9. One further point by which equation 9 may be tested is the expected absence of any dependence on the molecular weight of the polymer. This behavior was experimentally confirmed by showing that a polyelectrolyte sample of molecular weight 22,400 gave the same result in 0.35 M NaBr as did the sample whose molecular weight was 332,000 (see Table I and Fig. 2).

It is noteworthy that the lines in Fig. 2 are in the same order with respect to the cations as are the previously published intrinsic viscosity curves.[15] If one considers that both membrane equilibria and intrinsic viscosity values depend on excluded volume effects, the former on the volume excluded by the polymer to the salt, the latter on the volume excluded by one polymer segment to another,[32] this similarity is not surprising. Extension of the treatment used in this paper for polyelectrolyte–salt interactions to segment–segment interactions and hence to molecular dimensions and second virial coefficients of polyelectrolytes may be possible and is under consideration.

Acknowledgment.—The authors wish to express their appreciation to Dr. Moshe Levy for his exploratory experimental work on this problem while a post-doctoral fellow at Rutgers University during 1955 to 1956.

[32] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. XIV.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS, THE STATE UNIVERSITY]

On the Potential of Polyelectrolyte Molecules in Solutions Containing Simple Electrolyte[1]

BY ULRICH P. STRAUSS

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The applicability of recent theories involving a polyelectrolyte model in which the macroion charge is uniformly distributed over a sphere has been tested by comparing the theoretically predicted electrical potential with experimental zeta potential values. The results indicate that the zeta potentials obtained with long-chain polyphosphates in solutions containing simple electrolyte are considerably larger than the theoretical maximum potentials. The discrepancy is explained on the basis that the potential inside a polyelectrolyte coil fluctuates widely, being high near the polymer chain and low in regions which are more than one Debye–Hückel length removed from any portion of the chain. The zeta potential is a measure of the potential very near the polymer chain, while the theoretical potential represents an average over the domain of the polymer coil. As such, the latter gives an over-simplified, unrealistic picture. It is concluded that a more appropriate theoretical model of a polyelectrolyte in solutions of simple electrolyte would be a rather loosely coiled chain, each segment of which is surrounded by a cylindrical double layer.

It is becoming increasingly clear that knowledge concerning the electrical potential of polyelectrolyte molecules is necessary for an understanding of most other polyelectrolyte properties, such as molecular dimensions, molecular interactions and the binding of counterions. The theoretical treatment of this problem usually involves an exact or approximate solution of the Poisson–Boltzmann (P.B.) equation. Two models of the polyelectrolyte molecule generally are used. In the absence of or at low concentrations of simple electrolyte, a cylindrical rod model is employed,[2–4] while at higher electrolyte concentrations a model in which the electrical charge of the polyion is assumed to be uniformly distributed over a sphere is generally believed to be appropriate.[4–9] In this paper data are presented which indicate that the latter model does not give a realistic picture of the potential in long-chain polyphosphate molecules even when the concentration of simple electrolyte is high.

While an exact analytical solution of the P.B. equation for the spherical model is not available, an excellent approximation has been developed recently[9] which is in very close agreement with the numerical solution of Wall and Berkowitz[8] and which allows comparison with experimental data. As an experimental measure of the potential, the zeta potential, based on electrophoresis measurements of long-chain polyphosphates in NaBr and tetramethylammonium bromide (TMABr) solutions,[10] is used. The adequacy of the zeta-potential for this purpose has been demonstrated from a theoretical point of view by Overbeek and Stigter[11] and on experimental grounds by Katchalsky.[12] The volume occupied by the polyelectrolyte molecule, which one must know for the application of the theory, is obtained from viscosity data.[13]

The comparison between the experimental and theoretical values of the potential at 0° is shown in Tables I and II. Table I contains the data for sodium polyphosphate, NaPP-NK8, in aqueous NaBr solutions, while Table II contains the data for

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[1] This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT(30-1)1018.

