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A Chain Model for Polyelectrolytes. VI. Some Studies of Counterion Activity and Counterion Binding in Polyethyleneimine Salts^{1a}

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In this paper we report measurements of Cl^- activity coefficients, γ_{Cl^-} , for the hydrochloride of polyethyleneimine, ethylenediamine, diethylenetriamine, triethylenetetramine and tetraethylenepentamine. A simple model of the doubly charged bolaform species in quantitative agreement with the dependence of γ_{Cl^-} on charge separation and in semiquantitative agreement with the absolute value of γ_{Cl^-} . A second model, designed for the discussion of highly charged ions, predicts correctly all trends in γ_{Cl^-} with increasing charge. As a result of the experiments and calculations, a new interpretation of the meaning and utility of counterion binding is presented. This new interpretation agrees with all known data and removes the apparent conflict between purely electrostatic and site binding theories.

I. Introduction

All current theories of polyelectrolyte behavior are based on highly simplified models of the structure of the macromolecule.^{1d} In contrast, most experimental investigations have dealt with complex polymers in which the charges are in separate side chains and in which purely steric effects may play a significant role in determining the polymer configuration. Further, examination of the literature readily reveals that although the differences between the properties of polyelectrolytes and of simple electrolytes are universally recognized, there have been no studies of the transition from one to the other. In this and subsequent papers we shall describe experimental and theoretical investigations of the polyelectrolytes formed from neutralized polyethyleneimine. This substance is of interest for two reasons. First, when charged it corresponds very closely to theoretical models since there are no side groups, the charge is on the chain, all bond angles are the same and, aside from the small difference in CN and CC bond lengths, the polymer skeleton is microscopically uniform. Second, very low molecular weight analogs may be obtained and the transition from simple electrolyte to polyelectrolyte studied. In this paper we report studies of counterion activity coefficients and counterion binding in the hydrochlorides of polyethyleneimine, ethylenediamine, diethylenetriamine, triethylenetetramine and tetraethylenepentamine, as well as a theoretical analysis of the results obtained. In future papers we shall report the results of nuclear resonance, diffusion, sedimentation, conductance, viscometric and osmotic experiments.

II. Experimental Details

A. Activity Coefficient Measurements.—Samples: The samples of ethylenediamine (ED), diethylenetriamine (DT), triethylenetetramine (TT) and tetraethylenepentamine (TP) were obtained from Eastman Kodak Co. They were purified by distillation under reduced pressure of nitrogen. The first two amines are colorless liquids whereas TT and TP are slightly yellow. These last two compounds were analyzed with the results: TT, found: C, 49.7; N, 37.4; H, 12.2. Calcd.: C, 49.3, N, 38.4; H, 12.3. TP, Found: C, 51.3; N, 35.1; H, 12.4. Calcd.: C, 50.8;

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N, 37.0; H, 12.2. Since the boiling points of ED and DT, respectively, were quite sharp, analysis was deemed to be unnecessary.² They were considered to be 100% pure. The hydrochlorides of ED and DT were prepared by adding equivalent amounts of hydrochloric acid. For the preparation of the hydrochlorides of TT and TP a different procedure³ was adopted, since the results of the analysis quoted indicated the presence of impurities. In these cases hydrochloric acid diluted with equal quantities of water and ethanol was added slowly to a solution of the amine in ethanol. The temperature of the container was maintained at less than 10° throughout the reaction. The product was filtered by suction and purified by repeated solution in a minimum volume of hot water and precipitation with cold ethanol. It was then washed with acetone and absolute ethanol.

The hydrochlorides were dried in a vacuum oven at 90° until constant weight was obtained. Assuming complete purity stoichiometric 0.1 *N* solutions of both salts were titrated potentiometrically with 0.1 *N* silver nitrate and within the limits of experimental error the concentrations were found to be identical. The hydrochlorides of TT and TP are white substances but yield upon dissolving in water slightly yellow solutions. In order to prepare the dihydrochlorides of TT and TP the tetra- and pentahydrochlorides, respectively, were converted to the respective bases by passing through a column containing anion exchange resin in the hydroxide form. To these bases hydrochloric acid was added while the pH was measured, use being made of the titration curves (see below). The polyethyleneimine (PEI) used was a gift from the Chemirad Corporation, East Brunswick, N. J. The sample was an aqueous solution containing about 50% of water; its molecular weight is estimated to be in the range 30–40,000. Since purification of PEI by distillation is not possible, the aqueous solution was passed through columns containing cation and anion exchange resins in the hydrogen and hydroxide forms, respectively. To obtain PEI(HCl) the solution of PEI prepared in this way was analyzed for nitrogen to determine the concentration and, thereafter, an equivalent amount of HCl was added.

All stock solutions were 1 *N* in chloride ions, the exact concentration being determined by a potentiometric titration with AgNO_3 . In order to obtain molalities, densities were measured.

There remain a few words to be said on the titration curves of these compounds (Fig. 1). In the case of ED and DT 0.1 *N* solutions were titrated with 0.1 *N* HCl. The titration curve of ED shows, as expected, two inflection points corresponding to the first and second hydroxyl groups, respectively. The titration curve of DT, on the other hand, has only one such point which appears at the place where two-thirds of the base has been neutralized, *i.e.*, when in all probability the two end nitrogens are charged. Since we did not have pure TT and TP, the respective 0.1 *N* solutions of hydrochlorides were back titrated with a 0.1 *N* solution of sodium hydroxide. In the titration curve of TT(HCl), two inflection points appear corresponding to half and three-quarters of the equivalent amount of NaOH being added.

(2) G. D. Jones, A. Langsjoen, M. M. C. Neumann and J. Zomlefer, *J. Org. Chem.*, **9**, 125 (1944).

(3) C. N. Reilly and J. H. Holloway, *THIS JOURNAL*, **80**, 2917 (1958).

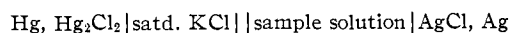
The titration curve of TP(HCl)₃ again has only one inflection point at the place where two-fifths of the equivalent amount of NaOH has been added. The aqueous solution of PEI was titrated with HCl. The rate of change of pH with added acid is rather large. This behavior has been described and interpreted by other authors.⁴

Electrodes.—Silver-silver chloride electrodes, used in the measurements of the activity of the chloride ions, were prepared from commercial Beckman silver electrodes. The electrodes were coated with AgCl by serving as anodes in the electrolysis of a saturated potassium chloride solution, another silver electrode being used as the cathode. In this way, silver-silver chloride electrodes were obtained whose standard potential was reproducible within ± 0.1 mv. This precision was considered to be satisfactory in view of the ambiguities arising from the liquid junction potential in our cell. Further aspects of this will be discussed below. While not in use, the electrodes were stored in dilute HCl.

As reference electrode, a saturated potassium chloride calomel electrode prepared in the standard way was used.

The hydrogen electrode was of the Hildebrand type. A finely divided deposit of platinum black was obtained by electrolysis of a 5% solution of chloroplatinic acid with the electrode serving as cathode. When not in use, it was stored in distilled water. In connection with it, electrolytic hydrogen was used from which carbon dioxide and oxygen, respectively, were removed by passage through tubes containing soda-lime and heated palladium on asbestos.

