A STUDY OF THE TRANSFERENCE METHOD FOR THE
DETERMINATION OF COUNTERION ASSOCIATION
WITH POLYELECTROLYTES AND ITS APPLICATION
TO POLY-4-VINYL-N,n-BUTYLPYRIDINIUM
BROMIDE IN HBr SOLUTIONS

DISSERTATION

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Introduction

Polyelectrolytes are an interesting class of compounds which combine in one molecule the typical properties of a high polymer and those of a simple electrolyte.

Several polyelectrolytes have been the object of intensive study over the past two decades, and the results of these studies have been summarized in recent reviews (1-6). Most of these studies have been concerned with the measurement of typical polymeric properties such as viscosity, osmotic pressure, sedimentation, diffusion, and light scattering, and deviations from normal polymeric behavior were attributed to charge effects.

(1) R. M. Fuoss, Discussions Far. Soc., 11, 125 (1951).

(2) P. Doty and G. Ehrlich, Ann. Rev. Phys. Chem., 3, 81 (1952).

(3) R. M. Fuoss and A. S. Fuoss, Ann. Rev. Phys. Chem., 4, 49 (1953).

(4) U. P. Strauss and R. M. Fuoss, Die Physik der Hochpolymeren, Vol. II, ed. H. A. Stuart, Springer, Berlin, 1953, p. 680.

(5) H. Eisenberg and R. M. Fuoss, Modern Aspects of Electrochemistry, ed. J. O'M. Bockris, Butterworths, Sci. Pub., London, 1954, p. 1.

(6) A. Katchalsky, J. Polymer Sci., 12, 159 (1954).

Fuoss and co-workers (7-9) studied the conductance of polyelectrolytes, and attributed deviations from the behavior of simple electrolytes to the polymeric nature of the compounds. The conductance curves resembled those of weak electrolytes, thus indicating that there is considerable association between the polyions and their counterions in water, even though the corresponding monomeric salts are completely dissociated.

Other measurements, especially viscosity, also indicated a high degree of association between polyion and counterions with increasing dissociation as the concentration was decreased.

A measurement of the actual degree of association in a polyelectrolyte system was made by Wall and co-workers (10-12), who used Hittorf-type transference experiments to

(7) R. M. Fuoss and U. P. Strauss, J. Polymer Sci., 3, 246 (1948).

(8) G. I. Cathers and R. M. Fuoss, ibid., 4, 121 (1949).

(9) D. Edelson and R. M. Fuoss, J. Am. Chem. Soc., 72, 306 (1950).

(10) J. R. Huizenga, P. F. Greiger and F. T. Wall, J. Am. Chem. Soc., 72, 2636 (1950).

(11) F. T. Wall and R. H. Doremus, ibid., 76, 1557 (1954).

(12) J. R. Huizenga, P. F. Greiger and F. T. Wall, ibid., 72, 4228 (1950).

determine the extent of sodium ion binding in solutions of polyacrylic acid which were partially neutralized by sodium hydroxide. They found an increase in the fraction of sodium ions associated with the polymer with increase in neutralization; about one-fourth at 25% neutralization, and about two-thirds at 100% neutralization. Diffusion experiments (12) on the same system using radioactive sodium gave similar results.

Wall also carried out transference experiments on polyvinylpyridine partially neutralized with hydroiodic acid (13), and found that from 30 to 60% of the iodine moved with the polymeric cation.

The increase in the fraction of counterions associated with the polyion as the degree of neutralization is increased, is primarily due to the increased charge density along the polymer chain. There is also a mass action effect, however, for the concentration of counterions eligible for association also increases with increasing neutralization.

Statement of Problem

The original purpose of the present investigation was to study the mass action effect in a polyelectrolyte system.

(13) F. T. Wall, J. J. Ondrejcin and M. Pikramenou, J. Am. Chem. Soc., 73, 2821 (1951).

To do so it was desirable to use a polyelectrolyte with a constant number of charge sites, and study the degree of association of counterions as a function of the concentration of a simple electrolyte containing the same counterion. The polyelectrolyte selected for this study was poly-4-vinyl-N,n-butylpyridinium bromide (hereafter abbreviated PVPBr), a compound which has been the object of numerous studies by Fuoss and co-workers (7, 14-16) as well as in this laboratory (17-21). It was decided to use hydrobromic acid as the simple electrolyte, since the solution can be readily analyzed for hydrogen ion. The method used was Hittorf-type transference experiments similar to those of Wall (10-12).

(14) R. M. Fuoss and R. Signer, J. Am. Chem. Soc., 73, 5872 (1951).

(15) R. M. Fuoss and D. Edelson, ibid., 6, 767 (1951).

(16) E. B. Fitzgerald and R. M. Fuoss, ibid., 14, 329 (1954).

(17) C. Bartell, doctoral dissertation, The Ohio State University (1951).

(18) P. Goodman, doctoral dissertation, The Ohio State University (1952).

(19) W. Ritchey, Master's thesis, The Ohio State University (1953).

(20) N. Maio, Master's thesis, The Ohio State University (1953).

(21) L. Bsharah, doctoral dissertation, The Ohio State University (1955).

While these studies were in progress, Wall and Eitel (22) published the results of a similar investigation of the mass action effect on partially neutralized polyacrylic acid. When the acid was neutralized with NaOH, they found that addition of NaCl did not appreciably affect the total sodium ion association. By neutralizing the acid with $\text{Sr}(\text{OH})_2$, however, they found a pronounced increase in the degree of association of the divalent strontium ions with $\text{Sr}(\text{NO}_3)_2$ concentration.

Because of the surprising results of Wall's experiments (i.e., no mass action effect with sodium ions), it was decided that a critical evaluation of the transference method for determining counterion association should be made. Also, because of the interest in polyvinylpyridinium bromide in this laboratory, it was decided to continue the studies of the mass action effect on this polyelectrolyte, and to use the results of these experiments to help evaluate the transference method.

(22) F. T. Wall and M. J. Eitel, J. Am. Chem. Soc., 79, 1556 (1957).

General Theory

Calculation of Degree of Association from Transference Experiments

The derivation which follows is essentially that of Wall (23, 24). The discussion will be simplified by assuming that only one species of polymeric ion is present in the solution (25), and that the counterions can exist either in the free state or in the bound state, with no intermediate states.

The polymeric ion will be designated by the subscript p, the counterions by the subscript c, and the by-ions (ions of same sign as the polyion) by the subscript b. Only the simplest case will be considered here, namely that in which there is only one species of counterions and one species of by-ions. It is further assumed that the simple electrolyte

(23) J. R. Huizenga, P. F. Greiger and F. T. Wall, J. Am. Chem. Soc., 72, 2636 (1950).

(24) F. T. Wall, J. J. Ondrejcin and M. Pikramenou, ibid., 73, 2821 (1951).

(25) Actually there is a distribution of molecular weights around some average value as well as a distribution of charges around some average value. For high degrees of polymerization the degree of association should not vary with molecular weight however.

which is present is symmetrical, i.e., that the ions B and C have equal (but opposite) charges.

It will be helpful to consider the solutions to be made up by dissolving the polyelectrolyte, PC_n , in a solution of the simple electrolyte BC.

The following symbols will be used:

- α = fractional charge per monomer unit (identical with the degree of dissociation for a weak electrolyte)
- $1 - \alpha$ = degree of association of the counterion, C, with the polyion
- t_i = transference number of ion i
- Q_i = net increase in the number of equivalents (26) of ion i in the cathode compartment during a transference experiment
- n = number of equivalents of electricity passed through the cell during a transference experiment
- C_i = stoichiometric concentration of the ion i in equivalents (26) per liter
- K = specific conductance of the polymer solution
- K_i = ionic specific conductance of ion i in the polymer solution
- Λ_i = ionic equivalent conductance of ion i in the polymer solution

(26) For the polymeric ion "one equivalent" is the same as a monomole, or one mole of monomer units.