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

[12] A. Katchalsky, *J. Polymer Sci.*, **12**, 159 (1954).

[13] D. Woodside, Ph.D. thesis, Rutgers, The State University, New Brunswick, New Jersey, 1957.

TABLE I

THE ELECTRICAL POTENTIAL OF NaPP-NK8 IN AQUEOUS NaBr AT 0°

$M_w = 1.02 \times 10^6$; $P_w = 10{,}000$; $L = 25{,}000$ Å.

m	$[\eta]^a$	$V_0 \times 10^{18}$ (cc.)	$\overset{\circ}{R}$	$c \times 10^{-18}$	$c_s \times 10^{-18}$	f	$\left(\frac{e\psi}{kT}\right)_m^b$	$\frac{e\zeta^c}{kT}$	$b \times 10^8$	$\frac{1}{\kappa} \times 10^8$	$b\kappa$
0.0286	5.05	343	434	29.2	17.2	0.851	0.77	2.31	66	18.2	3.6
.0704	2.60	177	348	56.6	42.3	.670	.63	1.99	48	11.6	4.1
.1320	1.54	104	292	95.9	79	.607	.57	1.77	37	8.5	4.4
.1966	0.910	62	245	162.0	118	.686	.64	1.62	28	7.0	4.0

[a] Ref. 13. [b] Calculated by means of equation 8a of ref. 9. [c] Ref. 10.

TABLE II

THE ELECTRICAL POTENTIAL OF TMAPP-K2 IN AQUEOUS TMABr AT 0°

$M_w = 415{,}000$; $P_w = 2700$; $L = 6750$ Å.

m	$[\eta]^a$	$V_0 \times 10^{18}$ (cc.)	$\overset{\circ}{R}$	$c \times 10^{-18}$	$c_s \times 10^{-18}$	f	$\left(\frac{e\psi}{kT}\right)_m^b$	$\frac{e\zeta^c}{kT}$	$b \times 10^8$	$\frac{1}{\kappa} \times 10^8$	$b\kappa$
0.0328	3.76	104	292	26	19.7	0.66	0.62	2.8	71	17.0	4.1
.0918	2.66	74	261	36	55	.33	.33	2.8	59	10.2	5.8
.319	1.83	51	230	53	192	.14	.14	2.8	49	5.46	9.0
.900	1.59	44	220	61	540	.057	.057	2.8	46	3.25	14.0

[a] Ref. 13. [b] Calculated by means of equation 8a of ref. 9. [c] Ref. 10.

tetramethylammonium polyphosphate, TMAPP-K2, in aqueous TMABr solutions. The preparation and characterization of both polyphosphate samples has been described previously.[10]

In each table, the first and second columns contain the molarity of the simple electrolyte, m, and the intrinsic viscosity of the polymer, $[\eta]$, in dl./g., respectively. The third column gives the volume of the effective Einstein sphere occupied by a polymer molecule, calculated from the equation

$$V_0 = \frac{[\eta] M_w}{0.025 N_A} \qquad (1)$$

where M_w is the weight-average molecular weight of the polyelectrolyte and N_A is the Avogadro number. The quantity $\overset{\circ}{R}$ in the next column is the radius of the effective Einstein sphere, expressed in Ångström units. Following Lifson's notation, the concentration c is the local number of fixed polyelectrolyte charges per ml. inside the Einstein sphere and equals P_w/V_0, where P_w is the weight-average degree of polymerization of the polyelectrolyte. The quantity f is defined as $c/2c_s$, where c_s is the simple salt concentration (expressed in molecules per ml.) at points far from the macromolecule where the potential ψ is zero. The theoretical and experimental values of the potential are compared in the eighth and ninth columns, respectively. The quantity $(e\psi/kT)_m$, where e, k and T are the electron charge, Boltzmann's constant and the absolute temperature, respectively, represents the theoretical maximum value of the potential, and has been calculated by means of equation 8a of reference 9.[14] The quantity ζ represents the zeta-potential which has been determined previously by electrophoresis.[10] It is evident that the theoretical maximum values are all considerably smaller than the experimental values.