Description of Cell and Measurements.—The cell used to obtain the Cl⁻ activity in our experiments was



This is a cell with transference. Assuming, however, that the liquid junction potential between a Cl⁻ solution and a saturated KCl solution has a constant (presumably small) value for different concentrations of the same sample, its electromotive force (e.m.f.) can be expressed as

$$E = E^0 - (RT/F) \ln a_{\text{Cl}^-} \quad (1)$$

where E^0 is the corrected standard e.m.f. of the above cell. Studies of liquid junction potentials in other solutions of polyelectrolytes suggest that their values are probably small.⁵ Thus, the activity coefficients of Cl⁻ in the solutions of PEI(HCl) should not be greatly influenced by this uncertainty. The case of the small amines is even more complicated. Since we have at our disposal no data on the transference numbers of these compounds, even an estimate of the error involved in neglecting the liquid junction potentials is hardly possible. However, we may assume that they do not differ too much from one another since the structures are similar and that those differences which do exist do not change with concentration. Such differences could cause only a parallel shift of the values of chloride activity obtained without altering the general trend with increasing distance between the charges (dihydrochlorides) or increasing number of charges, respectively. Furthermore, the use of a saturated potassium chloride bridge and the occurrence of chloride ion in the sample solutions renders such an assumption even more plausible.

The electrodes were immersed in the solutions contained in a glass cell having the form of the letter H. The e.m.f. was recorded one minute after immersion and then again after ten minutes. The difference between the two readings usually did not exceed ± 0.2 mv. The reproducibility was also of the same degree of precision. A longer contact between the silver-silver chloride electrode and the solutions was avoided to prevent any complexing of the electrode surface by the amines. The corrected standard e.m.f., E^0 , was determined in two ways. First, a series of measurements was made with solutions of KCl. The values of the e.m.f. measured were plotted *versus* $\log a_{\text{Cl}^-}$. As the result, a straight line was obtained with the slope 59.0 ± 0.2 mv., the intercept with the axis of ordinate giving E^0 .

Second, the potentials of both electrodes were determined using the standard hydrogen electrode and a solution of 0.1 N HCl. From these measurements a value of E^0 , differing only by ± 0.2 mv. from the value obtained by the first

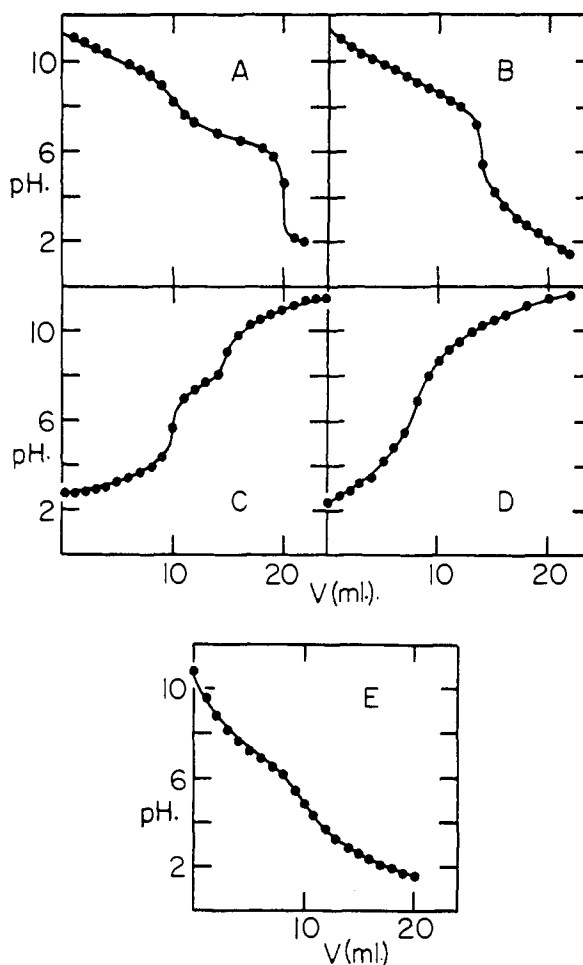


Fig. 1.—Titration curves of amines and PEI: A, ED (HCl); B, DT (HCl); C, TT (NaOH); D, TP (NaOH); E, PEI (HCl).

method, was found. The same agreement was also obtained in subsequent checks. However, it is not superfluous to repeat again that both determinations suffer from the same ambiguity owing to the occurrence of the liquid junction potential.

Apparatus.—The e.m.f.'s were measured with a Leeds-Northrup K-3 potentiometer in conjunction with a Leeds-Northrup Stabilized D-C Microvolt Amplifier serving as null detector, the maximum sensitivity of the latter being $1 \mu\text{v.}$ per mm. of scale deflection. All e.m.f. measurements were made in a water bath maintained at $25 \pm 0.02^\circ$. All pH measurements were made with a Beckman model GS pH meter.

B. Counterion Binding Measurements.—As in previous work,⁶ the extent of counter ion binding was determined by measurement of the tracer diffusion coefficient of the counterion using the method of Huizenga, Grieger and Wall.⁷

Apparatus and Methods.—The diffusion cell consists of a closed glass tube divided into two compartments by a glass frit sealed at the center. Polymer solution containing Cl³⁶ is placed in one side (side "a") and non-tagged solution in the other side (side "b"). Each compartment contains several pieces of glass rod whose stirring action, generated by continuous end over end rotation of the cell, limits diffusion to within the frit. At the end of a diffusion experiment, 2 ml. aliquots of the contents of side "b" were evaporated in dishes and the activity determined with a Baird-Atomic proportional counter. The ratio of this activity to that of the contents of side "a" at the start is used in eq. 6 of Huizenga,

(4) A. Katchalsky, J. Mazur and P. Spitnik, *J. Polymer Sci.*, **23**, 513 (1957); E. J. Shephard and J. A. Kitchener, *J. Chem. Soc.*, 2448 (1956).

(5) M. Nagagawa, S. Ozawa, K. Kimura and I. Kagawa, *Mem. Fac. Eng. Nagoya Univ.*, **8**, 50 (1956) (in English).

(6) M. Nagasawa and S. A. Rice, *THIS JOURNAL*, **82**, 5207 (1960).

(7) J. R. Huizenga, P. F. Grieger and F. T. Wall, *ibid.*, **72**, 4228 (1950).

Grieger and Wall to calculate the fraction of unassociated ions, $1 - f$. Five different cells were used; $1 - f$ for each solution was determined in duplicate diffusion runs, and duplicate aliquots of the solutions were always taken. The cells were continuously tumbled in an air conditioned room maintained at $25 \pm 2^\circ$.

The procedure followed was to add a small amount (less than 4% of the total Cl^- present) of HCl^{36} to the portion of polymer solution for side "a," and the concentration of the solution for side "b" was accordingly adjusted to prevent gradients in concentration for any of the species present. The cell constants were determined using 0.05 *N* NaCl; the tagged HCl added to the "a" solution was neutralized to prevent loss by evaporation and the concentration of the "b" solution was adjusted accordingly. With the procedure described the greatest source of imprecision was variations in the condition of the frits; the polymer tended to become trapped in the pores and ground glass could be loosened by strong alkaline cleaning agents. The cell constant of each cell was determined at intervals of 2-3 diffusion runs with polymer and was used to calculate $1 - f$ for these runs. The variations in cell constant were restricted to a spread of 5% when acid cleaning agents were used. Since activity determinations always involved more than 10^4 counts, the random counting error does not exceed 1%. With diffusion runs of 1.3 to 1.6 days, the over-all accuracy of the binding data may be taken as $\pm 5\%$.