K' , K'_1 , Λ' , Λ'_1 , t'_1 , etc., are the same quantities as defined above, except that the primed quantities refer to the simple electrolyte solution, BC, in which the polyelectrolyte was dissolved, while the unprimed quantities refer to the polymer solution.

$r = t'_0/t'_b$ = ratio of the counterion transference number to that of the by-ion in the simple electrolyte solution in which the polymer is dissolved.

The transference number of the polyion can be defined as the fraction of the charge carried

$$t_p = \frac{\alpha Q_p}{n} \quad (1)$$

or as a ratio of specific conductances

$$t_p = \frac{K_p}{K} \quad (2)$$

Upon eliminating t_p from equations 1 and 2, the following equation is obtained for α :

$$\alpha = \frac{nK_p}{Q_p K} \quad (3)$$

All the quantities in this expression can be determined experimentally except K_p , which can be obtained from

$$K_p = K - K_b - K_o \quad (4)$$

Wall assumed that Kohlrausch's rule of independent migration of ions was valid, and thus that K_b and K_c could be calculated from the expression

$$K_1 = \frac{c_1 \Lambda_1}{1000} \quad (5)$$

the values of Λ_1 being obtained from measurements on solutions of simple electrolytes.

For the counterions, the concentration used in equation 5 must be the total concentration of free counterions. Thus

$$K_c = \frac{(c_c)_{\text{free}} \Lambda_c}{1000} = \frac{(c_b + \alpha c_p) \Lambda_c}{1000} \quad (6)$$

By combining equations 3, 4, 5 and 6, the following expression is obtained for α :

$$\alpha = \frac{10^3 K - c_b \Lambda_b - c_b \Lambda_c}{\frac{10^3 Q_p K}{n} + c_p \Lambda_c} \quad (7)$$

Equation 7 has been derived because it will serve a useful purpose, although the validity of the assumption involved in its derivation will now be questioned. Onsager and Fuoss (27) have pointed out that "Kohlrausch's rule of independent migration of ions, valid as a limiting law for simple binary electrolytes, does not apply to mixtures, nor are the conductances additive." Using experimental data on

(27) L. Onsager and R. M. Fuoss, J. Phys. Chem., 36, 2689 (1932).

HCl and KCl, they showed that the observed conductance of mixtures of these two electrolytes was always less than that calculated from the individual ionic equivalent conductances obtained from experiments on separate solutions of the two electrolytes. The deviation between the observed conductance and that calculated on the basis of additivity increased with concentration of the solutions.

It is therefore evident that values of α calculated from equation 7 will be too low, if the ionic conductances are obtained from data on simple binary electrolytes.

Equation 4 is still valid if the values of K_b and K_o are determined in the polymer solution, however. If the concentration of by-ions in the solution can be determined, then the transference number of the by-ion in the polymer solution can be calculated from the transference data, and the conductance of the by-ions can be obtained from the expression

$$K_b = t_b K \quad (8)$$

where K is the experimentally measured conductance of the solution.

The counterion conductance cannot be determined from an expression similar to equation 8, however, because some of the counterions migrate with the polyion, and thus t_o is dependent on α .

A relationship between the conductance of the counter-ions and that of the by-ions will now be developed.

Onsager and Fuoss (27) derived a general equation for the equivalent conductance of an ion in the presence of an arbitrary mixture of ions. The form of the equation which will be used here is a simplified version of that given by Harned and Owen (28), and may be written

$$\Lambda_i = \Lambda_i^0 - \left[B \Lambda_i^0 |Z_i f| + B_1 |Z_i| \right] \sqrt{I} \quad (9)$$

where B and B_1 are constants depending only on the solvent and the temperature, Z_i is the valence of the ion, and $I = \sum C_i Z_i^2$ is twice the ionic strength of the solution. The quantity f is a complex function involving the mobilities and charges of all the ions present in the solution.

For a solution containing only two kinds of ions, the quantity $Z_i f$ can be replaced by

$$\frac{|Z_1 Z_2| q}{1 + \sqrt{q}}$$

where q is given by the expression

$$q = \frac{|Z_1 Z_2|}{|Z_1| + |Z_2|} \cdot \frac{\Lambda_1^0 + \Lambda_2^0}{|Z_2| \Lambda_1^0 + |Z_1| \Lambda_2^0}$$

(28) H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 2nd ed., Reinhold Publishing Corp., New York, 1950, p. 141.

For a symmetrical binary electrolyte, B_nC_n , it may readily be shown that $q = \frac{1}{2}$, and

$$\frac{|Z_1 Z_2|^q}{1 + \sqrt{q}} = \frac{\frac{1}{2}n^2}{1 + \sqrt{\frac{1}{2}}} = \frac{n^2}{3.414}$$

Thus for a symmetrical binary electrolyte equation 9 may be written

$$\Lambda'_i = \Lambda_i^o - \left[B \Lambda_i^o \frac{n^2}{3.414} + B_1 |n| \right] \sqrt{\Gamma} \quad (10)$$

The difference between the conductance of ion i in an arbitrary mixture of ions and that in a symmetrical binary electrolyte solution may therefore be written as

$$\begin{aligned} \Lambda_i - \Lambda'_i &= -B_1 \Lambda_i^o \left[|Z_i f| - \frac{n^2}{3.414} \right] \sqrt{\Gamma} \\ \text{or } \Lambda_i &= \Lambda'_i - B_1 \Lambda_i^o \left[|Z_i f| - \frac{n^2}{3.414} \right] \sqrt{\Gamma} \\ &= \Lambda'_i - \Lambda_i^o F(\Gamma) \end{aligned} \quad (11)$$

The complex function $F(\Gamma)$ must have a value greater than one, because it is experimentally observed that $\Lambda_i > \Lambda'_i$.

Equation 11 can be used to write a relationship between Λ_b and Λ_o . Thus

$$\frac{\Lambda_o}{\Lambda_b} = \frac{\Lambda'_o - \Lambda_o^o F(\Gamma)}{\Lambda'_b - \Lambda_b^o F(\Gamma)} \quad (12)$$

From equation 12 it may readily be shown that

$$\frac{\Lambda_c}{\Lambda'_c} = x \frac{\Lambda_b}{\Lambda'_b} \quad (13)$$

where

$$\begin{aligned} 1 < x & \quad \text{if } \Lambda_c^o < \Lambda_b^o \\ 0 < x < 1 & \quad \text{if } \Lambda_c^o > \Lambda_b^o \end{aligned} \quad (14)$$

If $\Lambda_c^o = \Lambda_b^o$ then

$$\begin{aligned} 0 < x < 1 & \quad \text{if } \Lambda'_c < \Lambda'_b \\ 1 < x & \quad \text{if } \Lambda'_c > \Lambda'_b \end{aligned} \quad (15)$$

It should be noted that x can never have a value of one, for in such a case the mixture effect would have to disappear (i.e., the system would reduce to one in which there are only two ions) and equation 13 would reduce to

$$\frac{\Lambda'_c}{\Lambda'_c} = \frac{\Lambda'_b}{\Lambda'_b}$$

The quantity x is a complicated variable, which one cannot hope to evaluate for a polyelectrolyte system. Nevertheless, equation 13 together with the limits imposed upon x by equations 14 and 15 can be used to indicate the nature of the corrections which must be applied to data obtained from equation 7.

