Fig. 5.—Dielectric constant of cyclohexane at the freezing point.

(point R to S). After some decrease had taken place, the temperature was further lowered (point S to T), whereupon the rate of decrease of dielectric constant with time became zero. In successive runs, any value of the dielectric constant between 2.0 and 2.1 could be obtained. The longer the cyclohexane was kept in the range of 5.0 to 6.0° the lower value for the dielectric constant could be obtained. No drift in the dielectric constant over several hours was noted at 3° or below.

Discussion of Results

The disagreement between the values obtained in this investigation and those obtained by Seyer and Barrow[1] is largely due to the fact that the value of the dielectric constant for benzene 2.289 accepted at that time was too high. The present value is given as 2.2836 at 20°. Qualitatively, the behavior of the dielectric constant of the three hydrocarbons has been confirmed during the freezing and melting process. During freezing the value of the dielectric constant for the cis-decahydronaphthalene decreases in going from liquid to solid whereas that of the trans form rises as does that of cyclohexane (Figs. 6 and 7).

It has been drawn to our attention that Smyth and Crowe could find no anomalous behavior of cyclohexane during the freezing process.[5] Since
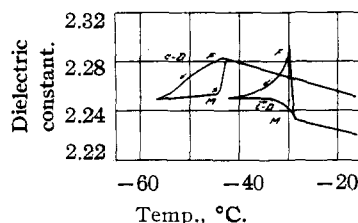

Fig. 6.—Freezing, F, and melting M, of cis- and trans-decahydronaphthalene after Seyer and Barrow.

the m.p. in both cases was 6.5, the divergence in the results may be due to the rate of cooling employed or possibly due to the presence of minute impurities. Thus it has been shown that there is a large increase
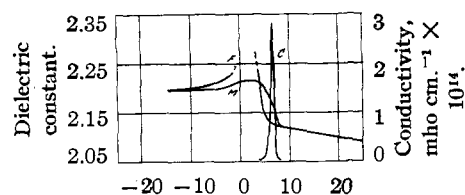

Fig. 7.—Dielectric constant of cyclohexane during freezing, F, and melting, M, after Seyer and Barrow and conductivity of cyclohexane C with excess of water during freezing after Staudhammer and Seyer.

in the electrical conductivity of cyclohexane during the freezing process with traces of water present.

In conclusion, we wish to acknowledge the financial assistance of the Paper-Mate Company of the Gillette Corporation.

Los Angeles 24, California

A Simple Interpretation of Donnan Equilibria Obtained with Long Chain Polyphosphates[1]

By Ulrich P. Strauss and Paul Ander

The distribution of electrolyte across a semi-permeable membrane has been measured carefully for long-chain polyphosphates in aqueous solutions of lithium, sodium, potassium and tetramethylammonium bromide as a function of both polymer and salt concentrations. The conventional interpretation of the results in terms of an effective degree of ionization i leads to an increase of i with increasing electrolyte concentration. A more satisfactory interpretation is obtained by considering the Donnan equilibrium as arising from the volume excluded to the salt by the polyelectrolyte chain and its cylindrical ionic atmosphere.

The interactions between polyelectrolytes and simple electrolytes have been the subject of many

experimental[2-6] and theoretical[7-14] studies. Yet there is still a considerable lack of understanding of

(2) R. M. Fuoss and U. P. Strauss, Ann. N. Y. Acad. Sci., 51, 836 (1949).

(3) D. T. F. Pals and J. J. Hermans, Rec. trav. chim., 71, 433, 458 (1952).

(4) R. Arnold and J. T. G. Overbeek, ibid., 69, 192 (1950).

(5) A. Oth and P. Doty, J. Phys. Chem., 56, 43 (1952).