III. Experimental Results

The ionic molal activity coefficients of Cl^- for the dihydrochlorides are given in Table I. The most characteristic feature of the tabulated values

TABLE I

MOLAL ACTIVITY COEFFICIENTS OF CHLORIDE IONS IN SOLUTIONS OF DIHYDROCHLORIDES

	Molality	ED(HCl) ₂	DT(HCl) ₂	TT(HCl) ₂	TP(HCl) ₂
1	1.0	0.437	0.428		
2	0.8	.453	.451		
3	.6	.479	.482		
4	.5	.497	.501	0.484	
5	.4	.525	.525		
6	.3	.565	.557		
7	.2	.610	.602	.601	0.591
8	.1	.683	.686	.680	.685
9	.08	.703	.709	.702	.712
10	.06	.736	.741	.735	.749
11	.05	.754	.757	.756	.767
12	.04	.774	.778	.770	.792
13	.03	.796	.800	.801	.823
14	.02	.820	.828	.836	.856
15	.01	.873	.879	.890	.900
16	.009	.875	.886	.896	.907
17	.008	.878	.896	.901	.918
18	.007	.882	.908	.914	.929
19	.006	.891	.921	.925	.943
20	.005	.904	.936	.942	.960

is that below a certain concentration ($0.03 m$), the sequence is such that γ_{Cl^-} for ED(HCl)₂ is the smallest and for TP(HCl)₂ the largest. The differences between the values generally are too large to be accounted for by the experimental error inherent in all measurements, *i.e.*, ambiguities arising from the occurrence of the liquid junction potential. If we further assume that the two end nitrogen atoms are charged, an assumption which seems justified from the point of view of interaction energy considerations and which seems to be confirmed by the form of the titration curves, we may conclude that at the same concentration activity coefficients of Cl^- increase with increasing distance between the changes on the cation. A

theoretical discussion of this case will be given below.

The ionic molal activity coefficients of Cl^- in solutions of fully neutralized amines and PEI(HCl) are given in Table II. Here, the general trend is in accord with expectation. With increasing number of charges on the cation, the counterion activity coefficients at the same concentration become smaller. The differences between the activity coefficients of Cl^- in the solutions of the amines are seen to be rather small. In the case of DT(HCl)₃ an anomaly has been encountered: in the concentration range below $0.7 \times 10^{-3} m$ the activity coefficients of Cl^- are seen to be slightly larger than those of DT(HCl)₂. This we believe can be attributed to experimental error.

TABLE II

MOLAL ACTIVITY COEFFICIENTS OF CHLORIDE IONS IN SOLUTIONS OF AMINE HYDROCHLORIDES AND PEI(HCl)

	Molality	ED-(HCl) ₂	DT-(HCl) ₂	TT-(HCl) ₂	TP-(HCl) ₂	PEI-(HCl)
1	1.0	0.437	0.414	0.382	0.365	0.298
2	0.8	.453	.437	.401	.382	.300
3	.6	.479	.465	.426	.408	.302
4	.5	.497	.481	.442	.423	.304
5	.4	.525	.502	.464	.441	.308
6	.3	.565	.531	.492	.479	.314
7	.2	.610	.566	.538	.528	.321
8	.1	.683	.649	.607	.589	.337
9	.08	.703	.675	.634	.610	.339
10	.06	.736	.707	.667	.638	.343
11	.05	.754	.727	.685	.655	.351
12	.04	.774	.750	.710	.676	.360
13	.03	.796	.779	.744	.702	.374
14	.02	.820	.813	.786	.758	.391
15	.01	.873	.866	.844	.823	.428
16	.009	.875	.870	.849	.828	.433
17	.008	.878	.876	.859	.836	.440
18	.007	.882	.886	.869	.848	.448
19	.006	.891	.898	.883	.864	.457
20	.005	.904	.908	.901	.883	.467
21	.004					.479
22	.003					.496
23	.002					.516
24	.001					.562

Though in solutions of TP(HCl)₅ the cation already has 5 charges its influence on the activity coefficients of Cl^- is not nearly so large as in the case of the polyion. In other words, the differences between the respective counterion activity coefficients are still large. A plot of the activity coefficients of Cl^- in PEI(HCl) and TP(HCl)₅ solutions *versus* m_{Cl^-} is given in Fig. 2. It may be seen that the values of activity coefficients increase rather slowly and that even at a concentration of $1 \times 10^{-3} m$ the counterion activity is still low. There is another feature which should be noted. It has been reported in some cases that the activity coefficients of counterions to polyelectrolytes decrease with decreasing concentration.⁸ For the compounds described herein, such behavior has not been observed. But, the case of PEI(HCl) is somewhat different from those previously reported. Whereas the amines are mod-

(8) M. Nagasawa and I. Kagawa, *J. Polymer Sci.*, **24**, 61 (1957).

erately strong bases and hydrolysis in solutions of their respective hydrochlorides may be neglected, PEI, on the other hand, is a very weak base and a non-negligible amount of hydrolysis occurs. The degree of hydrolysis can be estimated by measuring the pH of single solutions. These values are given in Table III. We may compare this situation with that of a polyelectrolyte solution with added simple electrolyte, in which case behavior similar to that described above has been observed.⁹

TABLE III
 pH AND DEGREE OF HYDROLYSIS OF SOLUTIONS OF PEI(HCl)

	Molarity	pH	Degree hydrolysis
1	1.0	0.79	0.16
2	0.8	.82	.19
3	.6	.90	.21
4	.5	.99	.21
5	.4	1.09	.21
6	.2	1.34	.23
7	.1	1.61	.25
8	.08	1.68	.26
9	.06	1.79	.27
10	.05	1.89	.26
11	.04	1.99	.26
12	.02	2.28	.26
13	.01	2.59	.26
14	.008	2.69	.26
15	.006	2.78	.28
16	.005	2.86	.28
17	.004	2.93	.29
18	.002	3.18	.33
19	.001	3.44	.36

We turn now to a discussion of the results of the counterion binding experiments as listed in Table IV. It is readily seen that the degree of binding parallels the behavior of the counterion activity coefficient, *i.e.*, there is a slow increase as the number of charges on the polyion increases, but the values for TP(HCl)₅ are very far from those of PEI(HCl). This observation confirms and extends the results of Nagasawa and Rice⁶ which showed that the amount of counterion binding was not determined solely by the local charge density. The present experiments indicate that a charged chain of length greater than 5 is needed for any considerable amount of counterion binding. *In our opinion these results completely rule out previous suggestions of discrete ion-pair formation with a one to one correspondence between ion-pairs and charged sites along the polymer skeleton.* The experiments do not preclude an interpretation of binding in terms of loose association of counterion with long segments of charged chain. In this interpretation, the distribution of ions about the charged polymer skeleton is arbitrarily cut off at a given distance and ions within this radius are considered bound while those outside are considered substantially free. We note that this criterion is the same as that used by Fuoss in the theory of simple electrolytes.

Before closing this section it is pertinent to make two remarks. First, because the PEI(HCl) is partially hydrolyzed, the amount of binding

(9) M. Nagasawa, M. Izumi and I. Kagawa, *J. Polymer Sci.*, **37**, 375 (1959).