From equations 8 and 5,

$$c_b \Lambda_b = 10^3 K_b = 10^3 K t_b$$

By substituting this into equation 7, one obtains

$$\alpha = \frac{1 - t_B - \frac{c_b \Lambda_c}{10^3 K}}{\frac{Q_p}{n} + \frac{c_p \Lambda_c}{10^3 K}} \quad (16)$$

Combining equation 13 with equations 8 and 5, one may obtain

$$\Lambda_c = x \Lambda_b \frac{\Lambda'_c}{\Lambda'_b} = x \frac{10^3 t_B K}{c_b} \cdot \frac{t'_c c'_b}{t'_b c'_c}$$

Letting the symbol r represent the ratio t'_c/t'_b and noting that $c'_b = c'_c$, the above equation can be written

$$\frac{c_b \Lambda_c}{10^3 K} = x r t_B \quad (17)$$

By substituting equation 17 into 16, the following expression is obtained for α :

$$\alpha = \frac{1 - t_B - x r t_B}{\frac{Q_p}{n} + \frac{c_p}{c_B} x r t_B} \quad (18)$$

All of the quantities on the right side of this equation can be evaluated experimentally except x , and all that is known about x is that it must lie within the limits given by equations 14 and 15.

Since an exact solution to equation 18 cannot be obtained, several methods will be discussed now which will lead to approximate values of α . These methods will be numbered (i), (ii), (iii), etc., and will be so arranged that the accuracy of the value obtained for α will increase in the order given.

Method (i).---The easiest assumption to make from the experimental point of view is that Kohlrausch's rule of independent migration of ions is valid, and thus Λ_b and Λ_o can be obtained from data on simple binary electrolytes. This is the method used by Wall and co-workers (22-24).

Λ_o should be evaluated from data on a simple binary electrolyte in which the concentration is equal to the total concentration of free counterions in the polyelectrolyte solution, which is given by

$$(C_o)_{\text{free}} = C_b + \alpha C_p$$

Thus the values of α and Λ_o must be adjusted by a method of successive approximations. As a first approximation it may be assumed that $\Lambda_o = \Lambda'_o$, the equivalent conductance of the counterion in the simple electrolyte solution in which the polyelectrolyte is dissolved. Then α may be calculated from equation 7, after which the quantity $(C_o)_{\text{free}} = C_b + \alpha C_p$ can be calculated. A plot of

Λ_o vs. C_o in the simple electrolyte is then used to obtain a better value of Λ_o , and the process is repeated until there is no change in the resultant value of α .

Method (ii).--This method is similar to method (i) except that enough additional experimental data are obtained to calculate the actual value of by-ion conductance, Λ_b , in the polyelectrolyte solution. Λ_o is still obtained from data on simple electrolyte solutions, however.

Equation 16 may be used to calculate α by this method, but the values of α and Λ_o must be adjusted by a series of successive approximations as in method (i).

Method (iii).--The conductance of the by-ions in the polyelectrolyte solution can be determined if enough experimental data are obtained. It may then be assumed that Λ_o and Λ_b are decreased in the same proportion on addition of the polyelectrolyte. Thus

$$\frac{\Lambda_o'}{\Lambda_o} = \frac{\Lambda_b'}{\Lambda_b}$$

which is identical with equation 13 when $x = 1$. For this case equation 18 becomes

$$\alpha = \frac{1 - t_B - rt_B}{\frac{Q_p}{n} + \frac{C_p}{C_B} rt_B} \quad (19)$$

Method (iv).--This method involves the use of equation 18 using an appropriate value of x , as given by equations 14 and 15. The only difficulty with the method is that the values of α are very sensitive to small changes in x , and that the quantity x cannot be considered as constant over a wide range of experimental conditions.

This method can best be used in conjunction with method (iii), to indicate the direction and to estimate the magnitude of corrections which should be applied to the values of α obtained by method (iii).

Before indicating just how each of the above methods may be applied to solutions of PVPBr in HBr, the nature of the polyelectrolyte and the experimental procedure will be discussed.

Calculation of the polyion mobility

The mobility of the polyion may be calculated from the transference experiments without any assumptions.

If a solution contains several species of ions, such as PC_n , PC_{n-1} , PC_{n-2} , etc., all in rapid equilibrium, then under the influence of an electrical field these ions will migrate as a uniform substance with a mobility u_p , called the constituent mobility of the ion P.

According to Svensson (29), the constituent mobility of an ion may be defined in terms of a transference

(29) H. Svensson, Acta. Chem. Scand. 2, 841 (1948).

experiment as the mass transported relative to some plane of reference per unit time, unit cross section of the tube, unit field strength, and unit concentration of the constituent. Thus

$$u_p = \frac{m}{cAtX} \quad (20)$$

where

m = the transported mass of the constituent in grams

c = concentration of the constituent in grams/cm³ of solution

A = cross sectional area of the tube

t = time in seconds

X = field strength in volts/cm

The field strength X is given by

$$X = \frac{E}{l} = \frac{IR}{l} = \frac{I}{KA}$$

where E , I , and R are the potential, current, and resistance, l the length, and K the specific conductance of the solution. Substituting this expression into equation 20,

$$u_p = \frac{mK}{ctI} = \frac{mK}{cnF} \quad (21)$$

Here tI , the number of coulombs of electricity has been replaced by nF where

n = no. of equivalents of electricity passed through the cell

F = 96,500 coulombs per equivalent

This expression may be converted to one using the same notation as was used for the calculation of α in the preceding section by noting that

$$m = Q_P M_P$$

where M_P is the gram equivalent weight (i.e., the gram monomolecular weight) of the PVP⁺ ion, and that

$$c = \frac{M_P C_P}{1000}$$

Making these substitutions in equation 21, the following expression is obtained.

$$u_P = \frac{10^3 Q_P K}{C_P n F} \quad (22)$$

In equation 22, C_P should be expressed in equivalents per liter of solution, but since the analyses are made on a weight basis, C_P will be expressed in equivalents per 1000 grams of solution in the calculations. The error introduced by doing this is much smaller than the other experimental errors.

Preparation of the Polyelectrolyte

Polymerization of 4-Vinyl Pyridine

The vinyl pyridine was polymerized by the procedure developed by Erickson (30), who adapted it from Fuoss and Strauss (31), and Goodman (32). The monomer, 4-vinyl pyridine (Reilly Tar and Chemical Corporation), was distilled under vacuum (13 mm Hg) to remove inhibitor. One hundred milliliters of the water-clear monomer was dissolved in 457 ml of toluene, and 7.5 g of benzoyl peroxide was added as a catalyst. This solution was allowed to polymerize for one hour at 60°, with constant stirring in a nitrogen atmosphere. The product was washed with toluene, blended in a Waring blender, filtered, and finally dried in a vacuum oven at 40°C.

The products obtained from ten different runs were combined and then fractionated as described below.

(30) D. Erickson, doctoral dissertation, The Ohio State University (1956).

(31) R. M. Fuoss and U. P. Strauss, J. Polymer Sci., 3, 246 (1948).

(32) P. Goodman, doctoral dissertation, The Ohio State University (1952).

Fractionation of the Polymer

Ninety grams of the polyvinylpyridine (PVP) were dissolved in 3000 ml of tertiary butyl alcohol (TBA). Benzene was added to this solution slowly, with stirring, until the cloud point was reached (approximately 5350 ml benzene). An additional 50 ml of benzene was then added to precipitate the first fraction of polymer, H-1. The solution was allowed to stand overnight, after which the supernatant solution was siphoned off. An additional 75 ml of benzene was added to the supernatant to precipitate the second fraction of polymer, M-1. After standing overnight, the supernatant above M-1 was siphoned off, and an additional 150 ml of benzene was added to it, to precipitate the third fraction of polymer, L-1.

The above process was repeated with an additional 90 g of polymer, and each fraction was dried by lyophilization (freeze-drying). From four such fractionations, 56 g of H-1, 34 g of M-1 and 80 g of L-1 were obtained.

Each fraction was redissolved in enough tertiary butyl alcohol to give approximately a 2% solution, and was then refractionated by further addition of benzene as shown in Table 1. The products were lyophilized to give a white, spongy material, which was further dried in a vacuum oven at 40°C.