(6) U. P. Strauss, E. H. Smith and P. L. Wineman, THIS JOURNAL, 75, 3935 (1953).

such interactions. As part of our comprehensive investigation of the long-chain polyphosphates,[15,16] we have performed membrane equilibrium measurements with polyphosphates in solutions of tetramethylammonium (TMA), potassium, sodium and lithium bromide. The thermodynamic interactions determined in this manner are useful for several reasons. First, their interpretation throws further light on the adequacy of molecular models of polyions currently under consideration; second, a comparison with the interactions as determined by other methods, as for instance electrophoresis, clarifies the potentialities and limitations of the various methods; and third, such thermodynamic data are necessary for the proper interpretation of light scattering results.[16]

In this paper, we present results obtained by carefully equilibrating the electrolyte solution containing the polyphosphate against a solution of the same electrolyte without polyphosphate through a membrane impermeable to the macro-ion but permeable to all small ions. While the potassium form of the polyphosphate was used as the starting material in all experiments, conditions were adjusted so that in any experiment only one counter-ion species was present at equilibrium.

Experimental

Materials.—Potassium polyphosphate (KPP) of molecular weight 332,000, prepared by the method of Pfanstiel and Iler,[17] was used throughout this study. To determine the effect of molecular size on the measured quantities a sample of molecular weight 22,400 was included in the 0.35 M NaBr run. Molecular weights were determined from the known viscosity–molecular weight relationship.[18]

The salts used in this study included lithium bromide, C.P., Matheson Co.; sodium bromide, C.P., Matheson Co.; potassium bromide, C.P., Coleman and Bell; tetramethylammonium bromide, reagent grade, Eastman Organic Chemicals.

Membrane Equilibria.—A known volume of aqueous salt solution of the desired concentration was added to a previously weighed quantity of potassium polyphosphate in cellulose tubing (Visking Corp., No. 24). Two glass beads were inserted to aid mixing and the tubing was sealed. After placing the tubing in a large test-tube which contained aqueous salt solution, the test-tube was stoppered and tumbled for approximately 60 hours in a water-bath thermostated at 25°.

Inasmuch as the experimental quantity determined, namely, the difference in bromide concentration between the outside salt solution and the inside salt solution which contained the polymer, was a small value, great care was taken in achieving equilibrium between the outside and inside solutions. Equilibrium was approached from opposite directions by first equilibrating the inside solutions of two different cellulose bags containing the same amount of polymer against solutions of higher and lower concentrations than that desired. During equilibration, the cations of the sol-

(7) J. J. Hermans and J. T. G. Overbeek, *Rec. trav. chim.*, **67**, 761 (1948).

(8) G. E. Kimball, M. Cutler and H. Samuelson, *J. Phys. Chem.*, **56**, 57 (1952).

(9) A. Katchalsky and S. Lifson, *J. Polymer Sci.*, **11**, 409 (1953).

(10) P. J. Flory, *J. Chem. Phys.*, **21**, 1962 (1953).

(11) S. A. Rice and F. E. Harris, *J. Phys. Chem.*, **50**, 725 (1954).

(12) F. Osawa, H. Imai and I. Kagawa, *J. Polymer Sci.*, **13**, 93 (1954).

(13) F. T. Wall and J. Berkowitz, *J. Chem. Phys.*, **26**, 114 (1957).

(14) F. T. Wall, *J. Phys. Chem.*, **61**, 1344 (1957).

(15) U. P. Strauss, D. Woodside and P. Wineman, *ibid.*, **61**, 1353 (1957).

(16) U. P. Strauss and P. L. Wineman, THIS JOURNAL, **80**, 2366 (1958).

(17) R. Pfanstiel and R. K. Iler, *ibid.*, **74**, 6059 (1952).

(18) U. P. Strauss and R. Hubbard, unpublished data.

vent exchanged for the potassium ions of the polyphosphate. The final elimination of potassium ions was confirmed by a flame test. Then, each bag was re-equilibrated against the salt solution of the desired concentration. A slightly modified procedure had to be used when aqueous KBr was the solvent since KPP does not dissolve in aqueous KBr. The polymer was first dissolved in an aqueous solution of NaBr or TMABr whose concentration was the same as that of the desired solvent. After dissolution, 15 to 20 changes of outside KBr solutions, at approximately 4 hour intervals, ensured removal of all cations except potassium. Then, the procedure for reaching equilibrium from opposite directions, as previously described, was employed.

Total phosphate analysis of the outside solvent revealed that diffusion of any phosphate species through the membrane was negligible.