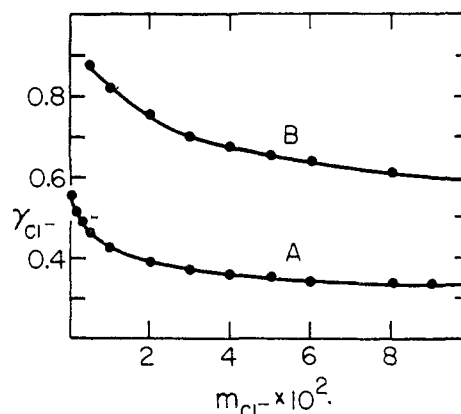


Fig. 2.—Activity coefficients of Cl⁻ in solutions of (A) PEI(HCl) and (B) TP(HCl)₅.

should be compared with that of, say, sodium polyacrylate at 75% neutralization. For this compound, at three-fourths full charge, f is approximately 0.5, in agreement with our results. Since the linear charge densities of PEI(HCl) and sodium polyacrylate are almost the same, this agreement

TABLE IV
FRACTION OF COUNTERIONS BOUND, f , TO AMINE HYDROCHLORIDES

Compound	f
ED(HCl) ₂	0.00 ± 0.01
DT(HCl) ₃	.00 ± .01
TT(HCl) ₄	.00 ± .01
TP(HCl) ₅	.10 ± .01
PEI(HCl)	.54 ± .02

is as expected. Second, we wish to point out that the extent of binding is not totally independent of the local charge density. In a series of experiments, Wall and Doremus¹⁰ determined the binding of sodium ion to various polyphosphates. They found that f was approximately 0.05, 0.21, 0.29 and 0.71 for Na₂HPO₄, Na₄P₂O₇, Na₅P₃O₁₀ and polymer, respectively. In this case the local charge density is inhomogeneous and the over-all linear charge density rather higher than in PEI(HCl). In view of the small increase in binding with considerable increase in linear charge density for sodium polyacrylate ($f = 0.5$ at $\alpha = 0.75$, $f = 0.6$ at $\alpha = 1$), we attribute the larger binding of the polymer and the larger binding of the low molecular weight analogs to the charge inhomogeneity. Further discussion is reserved to a later section of this paper.

IV. A Simple Model of the Doubly Charged Ions

Beginning with a paper on zwitterions in 1932,¹¹ Kirkwood has published extensively on the extension of the Debye-Hückel theory to complex electrolytes.¹² Most of the models dealt with have been of spherical symmetry, and those for which more general geometries were considered have been restricted to the case of zero net charge. In

(10) F. T. Wall and R. H. Doremus, *J. Am. Chem. Soc.*, **76**, 868 (1954).

(11) G. Scatchard and J. G. Kirkwood, *Physik. Z.*, **33**, 297 (1932).

(12) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934); "Proteins, Amino Acids and Peptides," Ed. E. J. Cohn and J. T. Edsall, Reinhold Publishing Corp., New York, N. Y., 1943, chapter 12.

the following we present a simple model of the doubly charged ion, idealized as an ellipsoid of revolution. For the substances considered in this paper, such a model is superior to those considered by other authors.

Consider then an ellipsoid of revolution with one charge at each focus. Inside the ellipsoidal surface and excluding the singularities due to the charges at the foci, the potential satisfies the Laplace equation

$$\nabla^2\psi = 0 \tag{2}$$

whereas external to the ellipsoidal surface the potential satisfies the linearized Poisson-Boltzmann equation

$$\nabla^2\psi = \kappa^2\psi \tag{3}$$

$$\kappa^2 = \frac{4\pi}{DkT} \sum_i c_i^0 (z_i q)^2 \tag{4}$$

with D the dielectric constant of the medium, q the unit charge, z_i the valence and c_i^0 the bulk concentration of the ionic species labelled i . Let the semi-major axis of the ellipsoid be \mathbf{m} . We seek solutions of eq. 2 and 3 in prolate spheroidal coordinates defined by

$$\xi = \frac{r_1 + r_2}{\mathbf{m}}; \mu = \cos \vartheta = \frac{r_1 - r_2}{\mathbf{m}} \tag{5}$$

with r_1 and r_2 the distances of a given point from the charges (foci). In this coordinate system the Laplacian operator ∇^2 becomes

$$\nabla^2 = \frac{4}{\mathbf{m}^2(\xi^2 - \mu^2)} \left[\frac{\partial}{\partial \xi} (\xi^2 - 1) \frac{\partial}{\partial \xi} + \frac{\partial}{\partial \mu} (1 - \mu^2) \frac{\partial}{\partial \mu} \right] \tag{6}$$

The use of eq. 6 in eq. 3 and the assumption that

$$\psi(\xi, \mu) = R(\xi) S(\mu) \tag{7}$$

leads to the equations

$$\frac{d}{d\xi} \left[(\xi^2 - 1) \frac{dR}{d\xi} \right] - [B - \mathbf{p}^2 \xi^2] R = 0 \tag{8}$$

$$\frac{d}{d\mu} \left[(1 - \mu^2) \frac{dS}{d\mu} \right] + [B - \mathbf{p}^2 \mu^2] S = 0 \tag{9}$$

where B is a separation constant and

$$2\mathbf{p} = i\mathbf{m}\kappa \tag{10}$$

with i the imaginary unit. When $\kappa = 0$, we obtain the formulation of the Laplace equation in this coordinate system. In this case we take the separation constant B to be $n(n + 1)$ whereupon eq. 8 and 9 reduce to the Legendre equation with solutions $\mathfrak{P}_n^{(0)}(\xi)$ and $\mathfrak{P}_n^{(0)}(\mu)$, respectively. The general solution inside the ellipsoid is then

$$\psi'' = \sum_{n=0}^{\infty} A_n P_n^{(0)}(\xi) P_n^{(0)}(\mu) \tag{11}$$

For our purposes we require the potential ψ' defined by

$$\psi' = \sum_{n=0}^{\infty} A_n P_n^{(0)}(\xi) P_n^{(0)}(\mu) + \psi_s \tag{12}$$

where ψ_s is the potential due to the point charges at the foci. Outside the ion, where $\kappa \neq 0$, the angular solution is¹³

$$\begin{aligned} S_{0l} &= \sum_{\nu=0}^{\infty} d_{2\nu}(\mathfrak{R}/l) T_{2\nu}^{(0)}(\mu); \quad l \text{ even} \\ &= \sum_{\nu=0}^{\infty} d_{2\nu+1}(\mathfrak{R}/l) T_{2\nu+1}^{(0)}(\mu); \quad l \text{ odd} \end{aligned} \tag{13}$$

where the d 's are coefficients of a series expansion explicitly displayed by Morse and Feshbach,¹³ and the functions are tesseral harmonics. For the radial solutions we take a linear combination of spherical Bessel functions, j_n and Neumann functions, n_n , *i.e.*

$$\begin{aligned} R_{0l} &= h e_{0l} = \sum' (i)^{n-l} d_n (\mathfrak{R}/l) [j_n + i n_n] \\ &= j_{c_{0l}(\mathfrak{R}\xi)} + i n_{e_{0l}(\mathfrak{R}\xi)} \end{aligned} \tag{14}$$

The solution indicated converges to $(\kappa\mathbf{m}\xi/2)^{-1} \exp(-\frac{\kappa\mathbf{m}\xi}{2})$ in the limit as $\xi \rightarrow \infty$, which is the desired behavior. In eq. 14, the prime on the summation indicates that n runs over even integers if l is even and over odd integers if l is odd. The combination in parentheses on the right hand side of eq. 13 is the Hänkel function of order n with generating function

$$\begin{aligned} h_n(\mathbf{Z}) &= -i\mathbf{Z}^n (-)^n \left(\frac{d}{Z dZ} \right)^n \left(\frac{e^{iZ}}{Z} \right) \\ h_n &= j_n + i n_n \end{aligned} \tag{15}$$