Table 1
Second Fractionation of PVP

Fraction used	Weight of fraction used in grams	Volume of TBA in ml.	Volume of benzene added in ml.	Remarks
H-1	56	2900	4765	Initial cloud point
			4768	Fraction H-2 (discarded)
			4932	Fraction HM-2 (9.8g)
M-1	34	1700	2994	Initial cloud point
			3074	Fraction MH-2 (15.7g)
			3354	Fraction ML-2 (4.7g)
L-1	80	3200	5375	Initial cloud point
			5975	Fraction LM-2 (60.5g)

Quaternization with n-Butyl Bromide

Commercial grade nitromethane, which was used as the solvent, was purified by fractional distillation and used immediately. The 1-bromobutane was obtained from Eastman Kodak Company (EK-51), and was used without further purification. Dioxane was dried over sodium and distilled before use.

Fifty-eight grams of polyvinylpyridine (fraction LM-2) were dissolved in 1100 ml of nitromethane, and 853 ml of 1-bromobutane was added. This solution was allowed to stand under a nitrogen atmosphere for one week, during which time the temperature was maintained at 60°C. The viscous brown solution was then lyophilized to give a solid product which was dissolved in 425 ml of absolute alcohol. This solution was slowly poured into 8.6 liters of dioxane with stirring, to produce a white flocculent precipitate. The solvent was squeezed from the precipitate which was then dried in a vacuum oven at 40°C for three and one-half days and stored in a vacuum dessicator.

Characterization of the Poly-4-vinyl-N,n-butylpyridinium Bromide

Chemical analysis.--A sample of the PVPBr was analyzed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. The results of duplicate analyses are shown in Table 2.

From an average of the two analyses one can calculate a formula for the molecule of $C_{11.04} H_{18.08} N_{1.000} Br_{1.004}$ as compared with the theoretical formula $C_{11}H_{16}NBr$.

From the 1:1 ratio of Br and N atoms as shown by analysis, one might conclude that the polymer was 100%

Table 2
Analysis of PVPBr

%C	%H	%N	%Br
51.41	7.03	5.39	31.03
51.59	7.12	5.49	31.27

quaternized. Titration with $AgNO_3$ does give 100% Br^- , but titration with NaOH shows that about 2.25% of the Br^- ions are associated with H^+ rather than P^+ . Therefore it is believed that 97.75% of the nitrogens are quaternized with butyl bromide, and the additional 2.25% are quaternized with HBr.

Assuming the activity coefficients are unity, pH measurements on 1% and 0.5% solutions of PVPBr in water indicate that 35% of this HBr is hydrolyzed in a 1% solution

and 48% is hydrolyzed in a 0.5% solution (33). Very little hydrolysis would be expected when the polymer is dissolved in an HBr solution, however.

Molecular weight.--Light scattering studies were made on the unquaternized polymer in nitromethane by the dissymmetry method. A random coil shape was assumed, which gave a molecular weight of 116,000. If the polymer is assumed to be 100% quaternized, then the molecular weight of the PVPBr would be $116,000 \times 242/105 = 267,000$, corresponding to a weight average degree of polymerization of 1100.

(33) It will be shown in the discussion section that a better estimate of the amount of hydrolysis indicates that 46.6% of this HBr is hydrolyzed in a 1% solution, and 64% is hydrolyzed in a 0.5% solution.

Experimental Procedure

Preparation of Solutions

Studies were made on 1%, 0.5%, 0.3% and 0.1% solutions of PVPBr in 0.04, .025, .01, .005 and .0025N HBr and in water.

The three most concentrated HBr solutions were standardized against NaOH and found to be 0.04065, 0.02504 and 0.01020 N. The .005 and .0025 N solutions were prepared by dilution of 0.025 N HBr to give the required solution. Demineralized double distilled water was used to prepare solutions of PVPBr in water.

To prepare a 1% solution, the PVPBr was weighed out and dissolved in the required volume of solvent. Other solutions were prepared either by weighing out the PVPBr and dissolving in the appropriate solvent, or more frequently, by dilution of a 1% solution with the appropriate solvent.

The exact concentrations of the solutions were determined by analysis and are given in Table 3. (See page 45.)

Analysis of Solutions

Determination of total Br⁻ concentration.--The Volhard method was used for the Br⁻ analyses. This method consists

of titration with AgNO_3 followed by a back titration with NH_4SCN . The back-titration procedure permitted the endpoint to be observed three times for each sample. In addition two samples were analyzed for each solution, and the average of the six results was used as the Br^- concentration of the solution.

The AgNO_3 solutions (.01 and .02N) were prepared (34) by accurately weighing out the required amount of AgNO_3 (Merck, Primary Standard) and diluting to volume. The NH_4SCN solution (.01N) was prepared (34) by accurately diluting standard 0.1 N NH_4SCN , and was checked against the standard AgNO_3 solutions before use.

Determination of H^+ concentration.--The H^+ was titrated with standard .02N NaOH using phenolphthalein as indicator. In most cases two samples of each solution were analyzed.

The NaOH solutions were prepared (34) from a saturated solution of CO_2 -free NaOH, and were standardized against potassium acid phthalate (Mallinckrodt, Primary Standard). The solutions were restandardized frequently, and special precautions were taken to exclude CO_2 from the bottle in which the base was stored and from the buret used for the titration. The base was always checked before use, and was discarded if it gave a precipitate with 0.5M BaCl_2 .

(34) Prepared by the Ohio State University Control and Reagent Laboratory.

Determination of PVP⁺ concentration.--The concentration of PVP⁺ was obtained from the equation

$$C_P = C_{Br} - C_H$$

where C_{Br} and C_H are the concentrations of Br^- and H^+ in the same units. All analyses were made on a weight basis (equivalents per 1000 g solution) and were converted to equivalents per 1000 g water for the transference calculations.

Since C_P is often a small difference between two much larger quantities, C_{Br} and C_H must be determined quite accurately to give reliable values of C_P .

Transference Experiments

The transference cell consisted of a modified Hittorf apparatus as shown in Fig. 1. The right angle bends were inserted to help eliminate convection currents (35). The anode, middle, and cathode compartments, which are indicated by the letters A, M and C, had volumes of 60, 30 and 70 ml, respectively. Vent tubes V and V' facilitated draining the various compartments without mixing.

The electrodes were made from bright platinum wire (20 gauge), the anode being a coil made from a 3 cm length,

(35) D. A. MacInnes and M. Dole, J. Am. Chem. Soc., 53, 1357 (1931).

Fig. 1. — Transference cell.

while the cathode was only 2 mm long. The electrode reactions are shown below:

At the anode, oxidation of Br^- and H_2O occurred simultaneously, the relative amounts depending upon the concentrations of both HBr and PVPBr . A bright yellow precipitate also formed at the anode which is believed to be PVPBr_3 (36) as indicated above. Because of the presence of the yellow precipitate and Br_2 , the anode solution was not analyzed.

Originally the cell was designed for use with a non-gassing AgBr cathode, but it was found that the polymer was

(36) This yellow precipitate is also formed when Br_2 water is added to a solution of PVPBr . Upon drying it forms a bright orange salt which is insoluble in water, but dissolves readily in ethylene glycol monomethyl ether. When SO_3^{2-} is added to the precipitate in water, the yellow color is immediately discharged and the precipitate disappears, indicating that Br_2 is readily given up by the compound PVPBr_3 . Dr. M. P. Cava of this laboratory has prepared a similar salt of pyridine (PH^+ , Br_3^-) which is a stable orange-red salt, less soluble than ($\text{PH}^+ \text{Br}^-$), and acts as a source of free Br_2 toward reducing agents.

adsorbed on the surface of the AgBr. Therefore a platinum electrode was used and the size was kept small so that H₂ bubbles coming off the small surface might help prevent adsorption of polymer. The cathode was weighed at the beginning and end of about half of the experiments, and no change in weight was noted.