Bromide Analysis.—The bromide concentration was determined potentiometrically by titration with silver nitrate. Silver–silver bromide[19] and glass electrodes were employed. Weighed aliquots of solutions taken from inside and outside the bag were used for analysis. Two milliliters of approximately 6 M nitric acid was introduced into the aliquot. Titration was carried out to near the end-point with an approximately 0.3 M silver nitrate solution, delivered from a weight buret. The titration was completed volumetrically with a semi-micro buret containing silver nitrate of approximately 0.01 M. The silver nitrate solutions were standardized against a standard KBr solution. Rapid magnetic stirring and an electrode striker were used. Duplicate analysis on all samples was carried out to a precision of better than one part in a thousand.

Results and Discussion

Thermodynamics of Membrane Equilibrium.[20]—If we denote the water, the polyelectrolyte and the simple electrolyte as components 1, 2 and 3, respectively, and equate the chemical potentials of component 3 on the two sides of the membrane, we obtain, after power series expansion on the polyelectrolyte side up to first-order terms, the relation

$$\mu_3' = \mu_3 = \mu_3' + \left(\frac{\partial \mu_3}{\partial m_2}\right) m_2 + \left(\frac{\partial \mu_3}{\partial m_3}\right)(m_3 - m_3') \quad (1)$$

Here m_j and μ_j are the molarity and chemical potential of component j, respectively, and the primes indicate quantities on the side without the polyelectrolyte. Equation 1 leads to the working relation

$$\frac{m_3' - m_3}{C_2} = \frac{10 a_{23}}{M_2 a_{33}} \quad (2)$$

where C_2 is the polymer concentration in grams per 100 ml., M_2 is the molecular weight of the polymer and

$$a_{jk} = (1/RT)(\partial \mu_k / \partial m_j)$$

Since higher than first-order terms were neglected in equation 1, equations 1 and 2 are strictly accurate in the limit of infinite dilution of polymer only. If one defines the polyelectrolyte component so that iP of its P phosphate groups are ionized and the remaining $(1 - i)P$ groups un-ionized, equation 2 can be expanded into the form

$$\frac{m_3' - m_3}{C_2} = \frac{10}{M_2} \frac{iP + \beta_{23} m_3}{2 + \beta_{33} m_3} \quad (3)$$

where $\beta_{jk} = \partial \ln \gamma_j / \partial m_k$, γ_j being the activity coefficient of component j. Frequently, β_{23} and β_{33} are assumed to be zero, i.e., all the deviations from ideality are lumped into an effective "thermodynamic" degree of ionization, which, in our case,

(19) A. S. Keston, THIS JOURNAL, **57**, 1671 (1935).

(20) A similar treatment has been given by G. Scatchard [*ibid.*, **68**, 2315 (1946)].

would be given by the expression

$$i = 23.6 \left(\frac{m_3' - m_3}{C_2} \right) \tag{4}$$

since M_2/P is 118, the molecular weight of a KPO_3 unit. It is one of the aims of this work to test the validity of the assumptions needed to obtain equation 4 from equation 3.

Effect of Polymer Concentration.—The dependence of the quantity $(m_3' - m_3)/C_2$ on C_2 is illustrated in Fig. 1 with the behavior of the poly-
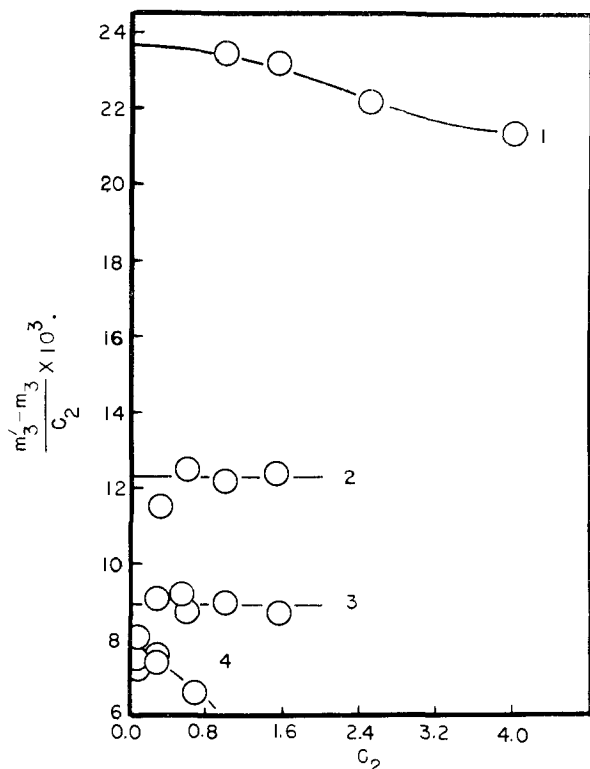