In our case, $\mathbf{Z} = \left(\frac{i\kappa\mathbf{m}\xi}{2} \right)$ whereupon the first few Hänkel functions are

$$\begin{aligned} h_0 &= -\frac{2}{\kappa\mathbf{m}\xi} e^{-\kappa\mathbf{m}\xi/2} \\ h_1 &= \frac{2\kappa\mathbf{m}\xi + 4}{(\kappa\mathbf{m}\xi)^2} e^{-\kappa\mathbf{m}\xi/2} \\ h_2 &= -\frac{24 + 12\kappa\mathbf{m}\xi + 2(\kappa\mathbf{m}\xi)^2}{(\kappa\mathbf{m}\xi)^3} e^{-\kappa\mathbf{m}\xi/2} \end{aligned} \tag{16}$$

For small values of \mathbf{p} , Morse and Feshbach¹³ give approximate formulas for the d_n from which we find

$$\begin{aligned} d_0 &\cong 1 - \frac{(\kappa\mathbf{m})^2}{36} + \frac{7}{16,200} (\kappa\mathbf{m})^4 \\ d_1 &\cong 1 - \frac{(\kappa\mathbf{m})^2}{100} + \frac{144}{16 \times 55,125} (\kappa\mathbf{m})^4 \\ d_2 &\cong \frac{(\kappa\mathbf{m})^2}{36} + \frac{5}{16 \times 567} (\kappa\mathbf{m})^4 \end{aligned} \tag{17}$$

The complete solution outside the ellipsoid is then

$$\psi = \sum_{l=0}^{\infty} C_l S_{0l}(\mu) R_{0l}(\xi) \tag{18}$$

We shall assume that it is a sufficiently accurate approximation to truncate the potential defined by eq. 18 after the $l = 1$ term

$$\psi = C_0 S_{00} R_{00} + C_1 S_{01} R_{01} \tag{19}$$

With the neglect of powers of $\kappa\mathbf{m}$ higher than the second

$$\begin{aligned} S_{00} &= \left(1 - \frac{(\kappa\mathbf{m})^2}{36} \right) P_0^{(0)}(\mu) + \frac{(\kappa\mathbf{m})^2}{36} P_2^{(0)}(\mu) \\ S_{01} &= \left(1 - \frac{(\kappa\mathbf{m})^2}{100} \right) P_1^{(0)} + \frac{(\kappa\mathbf{m})^2}{100} P_3^{(0)}(\mu) \\ R_{00} &= -2 \left(1 - \frac{(\kappa\mathbf{m})^2}{36} \right) \frac{e^{-\kappa\mathbf{m}\xi/2}}{\kappa\mathbf{m}\xi} - \\ &\quad \frac{(\kappa\mathbf{m})^2}{36} \left(24 + 12\kappa\mathbf{m}\xi + 2(\kappa\mathbf{m}\xi)^2 \right) \times \frac{e^{-\kappa\mathbf{m}\xi/2}}{(\kappa\mathbf{m}\xi)^3} \\ R_{01} &= 4 \left(1 - \frac{(\kappa\mathbf{m})^2}{100} \right) \left(1 + \frac{\kappa\mathbf{m}\xi}{2} \right) \frac{e^{-\kappa\mathbf{m}\xi/2}}{(\kappa\mathbf{m}\xi)^2} \end{aligned} \tag{20}$$

which may be substituted into eq. 19 to obtain the potential ψ . The corresponding expansion of the

(13) P. M. Morse and H. Feshbach, "Methods of Theoretical Physics," McGraw-Hill Book Co., New York, N. Y., 1953.

potential inside the ellipsoid yields

$$\psi' = \frac{4zq}{D\mathbf{m}} \frac{\xi}{\xi^2 - \mu^2} + A_0 + A_1\xi\mu \quad (21)$$

To evaluate the coefficients (*A*'s and *C*'s) we neglect powers of μ greater than the first and use the two boundary conditions, at the surface of the ellipsoid.

$$\begin{aligned} \psi'(\xi_0 = 2) &= \psi(\xi_0 = 2) \\ \nabla\psi'(\xi_0 = 2) &= \nabla\psi(\xi_0 = 2) \end{aligned} \quad (22)$$

This gives the relations

$$\begin{aligned} A_0 &\cong \frac{4zq}{D\mathbf{m}} \left[\frac{39 + 3\kappa\mathbf{m}}{90 + 90\kappa\mathbf{m} + 10(\kappa\mathbf{m})^2} - \frac{1}{2} \right] \\ C_0 &\cong -\frac{4zq}{D\mathbf{m}} \left[\frac{72\kappa\mathbf{m}e^{-\kappa\mathbf{m}}}{180 + 180\kappa\mathbf{m} + 15(\kappa\mathbf{m})^2} \right] \end{aligned} \quad (23)$$

In the limit as $\kappa \rightarrow 0$, the coefficient A_0 should vanish. In fact, due to the truncation error in the several expansions used, A_0 tends to the small value 0.06 as $\kappa \rightarrow 0$. This is a measure of the limited accuracy of our two term expansion for the potential

V. A Simple Model of Multiply Charged Linear Ions

It is clear that the considerations of the previous section may be extended to more highly charged ions. However, it is also clear that such an extension runs afoul of very complex algebra. In view of this situation we present in this section a simplified model of linear multiply charged ions. The principal simplifying assumption which we shall use is that end effects may be neglected. With this assumption, each charge may be treated as being exactly equivalent to every other charge.

Consider a linear array of $Z + 1$ charges. As depicted in Fig. 3 we represent the coordinates of each charge with respect to an arbitrary point by the variables ϑ_i and r_i . Let there be $Z/2$ charges to each side of the charge labelled zero. Then the distance of the j 'th charge from an arbitrary point P is

$$r_j^2 = r_0^2 + j^2R^2 - zjr_0R \cos \vartheta_0 \quad (24)$$

where r_0 , ϑ_0 represent the distance of charge zero from P and the angle between the molecular axis and the vector r_0 . The distance between any pair of adjacent charges is taken to be the constant R . Thus

$$\cos \vartheta_j = \frac{jR - r_0 \cos \vartheta_0}{r_j} \quad (25)$$

As before we solve the linearized Poisson-Boltzmann equation outside the ion, and the Laplace equation inside. In particular, let the polyion be represented as a linear array of charged spheres of radius a and near pair separation, R . The solution to both equations may be written in terms of Legendre polynomials, as in eq. 11. Let the coefficients of the expansion be C_i outside and A_{ij} inside, with i the order of the polynomial and j the ion label. Using the boundary condition $\psi'(a) = \psi(a)$ on the surface of each charge and neglecting end effects leads to

$$\begin{aligned} C_0' \frac{e^{-\kappa R a}}{R x} + C_1' \frac{1 + \kappa R x}{(R x)^2} \cos \vartheta_0 + \\ 2C_0' \sum_{j=1}^{Z/2} \frac{e^{-j\kappa R}}{jR} \left[1 + \frac{1}{2} (1 + j\kappa R) y_j \right] + \end{aligned}$$

$$\begin{aligned} 2C_1' \sum_{j=1}^{Z/2} \frac{(1 + y_j)}{(jR)^2} + 2C_1' \kappa \sum_{j=1}^{Z/2} \frac{(1 + 1/2 y)}{jR} \\ = \frac{zq}{DRx} + (Z + 1)A_{00}' + A_{10}' R x \cos \vartheta_0 + \\ \frac{2zq}{D} \sum_{j=1}^{Z/2} \frac{(1 + 1/2 y)}{jR} + 2A_{10}' \sum_{j=1}^{Z/2} jR \left(1 - \frac{y_j}{2} \right) \end{aligned} \quad (26)$$

where

$$\begin{aligned} y_j &= (2x/j) \cos \vartheta_0 \\ x &= r_0/R \end{aligned} \quad (27)$$

and we have truncated the series after terms in $P_1^{(0)}$ and have further assumed that x^2 is negligible