The electrodes were held in place by rubber stoppers which also contained stopcocks which were left open to permit escape of gases during a run, but were closed while the cell was being removed from the bath and drained.

A constant-voltage power supply was used, the current being regulated between 6 and 12 ma by means of a variable resistance in series with the cell. The quantity of electricity passed through the cell could be estimated from current-time observations, but was measured accurately by means of two iodine coulometers, one in series with each electrode.

During the transference experiments the cell was immersed in a water bath maintained at $25.00 \pm 0.01^\circ\text{C}$. The cell was mounted on a hydraulic lift to permit removal from the bath with a minimum of vibration.

Conductance Measurements

A Jones-type bridge manufactured by Leeds and Northrup Company was used for the conductance measurements.

The cells were designed according to the recommendations of Jones and Bollinger (37), but in order to minimize adsorption of polymer on the electrodes, the latter were not platinized.

Two cells were used (Fig. 2), cell A having a cell constant of 39.968, while cell B had a cell constant of about 2.8247. Cell B was used for the solutions of PVPBr in water, while cell A was used for all solutions containing HBr. The cell constants were accurately determined before each series of measurements by using a standard .01 normal KCl solution.

All resistance measurements were made at 1000 cycles per second with the cell in a water bath which was maintained at $25.000 \pm 0.005^{\circ}\text{C}$.

(37) G. Jones and G. M. Bollinger, J. Am. Chem. Soc. 53, 411 (1931).

Cell A

Cell B

Fig. 2. — Conductance cells.

Application of the General Theory
to Solutions of PVPBr in HBr

Calculation of the Degree of
Association of Br⁻ Ions

The equations developed in the general theory section will be used here with the counterion, C, being replaced by Br⁻, and the by-ion, B, being replaced by H⁺.

The nature of the polyelectrolyte--specifically the partial quaternization with HBr rather than butyl bromide--introduces a few complications which will be considered before proceeding with the theory.

Throughout the derivation of the general theory, it was assumed that none of the by-ions were associated with the polyelectrolyte. In the system studied, however, some HBr was associated with the polymer, since 2.25% of the nitrogens were quaternized with HBr rather than butyl bromide. The analytical procedure used gives the total H⁺ concentration (free H⁺ plus bound H⁺), while it is only the concentration of free H⁺ which should be used in the calculation of α . When the polymer is dissolved in water, an estimate of the free H⁺ can be made from pH measurements along with some other considerations to be presented in the discussion section. For solutions of PVPBr in HBr, pH

measurements are not sensitive enough to determine whether any of the HBr is removed from the nitrogens of the polymer or not. The extent of such hydrolysis in HBr solutions would be small, however, so it will be assumed that it is negligible, and the free H^+ concentration will be assumed to be equal to C'_H , the concentration in the HBr solution in which the polyelectrolyte was dissolved. In all the equations used to calculate α the by-ion concentration will therefore be written as C'_H to emphasize that it is the concentration of free H^+ ions which is to be used. Values of C'_H for all the solutions used are tabulated in Table 4.

Ordinarily the by-ion transference number would be calculated from the equation

$$t_b = \frac{Q_b}{n}$$

The hydrogen ion transference number must be corrected for the small fraction of the total H^+ which is carried by the polymer, however, and thus the correct expression is

$$t_H = \frac{Q_H - Q_p(\%H/100)}{n} \quad (23)$$

where $\%H$ represents the percentage of the nitrogen atoms in the polymer which carry H^+ rather than a butyl group. For solutions of PVPBr in HBr, $\%H$ is assumed to be 2.25%, while for solutions of PVPBr in water this must be corrected for

hydrolysis. In all cases the correction was smaller than the experimental errors involved in measuring t_H .

The equations for α as developed in the general theory section will now be applied to solutions of PVPBr in HBr, and the methods of calculation will be discussed in more detail.

Method (1).--Equation 7 can now be written

$$\alpha = \frac{10^3 K - c'_H \Lambda'_H - c'_H \Lambda_{Br}}{\frac{10^3 Q_p K}{n} + c_p \Lambda_{Br}} \quad (24)$$

where Λ_H has been written as Λ'_H to indicate that it is calculated from data on the HBr solutions rather than in the polymer solution itself.

Λ'_H and Λ'_{Br} could be determined from experimental data (transference numbers and conductances of HBr solutions), but data on HBr solutions are scarce in the literature. Separate transference experiments could have been made on HBr solutions, but the Hittorf method which was used in this work does not give very accurate results. Theoretical equations are available which give Λ_1 as a function of concentration, and it was decided that such an equation would give more accurate results than Hittorf-type transference experiments.

The equation used was that given by Robinson and Stokes (38, 39) for a 1-1 electrolyte.

$$\Lambda_1 = \Lambda_1^0 - (B_1 \Lambda_1^0 + \frac{1}{2} B_2) \frac{\sqrt{C}}{1 + Ba \sqrt{C}} \quad (25)$$

where $B = 0.3286$, $B_1 = 0.2289$ and $B_2 = 60.32$. The quantity a is the ion size parameter in Angstroms, for which a value of 5.10 was used. This compares well with the value of 5.18 obtained for HBr over the range 0.1-1.0 molal from activity coefficient data (40).

Values of 78.14 and 349.81 were used for Λ_{Br}^0 and Λ_H^0 , so equation 25 can be written

$$\Lambda_{Br} = 78.14 - \frac{48.05 \sqrt{C}}{1 + 1.68 \sqrt{C}} \quad (26)$$

$$\Lambda_H = 349.81 - \frac{110.2 \sqrt{C}}{1 + 1.68 \sqrt{C}} \quad (27)$$

The values of Λ_H obtained from the above equation are tabulated in Table 4 under the column labeled Λ'_H .

(38) R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Academic Press, New York, 1955, p. 150.

(39) Literature data is lacking for HBr, but for HCl, the values of Λ_{Cl}^0 calculated from this equation agree with observed values within 0.07% for a .01 N solution and within 0.6% for a .1 N solution.

(40) R. A. Robinson and R. H. Stokes, *loc. cit.*, p. 247.

Since the free Br^- concentration depends on α , an estimate of Λ_{Br} must be made, which is then used in equation 24 to calculate an approximate value of α . From the value of α so obtained, the free Br^- concentration is calculated

$$(\text{C}_{\text{Br}})_{\text{free}} = \text{C}'_{\text{H}} + \alpha \text{C}_{\text{p}}$$

and using this concentration, a new value of Λ_{Br} is obtained from equation 26. The process is repeated until there is no change in the resultant value of α .

Method (ii).--Equation 16 may now be written

$$\alpha = \frac{1 - t_{\text{H}} - \frac{\text{C}'_{\text{H}} \Lambda_{\text{Br}}}{10^3 \text{K}}}{\frac{Q_{\text{p}}}{n} + \frac{\text{C}_{\text{p}} \Lambda_{\text{Br}}}{10^3 \text{K}}} \quad (28)$$

In using this method, t_{H} is obtained from equation 23, and α and Λ_{Br} are adjusted by successive approximations as in method (i).

Method (iii).--Equation 19 may now be written as follows:

$$\alpha = \frac{1 - t_{\text{H}} - r t_{\text{H}}}{\frac{Q_{\text{p}}}{n} + \frac{\text{C}_{\text{p}}}{\text{C}'_{\text{H}}} r t_{\text{H}}} \quad (29)$$

All of the quantities in this expression can be determined from a transference experiment except r , and it can be determined from a separate transference experiment on the HBr solution. A better (41) method for calculating r is to use an equation for the variation of transference number with concentration. For a 1-1 electrolyte such an equation may be written (42)

$$t_1 = \frac{\Lambda_1^0 - \frac{1}{2}B_2 \frac{\sqrt{C}}{1 + Ka}}{\Lambda^0 - B_2 \frac{\sqrt{C}}{1 + Ka}} \quad (30)$$

where $B_2 = 60.32$, and $Ka = 0.3286a\sqrt{C}$, a being the ion size parameter in Angstroms. A value of 5.10 (43) was used for a , as in the preceding section.