Fig. 1.—Dependence of $(m_3' - m_3)/C_2$ on the polymer concentration C_2 in: (1) 1.49 M LiBr; (2) 0.40 M LiBr; (3) 0.10 M LiBr; (4) 0.02 M LiBr.

phosphate in four lithium bromide solutions. At intermediate electrolyte concentration, the lines are horizontal, but at both very high and very low electrolyte molarity, $(m_3' - m_3)/C_2$ decreases with increasing C_2. While this negative slope in the 0.02 M LiBr is based on only one point corresponding to the highest polymer concentration—(the point, however, being the result of two independent experiments in which equilibrium was approached from opposite direction)—negative slopes under similar conditions were also observed in the solutions of the other electrolytes and hence seem significant.[21]

Effect of Simple Electrolyte.—The effect of the simple electrolyte on $[(m_3' - m_3)/C_2]_0$, the value of $(m_3' - m_3)/C_2$, extrapolated to infinite dilution of polymer, is given in Table I.

An important feature of these results is the increase of $[(m_3' - m_3)/C_2]_0$ with the electrolyte con-

(21) In the light of the subsequent discussion, we believe the decrease of $(m_3' - m_3)/C_2$ at the higher polymer concentrations to be due to overlap of the ionic atmospheres of different polyions.

TABLE I

MEMBRANE EQUILIBRIUM RESULTS

Electrolyte	m_3'	$[(m_3' - m_3)/C_2]_0$ $\times 10^3$	i^a
LiBr	0.02013	7.7 ± 0.8	0.18
	.10236	8.9 ± .5	.21
	.3968	12.0 ± .8	.28
	1.4898	23.5 ± 1.0	.56
NaBr	0.02043	6.5 ± 1.5	.15
	.07913	7.2 ± 0.5	.17
	.2507	9.1 ± .7	.22
	.3469	9.7 ± .8	.23
	.3449^b	9.8 ± .3	.23
	.3991	9.6 ± .3	.23
KBr	.01965	6.8 ± .7	.16
	.10160	8.2 ± .4	.19
	.2377	9.7 ± .5	.23
TMABr	.02019	11.0 ± .8	.26
	.05659	12.4 ± .9	.39
	.19306	18.2 ± .5	.43
	.5216	29.4 ± .5	.69
	.9692	43.0 ± 1.2	1.02

^{a} Calculated by means of equation 4. ^{b} In this run potassium polyphosphate of molecular weight 22,400 was used.

centration.[22] Therefore, the effective thermodynamic degree of ionization i determined by equation 4 does not behave according to the law of mass action.[23] Also the value of i at the highest TMABr concentration is unreasonably large. Thus, the treatment of this type of membrane equilibrium data to obtain information about counterion binding according to equation 4 appears to be unsound.[24]

It therefore appears that the β_{jk}-terms in equation 3 cannot be neglected. While the β_{33}-term can be determined experimentally, the β_{23}-term has to be arrived at by theoretical considerations. If the distribution of ions in the neighborhood of the polymer chain were known, the activity coefficients could be calculated.[25] On the basis of experimental results, it can be shown[26] that the most appropriate and realistic model 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.[27] Since the curvature of the coil is generally small compared to the dimensions of the double layer and the double layers belonging to different chain segments do not overlap, a uniformly charged rod would be a good approximate model for the purpose of calculating poly-

(22) Malmgren found the quantity $(m_3' - m_3)/C_2$ to be essentially constant with an increase in salt concentration for the system potassium polyphosphate–sodium chloride–water. Although his values below 0.1 molar salt concentration approximate ours, those above are in disagreement with our experimental results. There is nothing in Malmgren's paper to indicate that his solutions were tumbled. We therefore suspect that in some of his experiments equilibrium was not attained [H. Malmgren, Acta Chem. Scand., 6, 1 (1952)].