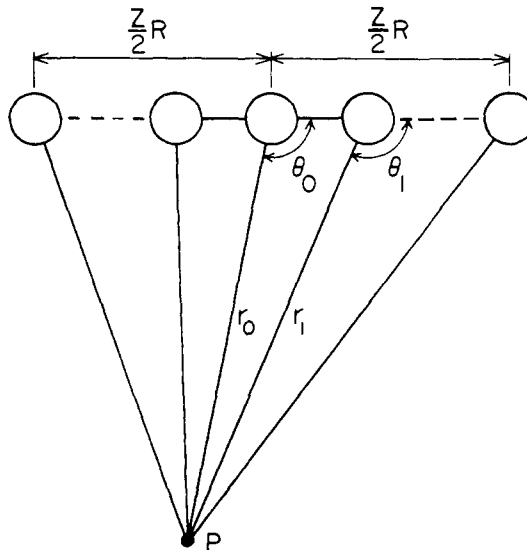


Fig. 3.—The multiply charged linear model ion.

relative to x . If we now apply the second boundary condition, namely, $\nabla\psi'(a) = \nabla\psi(a)$, then it is found that

$$\begin{aligned} C_0' &= \frac{zq}{D} \frac{e^{\kappa a}}{1 + \kappa a} \\ C_1' &= 0 \end{aligned} \quad (28)$$

$$\begin{aligned} A_{00}' &= \frac{zq}{(Z + 1)D} \left\{ \frac{e^{\kappa a}}{1 + \kappa a} \left[\frac{e^{-\kappa a}}{a} + 2 \sum_{j=1}^{Z/2} \frac{e^{-j\kappa R}}{jR} \right] - \frac{1}{a} - \right. \\ &2 \sum_{j=1}^{Z/2} \frac{1}{jR} - \frac{Z(Z/2 + 1)}{1 - Z} \left[\frac{e^{\kappa a}}{1 + \kappa a} \sum_{j=1}^{Z/2} \frac{e^{-j\kappa R}}{j^2 R} (1 + \kappa jR) - \right. \\ &\left. \left. \sum_{j=1}^{Z/2} \frac{1}{j^2 R} \right] \right\} A_{01}' = \frac{2zq}{(1 - Z)RD} \left\{ \frac{e^{\kappa a}}{1 + \kappa a} \right. \\ &\left. \left[\sum_{j=1}^{Z/2} \frac{e^{-j\kappa R}}{j^2 R} (1 + j\kappa R) \right] - \sum_{j=1}^{Z/2} \frac{1}{j^2 R} \right\} \end{aligned} \quad (29)$$

VI. The Counterion Activity

To utilize the preceding results we require a method for determining the chemical potentials of the ionic species in the solution. For the case under consideration the usual Debye charging process is extremely difficult to apply since the potential is a complex function of κ . It is possible to use an alternative argument which is valid within the same range as the approximations already made in solving the Poisson-Boltzmann equation.¹² We note that the definition of the chemical

potential of the polyion, μ_p

$$\frac{\partial A^{el}}{\partial n_p} = \mu_p \quad (30)$$

corresponds to the integral relation

$$\int_{A_0^{el}}^{A^{el}} dA^{el} = \int_{n_p=0}^{n_p} \mu_p dn_p \quad (31)$$

where A_0^{el} is the Helmholtz electrostatic free energy in the absence of the polyion. If μ_p varies only slowly with n_p , we can make the approximation

$$A^{el} = A_0^{el} + n_p \mu_p \quad (32)$$

which should be very good when there are several ionic species present. It is now easy to find a potential function for the counterion to the polyion, for, by definition

$$\psi_i = \frac{\partial A^{el}}{\partial q_i} = \psi_i^0 + n_p \frac{\partial \mu_p}{\partial q_i} \quad (33)$$

To complete the calculation we require the chemical potential of the polyion. It may be shown that¹¹

$$kT \ln \gamma_p^{(2)} = 2zqA_0 \quad (34)$$

for the bolion, and

$$\begin{aligned} kT \ln \gamma_p^{(Z+1)} &= \sum_{j=1}^{Z+1} \frac{zq_j}{2} (Z+1)A_{0j}' \\ &= \frac{1}{2} (Z+1)^2 zqA_{0j}' \end{aligned} \quad (35)$$

for the linear polyion (neglecting end effects as before). From this we find

$$\begin{aligned} kT \ln \gamma_{Cl^{-(2)}} &= -\frac{z^2 q^2 \kappa}{12D} \left[\frac{30 + \frac{13}{2} \kappa m + \frac{1}{6} (\kappa m)^2}{\left(\frac{5}{2} + \frac{5}{2} \kappa m + \frac{1}{6} (\kappa m)^2\right)^2} \right] \\ &\quad - \frac{z^2 q^2}{2D} \frac{\kappa}{1 + \kappa a_{Cl^-}} \end{aligned} \quad (36)$$

for the ellipsoidal model of the bolion, and

$$\begin{aligned} kT \ln \gamma_{Cl^{-(Z+1)}} &= -\frac{z^2 q^2}{2D} \frac{\kappa}{1 + \kappa a_{Cl^-}} + \\ &\quad \frac{z^2 q^2}{4D} \frac{Z+1}{Z} \left\{ -\frac{a}{(1 + \kappa a)^2} \times \left[\frac{1}{a} + 2 \sum_{j=1}^{Z/2} \frac{e^{-\kappa(jR-a)}}{jR} - \right. \right. \\ &\quad \left. \frac{Z(Z/2+1)}{1-Z} \sum_{j=1}^{Z/2} \frac{e^{-\kappa(jR-a)}}{j^2 R} (1 + \kappa j R) \right] + \\ &\quad \left. \frac{1}{1 + \kappa a} \left[-2 \sum_{j=1}^{Z/2} \frac{jR-a}{jR} e^{-\kappa(jR-a)} - \right. \right. \\ &\quad \left. \frac{Z/(Z/2+1)}{1-Z} \sum_{j=1}^{Z/2} \frac{e^{-\kappa(jR-a)}}{j} + \right. \\ &\quad \left. \left. \frac{Z(Z/2+1)}{1-Z} \sum_{j=1}^{Z/2} \frac{jR-a}{j^2 R} e^{-\kappa(jR-a)} (1 + \kappa j R) \right] \right\} \end{aligned} \quad (37)$$

for the linear array of charged spherical beads. For the cases $Z+1=3$ and $Z+1=5$ considered in this paper, the general formula reduces to

$$\begin{aligned} kT \ln \gamma_{Cl^{-(3)}} &= -\frac{z^2 q^2}{2D} \frac{\kappa}{1 + \kappa a_{Cl^-}} - \frac{3}{8} \frac{z^2 q^2}{D} \left\{ \frac{\kappa a}{(1 + \kappa a)^2} \left[\frac{1}{a} + \right. \right. \\ &\quad \left. \left. \left(\frac{6}{R} + 4\kappa \right) e^{-\kappa(R-a)} \right] + \frac{\kappa e^{-\kappa(R-a)}}{1 + \kappa a} \left[2 + \right. \right. \\ &\quad \left. \left. 6\kappa(R-a) - \frac{6a}{R} \right] \right\} \end{aligned} \quad (38)$$