(41) For salts for which experimental data are available (e.g., HCl, LiCl, NaCl, NaAc, KCl, KAc) the above equation gives results which are more accurate than those obtained from the Hittorf-type transference experiments used in this work. For 0.01 N and 0.10 N HBr, the equation gives the same results as were obtained experimentally in this laboratory, but the experimental values are accurate to only three significant figures, whereas the calculated values for the salts mentioned above agree with values obtained by the more accurate moving boundary method within 0.05% over the range 0.01-0.10 N.

(42) R. A. Robinson and R. H. Stokes, loc. cit., p. 157.

(43) t_H is not very sensitive to the choice of a . For .02N HBr, t_H varies from 0.8229 to 0.8226 as a is varied from 4.00 to 5.40.

In calculating r , the denominator of equation 30 cancels, and the expression for r becomes

$$r = \frac{t'_{Br}}{t'_H} = \frac{\Lambda^{\circ}_{Br} - \frac{1}{2}B_2 \frac{\sqrt{C}}{1+Ka}}{\Lambda^{\circ}_H - \frac{1}{2}B_2 \frac{\sqrt{C}}{1+Ka}} \quad (31)$$

Values of r calculated from this equation and of t'_H calculated from equation 30 are given in Table 4 for each of the HBr solutions used as solvent.

Method (iv).--Equation 18 can be rewritten in terms of the present notation to give

$$\alpha = \frac{1 - t_H - xrt_H}{\frac{Q_p}{n} + \frac{C_p}{C'_H} xrt_H} \quad (32)$$

with $x > 1$ since $\Lambda^{\circ}_{Br} < \Lambda^{\circ}_H$.

As stated previously, the quantity x is a complex variable and cannot be evaluated for the polyelectrolyte solution. Values of α will be calculated for different values of x , so that the effect of x on α may be determined. This in turn may indicate the nature of the error involved in method (iii), since the latter is really a special case of method (iv) in which $x = 1$.

Results

The Data

The experimental data are presented in Table 3. In Tables 4-8, the quantities needed to calculate α by each of the four methods discussed earlier are tabulated, along with the corresponding values of α . Table 9 gives a comparison of the values of α obtained by each of the four methods.

Methods (i) and (ii) involve the simultaneous adjustment of Λ_{Br} and α . The values of Λ_{Br} given in Tables 5 and 6 are the final values obtained by this method. Blank spaces in Table 5 indicate that the numerator in the expression for α was negative.

For method (iv) a parameter x must be chosen before α can be calculated. Table 7 gives values of α for several different values of x . If too high a value is chosen for x , the numerator in the expression for α becomes negative. This is indicated by a blank space in Table 7. It should be noted that method (iii) is merely a special case of method (iv) in which $x = 1$.

The binding data (44) are also shown graphically in Figs. 3-15, where the influence of both HBr and PVPBr concentrations on the value of α obtained by each method is shown.

In the graphs for which C_{HBr} is the abscissa, all the experimental points for a given HBr concentration should fall on the same vertical line, since C_{HBr} was the same for all. In some of the graphs the points were displaced slightly from the true value of C_{HBr} , however, so that the error lines would not overlap.

The quantities necessary to calculate the polyion mobility are tabulated in Table 10. Table 12 gives the values of K_H and Λ_H calculated in the polyelectrolyte solution.

Estimation of Errors

Errors in direct experimental observations (weighing, reading burets, determining end points, etc.) were

(44) If one wishes to be strictly correct, he should talk about binding data for a system in which the monomeric counterpart is a strong electrolyte, in terms of the degree of association of the counterions.

It is more convenient to graph and discuss the charge fraction α , however, particularly if one wishes to compare its behavior with that of simple weak electrolytes, for which α is also the degree of dissociation.

It is hoped, therefore, that the author will be excused if he occasionally refers to the quantity α as the degree of dissociation of the polyelectrolyte; for whether it is called the charge fraction or the degree of dissociation is a problem of semantics, not of interpretation.

estimated. Errors in indirect measurements and in calculated quantities were determined in the usual manner by combining the errors from different sources using the method of least squares.

The estimated errors in C_1 , Q_1 and t_H are presented in Table 10, for $i = \text{Br}^-$, H^+ and P^+ . The error in C_H and C_{Br} depends on the size of the sample analyzed. For C_H this is determined by C_{HBr} only, but for C_{Br} it depends on both C_{HBr} and C_{PVPBr} .

The large error in t_H deserves some explanation. At the cathode, H^+ is reduced to hydrogen gas, one equivalent of H^+ being reduced for each equivalent of electricity passed through the cell. Hydrogen ion migrates into the cathode compartment during a transference experiment, but the net change in H^+ concentration is small (and negative), because more H^+ is lost through reduction than is gained by transference. When n equivalents of electricity are passed through the cell, $t_H = Q_H/n$ where Q_H is the number of equivalents of H^+ which migrate into the cathode compartment. The quantity Q_H must be calculated from the expression

$$Q_H = Q'_H + n$$

where Q'_H is the net increase (a negative quantity) in H^+ in the cathode compartment. Q'_H and n are of the same order of magnitude, so the large error in Q'_H (which is a small

difference between two large quantities) produces a rather large error in Q_H and thus in t_H .

The estimated errors in α calculated by methods (ii) and (iii) are given in Tables 5 and 6 under the heading $\Delta\alpha$. In calculating the error in α , the only sources of error that need be considered are those due to errors in Q_P and t_H , since other sources of error are negligible compared to these two. It should be noted that the errors so calculated will be larger for method (iii) than for method (ii), because t_H is multiplied by $(1 + r)$ in the former case, and by only 1 in the latter. The estimated errors in α are indicated by the lengths of the vertical lines through the experimental points in Figs. 4, 5, 11 and 12.

Errors in α calculated by method (i) were not estimated. Since only experimental errors are considered, however, errors in α (i) will be less than those in α (ii) because one of the two main sources of error is t_H , and method (i) does not involve the use of t_H .

The errors in the values of α calculated by method (iv) were not estimated, because they depend upon the value of x which is used. The errors in α (iv) will be larger than those in α (iii) because t_H is multiplied by $(1 + xrt)$ in the former, and by only $(1 + r)$ in the latter.

Errors in u_P are given in the column marked Δu_P in Table 9, and are indicated in Figs. 11 and 12 by the length of the vertical lines through the points.

Table 3
Experimental Data

C _P	C _{HBr}	t _H	Q _P	n	C _P	K x 10 ³
%	eq/l		meq	meq	$\frac{\text{meq}}{10g \text{ soln}}$	$\frac{\text{mho}}{\text{cm}}$
0.1	0.0025	0.701	0.0150	0.07892	0.04129	1.1414
	.005	.753	.0106	.14218	.04155	2.1185
	.01	.7947	.0148	.42924	.04017	4.2088
	.025	.8119	.0052	.76214	.04251	10.170
	.04	.8150	.0028	1.2945	.04200	16.297
0.3	0.0025	0.606	0.0304	0.09723	0.12384	1.3535
	.005	.700	.0271	.15560	.12233	2.2984
	.01	.7519	.0347	.44621	.12180	4.3696
	.01	.7532	.0375	.44041	.12179	4.3462
	.025	.7972	.0122	.56159	.12503	10.276
	.04	.8019	.0267	1.4978	.12353	16.357
0.5	0	0.117	0.0209	0.02232	0.20532	0.64572
	0	.165	.0239	.02522	.20345	0.65215
	0.0025	.512	.0520	.12285	.22133	1.6041
	.005	.631	.0529	.21886	.20857	2.5048
	.01	.7185	.0540	.44396	.20547	4.4987
	.025	.7783	.0213	.56240	.20495	10.363
	.04	.7943	.0370	1.7380	.20631	16.415
1.	0	0.123	0.0279	0.03814	0.40942	1.2352
	0	.099	.0335	.03600	.41157	1.2427
	0.0025	.373	.0638	.11960	.41083	2.0908
	.005	.528	.0680	.19913	.41128	2.9604
	.01	.6463	.0936	.45132	.40883	4.8993
	.025	.7452	.0459	.66797	.40692	10.616
	.04	.7687	.0725	1.6197	.41134	16.538

Each of the quantities tabulated above contains two doubtful figures.

