nu^2 q^2}{D}\left[\frac{e^{-\kappa h_1}}{h_1} - \frac{e^{-\kappa h_0}}{h_0}\right] - \frac{\alpha^2\nu^2 q^2}{D} e^{-\kappa h_1}\left(\frac{1 + \kappa h_1}{h_1{}^2}\right)\frac{\partial h_1}{\partial \alpha} \quad (A\text{-}5)$$

If the free energy of expansion, eq. A-4, is minimized with respect to h_1, the equilibrium end to end separation becomes

$$\left(\frac{h_1}{h_0}\right)^2 = \left[1 + \frac{\nu^2\alpha^2 q^2 e^{-\kappa h_1}(1 + \kappa h_1)}{3DkTh_1}\right]\left[0.4 + \frac{0.6}{1 - (h_1/h_m)^2}\right]^{-1} \quad (A\text{-}6)$$

from which $(\partial h_1/\partial \alpha)$ may be evaluated readily. Numerical evaluation reveals that the free energy of expansion is small relative to the other contributions to the free energy (see reference 8 for details of a similar calculation).

As a final note, it is of interest to calculate the charge fluctuations. Differentiation of $\Xi(\lambda, T)$ leads to the relations

$$\frac{1}{\Xi(\lambda, T)}\frac{\partial \Xi(\lambda, T)}{\partial \ln \lambda} = <Q> \quad (A\text{-}7)$$

$$\frac{1}{\Xi(\lambda, T)}\frac{\partial^2 \Xi(\lambda, T)}{\partial (\ln \lambda)^2} = <Q^2>$$

from which one readily obtains for the fluctuations in charge

$$\Delta^2 = \frac{<Q^2> - <Q>^2}{N} = 4\alpha(1 - \alpha) - \frac{\lambda}{1 + 2\lambda + \lambda^2 e^{-\chi/hT}} \quad (A\text{-}8)$$

where $<Q>$ and $<Q^2>$ are the average and average square total charges. Note that this effect also exists in a bolion in which there are no interactions between the charges. Δ^2 is zero only when $\alpha = 0$, or $\alpha = 1$, when fluctuations are obviously physically impossible.

CAMBRIDGE, MASS.

(21) See P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953.

(22) W. Kuhn and F. Grun, *Kolloid Z.*, **101**, 248 (1942).

(23) Note that in eq. A-4 the convention assumed is that F_1 is computed with a charge separation of h_0, and $F_{\exp}$ includes both the free energy of stretching and the change in electrical free energy due to expansion. An obviously equivalent convention would be to compute F_1 for a charge separation h_1, whereupon $F_{\exp}$ becomes only the elastic free energy. Also note that the development given is for a single molecule.