and

$$\begin{aligned} kT \ln \gamma_{Cl^{-(6)}} &= -\frac{z^2 q^2}{2D} \frac{\kappa}{1 + \kappa a_{Cl^-}} - \frac{5}{16} \frac{z^2 q^2}{D} \left\{ \frac{\kappa a}{(1 + \kappa a)^2} \left[\frac{1}{a} + \right. \right. \\ &\quad \left. \left. \left(\frac{6}{R} + 4\kappa \right) e^{-\kappa(R-a)} + \left(\frac{2}{R} + 2\kappa \right) e^{-\kappa(2R-a)} \right] + \right. \\ &\quad \left. \frac{\kappa}{1 + \kappa a} \left[\left(\frac{6(R-a)}{R} - 4 + 4(R-a)\kappa \right) e^{-\kappa(R-a)} + \right. \right. \\ &\quad \left. \left. \left(\frac{2(2R-a)}{R} - 2 + 2(2R-a)\kappa \right) e^{-\kappa(2R-a)} \right] \right\} \end{aligned} \quad (39)$$

Equations 36 and 37 have been used to compute numerical values for $\ln \gamma_{Cl^-}$ as a function of concentration, of charge on the polyion and of separation between the two charges of the bolion. Consider first the variation in γ_{Cl^-} due to changing the charge separation in the bolion. Our experimental data are given in Table I and Curve B of Fig. 4. Curve A of Fig. 4 is the computed variation of $\ln \gamma_{Cl^{-(2)}}$. We observe that the theoretical slope is in quantitative agreement with experiment but that $\gamma_{Cl^{-(2)}}$ (theory) is about a factor of 1.10 too small at the concentration for which the data are plotted. This error of 10% arises from the truncation error in the potential and the resultant inaccuracy in the coefficients determined from the boundary conditions. It is our opinion that this agreement is satisfactory. As can be seen in Fig. 5, the predicted concentration dependence of $\gamma_{Cl^{-(2)}}$ is almost parallel to but displaced from the experimental values. The discrepancy is seen to be approximately linear in $\sqrt{m_{Cl^-}}$, again suggesting that the dominant source of error is the truncated potential.

Consider next the variation of γ_{Cl^-} with charge. As seen in Fig. 6, the expected increase in concentration dependence with increasing charge is obtained. Of more interest is the approach to the polymeric limit, *i.e.*, the dependence of γ on the number of charges. Here, the predicted variation is much more rapid than that observed (Fig. 7) although, of course, the direction predicted is correct. It should be noted that the multiple charge linear model with the neglect of end effects overestimates the electrostatic potential considerably for short chains. For each charge is assumed to be symmetrically surrounded by Z other charges. In a very rough estimate we may say that the computed potential is a factor of 3/2 too high at the end charges of the triple ion. For the ion of charge five, both the end and next to end charges have real potentials lower than the computed potential. In a very rough approximation, the computed activity coefficient should be (6/5) larger for the triple ion and (15/12.8) larger for the quintuple ion. These crude estimates are shown as crosses in Fig. 7. While the variation with Z is appreciably reduced, it is still too large when compared with experiment. We have no ready explanation of the remaining discrepancy.

VII. Discussion

In this paper we have attempted to study the transition from simple electrolyte to polyelectrolyte for a model series of compounds. In brief summary, we find that the transition region lies at degrees of polymerization in excess of 5; that a simple model of the doubly charged ion gives quan-

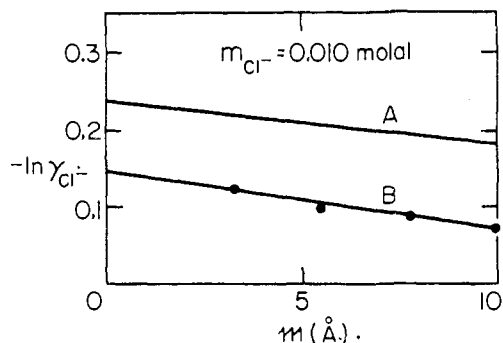


Fig. 4.—Dependence of $\ln \gamma_{Cl^-}$ on the length m of the semi-major axis of the two charge ellipsoidal model, $\kappa = 0.050 \times 10^8 \text{ cm.}^{-1}$.

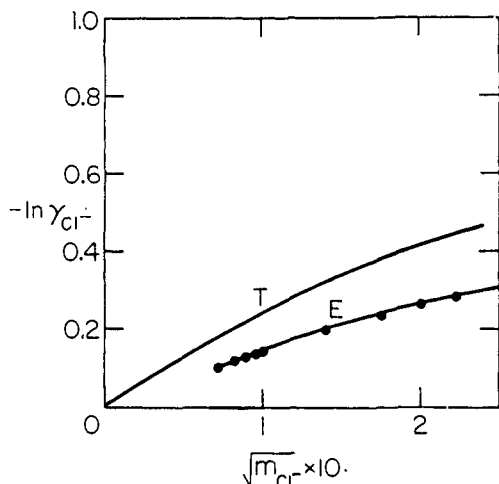


Fig. 5.—Concentration dependence of $\ln \gamma_{Cl^-}^{(2)}$; theory and experiment for ED $(\text{HCl})_2$.

titative agreement with the observed variation in $\gamma_{Cl^-}^{(2)}$ with charge separation but only semiquantitative agreement with the absolute value of $\gamma_{Cl^-}^{(2)}$; that a simple model of highly charged linear ions predicts all the proper trends but is quantitatively poor; and that the behavior of the counterion activity coefficient and the extent of counterion binding as a function of polyion charge are consistent with each other.

Consider first the possible interpretation of the results of the counterion binding experiments. We have already mentioned that ion-pair formation at charged sites seems to be ruled out, but there remains the possibility that the counterion distribution is sharply peaked about the polyion. Using the Fuoss-Bjerrum criterion of regarding ions closer than a given distance as bound and all others as free will have the following qualitative results. First, since the counterion distribution is very peaked close to the polymer skeleton, those ions classified as bound exclude a negligible fraction of the configurations ordinarily included in the Poisson-Boltzmann Debye-Hückel theory. Second, it seems reasonable, in view of the experimental results showing no discrete ion pairing, to regard the bound ions as forming a very highly mobile "monolayer" on the polymer skeleton "surface." When the charge density on the polymer skeleton has local peaks, as in the case of

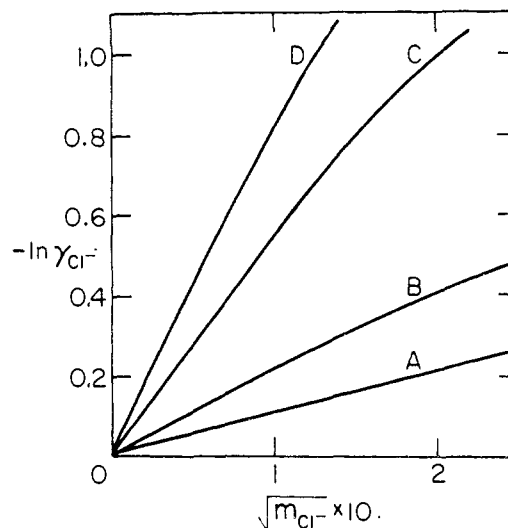


Fig. 6.—Dependence of $\ln \gamma_{Cl^-}$ on the $\sqrt{m_{Cl^-}}$ in the presence of: A, spherical univalent cation; B, bolaform ion; C, linear trivalent ion; D, linear pentavalent ion.