Table 4
Values of r , Λ'_{Br} , Λ'_H and t'_H for the Various
HBr Solutions Used as Solvent

C_{HBr}	r	Λ'_{Br}	Λ'_H	t'_H
0.04065	0.21371	70.90	333.21	0.82429
.02504	.21492	72.13	336.04	.82310
.01020	.21756	73.99	340.29	.82131
.00500	.21911	75.10	342.85	.82027
.00250	.22028	75.92	344.73	.81948
.000439(a)	.22202	77.16	347.87	.81832
.000306(a)	.22224	77.31	348.18	.81817

(a) Estimated values of free HBr present for solutions of 1% and 0.5% PVPBr in water. The PVPBr is partially quaternized (2.25%) with HBr rather than butyl bromide, and part of this HBr is hydrolyzed in water (see discussion section).

Table 5

Quantities Used to Calculate α
by Method (1)

$$\alpha = \frac{10^3 K - C'_H \Delta'_H - C'_H \Delta_{Br}}{\frac{10^3 Q_{PK}}{n} + C_P \Delta_{Br}}$$

C_P	C_{HBr}	Δ_{Br}	$10^3 K$	$C'_H \Delta'_H$	$C'_H \Delta_{Br}$	$\frac{10^3 Q_{PK}}{n}$	$C_P \Delta_{Br}$	α
0.1	0.0025	75.65	1.1414	0.8618	0.1891	0.2170	0.3124	0.171
	.005	75.04	2.1185	1.7143	.3752	.1579	.3193	.061
	.01	--	4.2088	3.4710	--	.1451	--	--
	.025	--	10.170	8.4144	--	.06936	--	--
	.04	--	16.297	13.545	--	.03520	--	--
0.3	0.0025	75.03	1.3535	0.8618	0.1876	0.4231	0.9292	0.225
	.005	74.62	2.2984	1.7143	.3731	.4004	.9128	.161
	.01	73.75	4.3696	3.4710	.7523	.3398	.8983	.118
	.01	73.79	4.3482	3.4710	.7527	.3701	.8987	.097
	.025	72.09	10.276	8.4144	1.8051	.2232	.9013	.050
	.04	--	16.357	13.545	--	.2916	--	--
0.5	0	75.04	0.6457	0.1065	0.0230	0.6054	1.541	0.241
	0	75.04	0.6522	0.1065	.0230	.6180	1.527	.244
	0.0025	74.45	1.6041	.8618	.1861	.6787	1.648	.239
	.005	74.20	2.5048	1.7143	.3710	.6054	1.548	.195
	.01	73.55	4.4987	3.4710	.7502	.5470	1.511	.135
	.025	71.99	10.363	8.4144	1.8026	.3924	1.475	.078
	.04	--	16.415	13.545	--	.3495	--	--
1.	0	73.81	1.2352	0.1527	0.0324	0.9035	3.022	0.267
	0	73.89	1.2427	.1527	.0324	1.1564	3.041	.254
	0.0025	73.70	2.0908	.8618	.1843	1.1152	3.028	.232
	.005	73.41	2.9604	1.7143	.3671	1.0110	3.019	.218
	.01	72.95	4.8993	3.4710	.7441	1.0161	2.982	.171
	.025	71.70	10.616	8.4144	1.7954	.7294	2.918	.111
	.04	70.79	16.538	13.545	2.8776	.7402	2.912	.032

Table 6

Quantities Used to Calculate α by Method (ii)

$$\alpha = \frac{1 - t_H - \frac{C'_H \wedge_{Br}}{10^3 K}}{1 - t_H - \frac{\beta \Omega^{3v}}{10^3 K}}$$

C_P	C_{HBr}	Δ_{Br}	t_H	$\frac{C_H \Delta_{Br}}{10^3 K}$	$\frac{C_P \Delta_{Br}}{10^3 K}$	$\frac{Q_P}{n}$	α	$\Delta\alpha$
0.1	0.0025	75.49	0.701	0.1653	0.2730	0.1901	0.289	0.057
	.005	74.77	.753	.1765	.1466	.07454	.319	.096
	.01	73.82	.7947	.1789	.07045	.03448	.252	.067
	.025	72.01	.8119	.1773	.03010	.00682	.293	.108
	.04	70.79	.8150	.1766	.01824	.00216	.412	.126
0.3	0.0025	74.93	0.606	0.1384	0.6856	0.3126	0.256	0.022
	.005	74.41	.700	.1619	.3960	.1742	.242	.035
	.01	73.47	.7519	.1715	.2048	.07777	.271	.025
	.01	73.50	.7532	.1725	.2059	.08515	.255	.024
	.025	71.85	.7972	.1751	.08744	.02172	.254	.050
	.04	70.65	.8019	.1756	.05335	.01783	.316	.030
0.5	0	74.96	0.117	0.0355	2.3837	0.9364	.255	0.017
	0	75.04	.165	.0352	2.3412	.9477	.243	.016
	0.0025	74.37	.512	.1159	1.0263	.4231	.257	.012
	.005	73.96	.631	.1476	.6159	.2417	.258	.016
	.01	73.21	.7185	.1660	.3344	.1216	.253	.015
	.025	71.64	.7783	.1731	.1417	.03787	.271	.031
	.04	70.53	.7943	.1747	.08867	.02129	.282	.017
1.	0	73.79	0.123	0.0262	2.4461	0.7315	0.268	0.012
	0	73.84	.099	.0261	2.4456	.9306	.259	.012
	0.0025	73.44	.373	.0878	1.4431	.5334	.273	.009
	.005	73.19	.528	.1236	1.0166	.3415	.256	.012
	.01	72.61	.6463	.1512	.6059	.2074	.249	.008
	.025	71.27	.7452	.1681	.2732	.06871	.254	.014
	.04	70.24	.7687	.1726	.1747	.04476	.267	.009

Table 7

Quantities Used to Calculate α by Method (iii)

$$\alpha = \frac{1 - t_H - rt_H}{\frac{Q_P}{n} + \frac{C_P}{C'_H} rt_H}$$

C_P	C_{HBr}	t_H	rt_H	$\frac{Q_P}{n}$	$\frac{C_P}{C'_H} rt_H$	α	$\Delta\alpha$
0.1	0.0025	0.701	0.1544	0.1901	0.25501	0.325	0.078
	.005	.753	.1650	.07454	.13712	.387	.129
	.01	.7947	.1729	.03448	.06809	.316	.086
	.025	.8119	.1745	.00682	.02962	.373	.135
	.04	.8150	.1737	.00216	.01795	.562	.160
0.3	0.0025	0.606	0.1335	0.3126	0.66131	0.267	0.033
	.005	.700	.1534	.1742	.37531	.267	.048
	.01	.7519	.1636	.07777	.19593	.309	.032
	.01	.7532	.1639	.08515	.19570	.295	.031
	.025	.7972	.1713	.02172	.08553	.294	.066
	.04	.8019	.1709	.01783	.05193	.390	.039
0.5	0	0.117	0.02600	0.9364	1.7445	0.320	0.118
	0	.165	.03667	.9477	2.4381	.236	.066
	0.0025	.512	.1128	.4231	.99864	.264	.020
	.005	.631	.1383	.2417	.57690	.282	.024
	.01	.7185	.1563	.1216	.31485	.287	.021
	.025	.7783	.1673	.03787	.13693	.297	.040
	.04	.7943	.1697	.02129	.08613	.335	.021
1.	0	0.123	0.02731	0.7315	2.5470	0.259	0.059
	0	.099	.02198	.9306	2.0607	.294	.080
	0.0025	.373	.08216	.5334	1.3501	.289	.021
	.005	.528	.1157	.3415	.95170	.276	.020
	.01	.6463	.1406	.2074	.56354	.276	.013
	.025	.7452	.1602	.06871	.26034	.287	.018
	.04	.7687	.1639	.04476	.16585	.320	.012