(23) In contrast, the degree of ionization as determined from electrophoresis measurements follows qualitatively the theoretical expectations, decreasing rapidly with increasing electrolyte concentration in the case of lithium, sodium and potassium bromide where there is specific site-binding, and decreasing extremely slowly in the case of TMABr where there is apparently no site-binding.[15]

(24) Under certain conditions, membrane equilibria involving more than one counterion may be used to measure counterion binding (U. P. Strauss and P. Ross, unpublished results).

(25) R. A. Marcus, J. Chem. Phys., 23, 1057 (1955).

(26) U. P. Strauss, THIS JOURNAL, in press.

(27) J. T. G. Overbeek and D. Stigter, Rec. trav. chim., 75, 543 (1956).

electrolyte–salt interaction. However, the distribution of ions around such a rod in the presence of simple electrolyte has not yet been theoretically treated.[28]

Nevertheless, it is possible to predict the form of the dependence of the membrane equilibrium results on the pertinent parameters by the following considerations. One imagines the polymer chain surrounded by a cylindrical shell of radius r chosen so as to include as many counterions as were part of the original polymer. The volume of the shell is considered to be excluded to the salt.[29] Thus the salt is compressed from its stoichiometric concentration, m_3, to an effective higher concentration m_3'. A salt solution containing no polymer which is in equilibrium with the salt–polymer solution through a membrane will then also have the concentration, m_3'.[30] These considerations can be expressed quantitatively by the relation

$$m_3' = m_3 \left(\frac{V_0}{V_0 - V_p} \right) \qquad (5)$$

where V_p is the volume of all the polymer molecules and their shells contained in a solution volume, V_0. Equation 5 can be simplified to the form

$$m_3' - m_3 = m_3' \left(\frac{V_p}{V_0} \right) \qquad (6)$$

If one expresses V_p/V_0 in terms of our cylindrical shell model, one obtains the relation

$$\frac{m_3' - m_3}{m_3'} = \frac{N_A \pi r^2 a C_2}{100 M_{20}} \qquad (7)$$

where N_A is Avogadro's number, a is the length of one monomer unit in the polymer chain and M_{20} is the equivalent weight of the polyelectrolyte.

In the absence of a complete quantitative theory, an assumption concerning the radius of the shell becomes necessary. Based on our model, the most likely form for this quantity is

$$r = d + \frac{s}{\kappa} \qquad (8)$$

where d represents the effective radius of the polyelectrolyte rod, κ is the reciprocal Debye–Hückel length and s is a constant with an expected order of magnitude of unity.

Substituting equation 8 into equation 7, expressing κ in terms of m_3' for water at 25°,[31] substituting the value of 2.5×10^{-8} for a and the value of 118 for M_{20}, and taking square roots, we obtain the

(28) In the absence of electrolyte, the Poisson–Boltzmann equation has been solved for the rod model [R. M. Fuoss with A. Katchalsky and S. Lifson, *Proc. Natl. Acad. Sci.*, **37**, 579 (1951); T. A. Alfrey, Jr., P. W. Berg and H. Morawetz, *J. Polymer Sci.*, **7**, 543 (1953)].

(29) Strictly speaking, the volume of the shell excludes the counterions of the salt. One could also focus one's attention on the distribution of by-ions which are repelled by the polyion, approximate this distribution by a step-function, and define an effective radius of a cylindrical shell from which the by-ions are excluded. This radius would be somewhat smaller than the radius excluding the counterions. For our purposes, it makes no difference whether one chooses either of these radii or their average value for the radius of the shell.

(30) This treatment assumes that the species inside the shell is electro-neutral. Actually, some by-ions will be inside the shell, so that this condition is not strictly fulfilled. However, the net-charge inside the shell will be so small that, to a first approximation, it can be neglected.