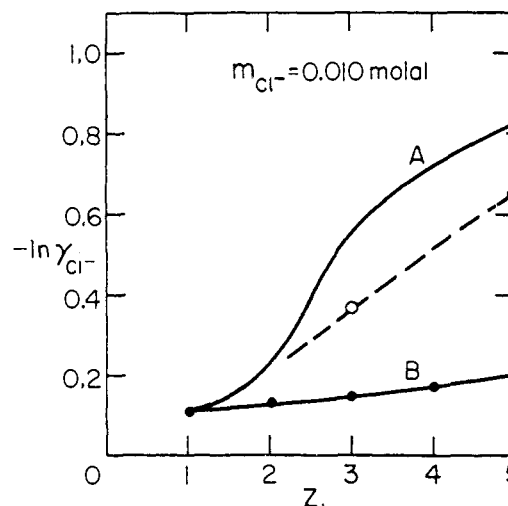


Fig. 7.—Dependence of $\ln \gamma_{Cl^-}$ on number of charges on "polymer" at fixed concentration: A, calculated; B, observed; ---, corrected.

the polyphosphates, it is to be expected that the counterion distribution has corresponding local maxima and therefore that a smaller section of chain is still large enough to attract the counterions. We note that the counterions in the "bound monolayer" should very effectively shield the fixed charges on the polymer skeleton. Finally, this point of view is in agreement with a rather different interpretation of our earlier theory of binding.^{14,15} That is, we now regard the Ising model calculations of binding as analogous to the use of the lattice gas model to discuss the properties of the real gas or of the quasi-lattice cell model of liquids to discuss the properties of real liquids.^{16,17} Such ap-

(14) F. E. Harris and S. A. Rice, *J. Phys. Chem.*, **58**, 725 (1954).

(15) S. A. Rice and F. E. Harris, *ibid.*, **58**, 733 (1954).

(16) J. Hirschfelder, C. Curtiss and R. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954.

(17) H. B. Levine, J. E. Mayer and H. Aroeste, *J. Chem. Phys.*, **26**, 201 (1957).

proximations can be very useful, even though the mathematical approximation of localizing the particles is not at all in accord with the real, very mobile molecular system. Of course, distinct from the binding question, the use of Ising methods to compute the electrostatic energy and other properties remains a valuable method of accounting for the discrete nature of the charges. The view proposed satisfies all the available criteria by which ion binding has been introduced: The high concentration in the "bound monolayer" insures very effective charge-charge shielding; the division in terms of the ionic distribution should, as in the case of simple electrolytes, be relatively field independent at low fields¹⁸ but yield a large Wien effect (as has been observed¹⁹); since we do not appeal to discrete ion-pair formation, it is clear that counterion binding and low counterion activity coefficients are but two descriptions of one phenomenon²⁰; we suggest that lattice gas calculations, which are in semiquantitative agreement with experiment, are useful mathematical approximations and that such a model should not be interpreted blindly in terms of pairs.

We now turn briefly to the possible extension of the models proposed herein to the case of coiled polyions. The results of Nagasawa and Rice⁶ indicated that the mean electrostatic field at a

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

(19) F. E. Bailey, A. Patterson and R. M. Fuoss, *J. Am. Chem. Soc.*, **74**, 1845 (1952).

(20) M. Nagasawa, *ibid.*, **83**, 1026 (1961).

charged site inside a polyion had major contributions from both the near neighbor and the rest of the polyion. This suggests that we take the multiply charged linear model and imbed it inside a polyion. Such a model would correspond to choosing an electrostatic Kuhn element and surrounding this element with a more or less spherical charge distribution. Qualitatively, we expect the potential due to the rest of the ion to be approximately constant throughout the polymer domain.²¹ Thus, we would anticipate that the activity coefficient of the counterion would be further depressed (over that calculated herein for the small compounds) and that its value would be independent of molecular weight. While these qualitative features are easily seen to follow from the physical nature of the model, the mathematical formulation of this problem is fraught with difficulties, and more details will be presented in a subsequent paper.²²

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(21) J. Hermans and J. T. G. Overbeek, *Rec. trav. chim.*, **67**, 761 (1949).

(22) See, however, the related earlier calculation: F. E. Harris and S. A. Rice, *J. Chem. Phys.*, **25**, 955 (1956).

[CONTRIBUTION NO. 642 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, INC., WILMINGTON, DELAWARE]

Perfluoroalkyl and Perfluoroacyl Metal Carbonyls

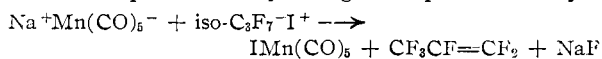
BY W. R. McCLELLAN

RECEIVED OCTOBER 19, 1960

Perfluoroacyl and perfluoroalkyl derivatives of manganese pentacarbonyl, $R_f\text{-CO-Mn(CO)}_5$ and $R_f\text{-Mn(CO)}_5$, respectively, where $R_f = \text{CF}_3$, $n\text{-C}_3\text{F}_7$ and $\text{iso-C}_3\text{F}_7$, and the perfluoromethyl-, -ethyl and - n -propyl derivatives of cobalt tetracarbonyl have been prepared by reaction of the appropriate perfluoroacyl halide with the lithium derivative of manganese or cobalt carbonyl hydride. The perfluoroalkylcobalt compounds have outstanding stability compared to their hydrocarbon analogs. The preparation of perfluoropropenylmanganese pentacarbonyl is also described.

Closson, Kozikowski and Coffield¹ have reported the preparation of alkyl- and acylmanganese pentacarbonyls by reaction of alkyl and acyl halides with sodium manganese pentacarbonyl. Certain of the acyl compounds lose the keto carbonyl on heating to give the corresponding alkyl derivatives and, in most cases, this reaction is reversed by carbon monoxide gas under high pressure.

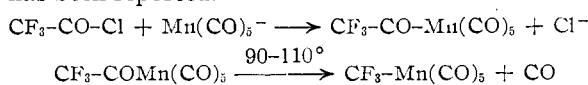
Because of the positive character of the halogen atom, reaction of perfluoroalkyl halides with sodium manganese pentacarbonyl does not provide a route to perfluoroalkylmanganese pentacarbonyls



The preparation of trifluoromethylmanganese pentacarbonyl, however, by thermal decarbonyla-

(1) R. D. Closson, J. Kozikowski and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957).

tion of trifluoroacetylmanganese pentacarbonyl has been reported.²



We have used this route to prepare several other perfluoroacyl and perfluoroalkylmanganese pentacarbonyl derivatives described in Table I.

The only previously described cobalt tetracarbonyls have been the methyl,^{3,4} ethyl⁴ and benzyl derivatives which, because of their high degree of instability, have been prepared and isolated at sub-zero temperatures. We have prepared several

(2) T. H. Coffield, J. Kozikowski and R. D. Closson, International Conference on Coordination Chemistry (London, 1959), p. 126 (Abstract), Burlington House, London, 1959.

(3) W. Hieber, *Z. Naturforsch.*, **13b**, 192 (1958).

(4) D. S. Breslow and R. F. Heck, *Chem. and Ind. (London)*, 467 (1960).