In view of this discrepancy, an examination of the assumptions underlying the comparison is in order. The use of the zeta-potential as an experimental measure of the potential already has been justified, as has also the use of Lifson's approximation for the calculation of the theoretical value of the potential. The use of equation 1 to calculate V_0 depends on the polymer coil really being a sphere. If the coil was an elongated ellipsoid instead, the value of V_0 by equation 1 would be too large, which would make c and hence f and $(e\psi/kT)_m$ too small. However, in all cases, the Einstein radius R is seen to be very much smaller than the contour length L and under these conditions it is known that the shape of the coil is essentially spherical.[15] Moreover, if the deviation from sphericity of the coil was the cause of the discrepancy between $(e\psi/kT)_m$ and $e\zeta/kT$, one would expect this discrepancy to become smaller with increasing ionic strength. Yet in the case of TMAPP-K2, the discrepancy actually shows a striking increase with increasing electrolyte concentration.

The only remaining conclusion is that the difference between the theoretical and experimental potential is real and that we must look for the cause of the discrepancy in the fact that, in the theoretical treatment, the polyelectrolyte charge is smeared out over the spherical domain of the macro-ion. In reality, the polymer molecule is a chain which is very loosely coiled. Near the chain elements the potential is high, and this is the value of the potential which is measured as the zeta-potential in electrophoresis.[10-12] As one goes away from a chain element perpendicular to the chain, the potential drops off rapidly and vanishes at a distance of the order of $1/\kappa$, the Debye–Hückel radius. The potential stays zero until one comes near another chain element belonging to a different portion of the chain. Thus the potential inside the polymer sphere undergoes wide fluctuations which are completely smoothed out in the theoretical treatment. One would expect that the fluctuations in the potential depend on the relative magnitudes of the Debye–Hückel radius and the average distance between near-by portions of the chain. As a meas-

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(14) The quantity $(e\psi/kT)_m$ is equal to Lifson's function $u(r)$ at $r = 0$, where $u(r)$ has its largest value. It is of interest that the earlier theories[6,7] would give the same values of $u(0)$ as Lifson's theory with the data contained in Tables I and II.

(15) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. XIV.

ure of the latter one may consider the quantity $2b$, where b is defined by the expression

$$\pi b^2 L = V_0 \qquad (2)$$

i.e., one imagines the polymer chain surrounded by a cylindrical envelope of radius b, so that this envelope completely fills out the volume V_0 occupied by the polymer coil. The quantities b, $1/\kappa$ (in cm. units) and their ratio, $b\kappa$, are given in the last three columns of Tables I and II. It is seen that in all cases, b is considerably larger than $1/\kappa$.[16] This means that in a large portion of the solution inside the polymer sphere the potential is equal to or close to zero, just as it is in the solution outside the polymer sphere. If b were smaller than $1/\kappa$, *i.e.*, if $b\kappa < 1$, the potential fluctuations would be smaller and the theoretical treatment involving the smeared out charge would be more appropriate.[17] However, with the large values of $b\kappa$ encountered here, the smeared out charge model does not give even an approximately realistic picture of the behavior of the potential inside the polymer coil. In further support of this argument, it is seen in Table II that the discrepancy between $(e\psi/kT)_m$ and $e\zeta/kT$ increases rapidly with increasing $b\kappa$.