(31) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 33.

relation

$$\left(\frac{m_3' - m_3}{m_3' C_2} \right)^{1/2} = 0.0201 \times 10^8\, d + \frac{0.061 s}{(m_3')^{1/2}} \qquad (9)$$

This equation predicts correctly the increase of $(m_3' - m_3)/C_2$ with m_3'. It also predicts that a plot of the left-hand side against $(m_3')^{-1/2}$ should be linear. Such plots are shown in Fig. 2. Linearity
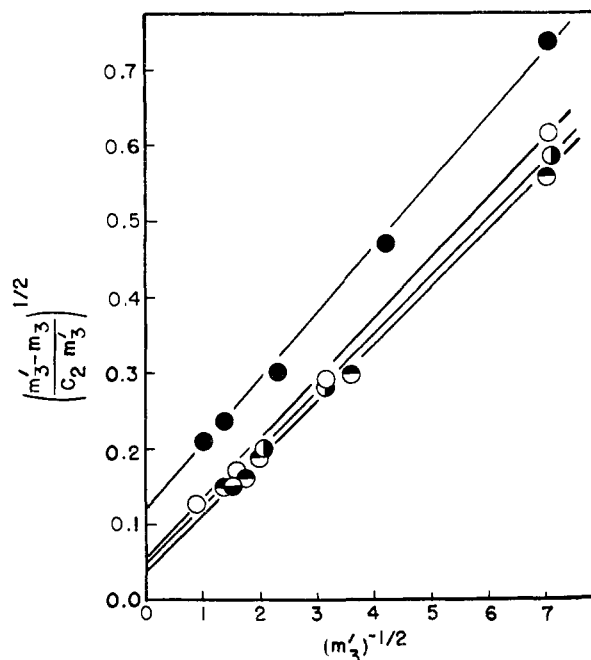

Fig. 2.—Test plot of equation 9 in: ●, TMABr ($M_2 = 332{,}000$); ○, LiBr ($M_2 = 332{,}000$); ◑, KBr ($M_2 = 332{,}000$); ◐, NaBr ($M_2 = 332{,}000$); ◒, NaBr ($M_2 = 22{,}400$).

is obtained over the whole range of salt concentrations investigated. The values of d and s, calculated from the intercepts and slopes of these lines, are listed in Table II.

TABLE II

PARAMETERS OF EQUATION 9

Salt	Intercept	Slope	$d \times 10^8$ (cm.)	s
LiBr	0.065	0.078	3.2 ± 0.4	1.28
NaBr	.049	.074	$2.4 \pm .3$	1.21
KBr	.050	.074	$2.5 \pm .3$	1.21
TMABr	.135	.083	$6.7 \pm .3$	1.36

The quantity s is of the order of unity, as expected, and seems to be fairly independent of the nature of the cation. The distance d is also of the right order of magnitude, and is about the same for the three alkali metal ions, but definitely larger for the TMA$^+$ ion. Possibly its interpretation as the radius of the polyelectrolyte rod should be broadened to include the effective diameter of any closely bound cations; or it might be the distance from the axis of the polyelectrolyte to the point where the potential has reached a certain value. In any case, d seems to be a measure of the short-range interactions between the polyion and the counterions.

The fact that d and s are of the expected order of magnitude is additional evidence for the essential soundness of the assumptions underlying equation

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.

[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

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

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

(2) R. M. Fuoss, A. Katchalsky and S. Lifson, *Proc. Natl. Acad.*, **37**, 579 (1951).

(3) T. Alfrey, P. W. Berg and H. Morawetz, *J. Polymer Sci.*, **7**, 543 (1951).

(4) F. Oosawa, *ibid.*, **23**, 421 (1957).

(5) J. J. Hermans and J. Th. G. Overbeek, *Rec. trav. chim.*, **67**, 761 (1948).

(6) G. E. Kimball, M. Cutler and H. Samelson, *J. Phys. Chem.*, **56**, 57 (1952).

(7) F. Oosawa, N. Imay and I. Kagawa, *J. Polymer Sci.*, **13**, 93 (1954).

(8) F. T. Wall and J. Berkowitz, *J. Chem. Phys.*, **26**, 114 (1957).

(9) S. Lifson, *ibid.*, **27**, 700 (1957).

(10) U. P. Strauss, D. Woodside and P. Wineman, *J. Phys. Chem.*, **61**, 1353 (1957).

(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.