It is therefore concluded that a more appropriate and realistic model of a polyelectrolyte in solutions containing fairly high concentrations of simple electrolyte would be a rather loosely coiled chain, each section of which is enveloped by a double layer of cylindrical symmetry as proposed by Overbeek and Stigter.[11] For many purposes, the curvature of the chain could be neglected and a uniformly charged rod substituted to obtain a first approximation. While the P.B. equation has not yet been solved for this case, a semi-theoretical treatment of Donnan equilibria using this model has produced good results.[18]

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[16] It is noteworthy that this is even true in the 0.1966 *M* NaBr solution in which the polymer is very close to the theta point.[15]

[17] It can be shown that $b\kappa$ is related to f by the equation $(b\kappa)^2 = (4e^2/DkT)(P_W/L)(1/f)$ which reduces to $b\kappa = 3.34\, f^{-1/2}$ in our case. Thus, $b\kappa < 1$ corresponds to $f > 11.2$.

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[CONTRIBUTION FROM THE WATSON LABORATORIES OF INTERNATIONAL BUSINESS MACHINES]

Observations on the Differential Thermal Analysis of Copper Sulfate Pentahydrate

BY ARNOLD REISMAN AND JOAN KARLAK

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An analysis of the applicability of differential thermal analysis to processes involving the depletion of one component is presented using $CuSO_4 \cdot 5H_2O$ as an example. It is demonstrated that the complex nature of the non-equilibrium dehydration process can readily lead to a misinterpretation of the nature of the observed differential peaks. In addition, it is shown that slight variations of experimental conditions affect the results considerably, thereby accounting for the apparent discrepancies between different studies.

Introduction

The thermal behavior of copper sulfate pentahydrate was described in 1936 by Taylor and Klug.[1] On the basis of DTA and weight loss experiments a new hydrate of $CuSO_4$, coördinating four molecules of water, was postulated. Borchardt and Daniels,[2] in a re-evaluation of the earlier work, showed that the differential peak attributed by Taylor and Klug to the transformation

$$CuSO_4 \cdot 4H_2O \xrightarrow{102°} CuSO_4 \cdot 3H_2O + H_2O(v)$$

was in reality due to the process

$$CuSO_4 \cdot 3H_2O + H_2O(l) \longrightarrow CuSO_4 \cdot 3H_2O + H_2O(v).$$

Several years ago, in conjunction with studies of other hydrates, DTA traces of $CuSO_4 \cdot 5H_2O$ were recorded in order to obtain characteristic heating curves of a "known" hydrate. These experiments gave results which were in disagreement with those of the 1936 work and when compared with the later effort, were found to agree insofar as the actual stages of dehydration were concerned, but to disagree markedly with respect to the reported dissociation temperatures.

$CuSO_4 \cdot 5H_2O$ frequently has been used as a classic example in describing isovolumic and isobaric dehydration phenomena. In order to account for the noted discrepancies, and thereby avoid further confusion, it was felt that a critical analysis of the DTA technique, as applied to the isobaric process, was necessary. The experiments to be recounted were not restricted to $CuSO_4 \cdot 5H_2O$. Studies of the hydrates of alkali metal carbonates and alkali niobates gave results which led to the same conclusions, but need not be discussed here.

Experimental Procedure

DTA.—The basic methods and apparatus have been described previously.[3-5] In order to facilitate weighing of the samples after each dehydration step, 1 cc. platinum or gold–20% palladium crucibles were employed which had the thermocouple protective capsules welded centrally in them. A $^1/_8$″ platinum spacer was placed at the bottom of each thermocouple protective well so that the junction rested in the center of the sample. Duplicate experiments were performed with the containers normally employed, and the resulting DTA graphs were identical within experimental limits.

Sample size was varied between 0.25 and 0.5 g., and heating rates of 0.4°/minute or less were used in most "equilibrium" experiments. The data were recorded on a Leeds and Northrop X-Y recorder having a basic X sensitivity of 2.5 mv./10″ and a Y sensitivity of 10 mv./10″. In order to resolve closely occurring heat effects, temperatures were generally measured on the X axis. Differential signals were amplified to provide final sensitivities of 5, 10 or 15 μv./inch. Alundum powder served as ballast in all experiments.

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