Table 8

Values of α Calculated by Method (iv)
for Several Values of x

$$\alpha = \frac{1 - t_H - xrt_H}{\frac{C_P}{n} + \frac{C_P}{C_H} xrt_H}$$

C_P	C_{HBr}	Value of x assumed					
		1.20	1.10	1.05	1.03	1.01	1.00
0.1	0.0025	0.229	0.275	0.299	0.309	0.320	0.325
	.005	.205	.291	.337	.357	.377	.387
	.01	--	.138	.225	.260	.297	.316
	.025	--	--	.129	.225	.324	.373
	.04	--	--	.124	.295	.473	.562
0.3	0.0025	0.211	0.238	0.252	0.258	0.264	0.267
	.005	.186	.224	.244	.253	.262	.267
	.01	.166	.232	.269	.275	.301	.309
	.01	.157	.221	.257	.272	.287	.295
	.025	--	.124	.205	.240	.276	.294
	.04	--	.135	.258	.310	.363	.390
0.5	0	0.281	0.299	0.309	0.313	0.318	0.320
	0	.204	.219	.227	.230	.234	.236
	0.0025	.217	.239	.251	.256	.261	.264
	.005	.217	.248	.264	.271	.278	.282
	.01	.188	.234	.260	.270	.281	.287
	.025	.103	.200	.253	.276	.299	.297
	.04	.017	.164	.246	.281	.317	.335
1.0	0	0.223	0.240	0.249	0.253	0.257	0.259
	0	.257	.274	.284	.288	.292	.294
	0.0025	.245	.266	.277	.282	.287	.289
	.005	.225	.248	.261	.267	.273	.276
	.01	.209	.241	.258	.265	.273	.276
	.025	.164	.221	.253	.267	.280	.287
	.04	.142	.224	.273	.290	.310	.320

Table 9
Comparison of α Values Obtained
by Methods (i), (ii), (iii) and (iv)

C_P	C_{HBr}	$\alpha(i)$	$\alpha(ii)$	$\alpha(iii)$	$\alpha(iv)$ with $x =$		
					1.01	1.05	1.20
0.1	0.0025	0.171	0.289	0.325	0.320	0.299	0.229
	.005	.061	.319	.387	.377	.337	.205
	.01	--	.252	.316	.297	.225	--
	.025	--	.293	.373	.324	.129	--
	.04	--	.412	.562	.473	.124	--
0.3	0.0025	0.225	0.256	0.267	0.264	0.252	0.211
	.005	.161	.242	.267	.262	.244	.186
	.01	.118	.271	.309	.301	.269	.166
	.01	.097	.255	.295	.287	.257	.157
	.025	.050	.254	.294	.276	.205	--
	.04	--	.316	.390	.363	.258	--
0.5	0	0.241	0.255	0.320	0.318	0.309	0.281
	0	.244	.243	.236	.234	.227	.204
	0.0025	.239	.257	.264	.261	.251	.217
	.005	.195	.258	.282	.278	.264	.217
	.01	.135	.253	.287	.281	.260	.188
	.025	.078	.271	.297	.299	.253	.103
	.04	--	.282	.335	.317	.246	.017
1.	0	0.267	0.268	0.259	0.257	0.249	0.223
	0	.254	.259	.294	.292	.284	.257
	0.0025	.232	.273	.289	.287	.277	.245
	.005	.218	.256	.276	.273	.261	.225
	.01	.171	.249	.276	.273	.258	.209
	.025	.111	.254	.287	.280	.253	.164
	.04	.032	.267	.320	.310	.273	.142

Table 10
Mobilities of the Polyion

$$u_p = \frac{10^3 Q_p K}{C_p n F}$$

C_P	C_{HBr}	Q_P	$K \times 10^3$	C_P	n	$10^4 \times u_p$	$10^4 \times \Delta u_p$
%	eq/l	meq	$\frac{mho}{cm}$	$\frac{meq}{10g\ soln}$	meq	$\frac{cm^2}{volt\ sec}$	
0.1	0.0025	0.0150	1.1414	0.04129	0.07892	5.44	0.87
	.005	.0106	2.1185	.04155	.14218	3.94	1.22
	.01	.0148	4.2088	.04017	.42924	3.74	.82
	.025	.0052	10.170	.04251	.76214	1.69	1.07
	.04	.0028	16.297	.04200	1.2945	0.87	1.12
0.3	0.0025	0.0304	1.3535	0.12384	0.09723	3.54	0.32
	.005	.0271	2.2984	.12233	.15560	3.39	.44
	.01	.0347	4.3696	.12180	.44621	2.89	.32
	.01	.0375	4.3462	.12179	.44041	3.15	.31
	.025	.0122	10.276	.12503	.56159	1.85	.59
	.04	.0267	16.357	.12353	1.4978	2.45	.37
0.5	0	0.0209	0.64572	0.20532	0.02232	3.05	0.26
	0	.0239	0.65215	.20345	.02522	3.15	.24
	0.0025	.0520	1.6041	.22133	.12285	3.18	.14
	.005	.0529	2.5048	.20857	.21886	3.01	.19
	.01	.0540	4.4987	.20547	.44396	2.76	.21
	.025	.0213	10.363	.20495	.56240	1.98	.38
	.04	.0370	16.415	.20631	1.7380	1.76	.19
1.	0	0.0279	1.2352	0.40942	0.03814	2.29	0.23
	0	.0335	1.2427	.41157	.03600	2.91	.25
	0.0025	.0638	2.0908	.41083	.11960	2.81	.15
	.005	.0680	2.9604	.41128	.19913	2.55	.15
	.01	.0936	4.8993	.40883	.45132	2.58	.13
	.025	.0459	10.616	.40692	.66797	1.86	.19
	.04	.0725	16.538	.41134	1.6197	1.86	.12

Table 11
Estimated Errors in C_1 , Q_1 and t_H

C _P	C _H	Estimated Error in						
		C _{Br}	C _H	C _P	Q _{Br}	Q _H	Q _P	t _H
%	eq/l	meq x 10 ⁵ 10 g soln			meq x 10 ⁴			
0.1	0.0025	14	20	24	14	20	24	0.025
	.005	14	30	33	14	29	33	.020
	.01	14	30	33	14	29	33	.0068
	.025	14	30	33	14	29	33	.0038
	.04	19	31	36	19	30	36	.0023
0.3	0.0025	18	20	37	18	20	27	0.021
	.005	22	30	37	22	29	36	.019
	.01	25	30	39	25	29	36	.0065
	.01	25	30	39	25	29	36	.0065
	.025	27	30	40	27	29	36	.0052
	.04	29	31	42	29	30	41	.0020
0.5	0	13	12	18	13	12	18	0.054
	0	13	12	18	13	12	18	.048
	0.0025	14	20	24	14	20	23	.016
	.005	14	30	33	14	29	33	.013
	.01	29	30	42	29	29	41	.0065
	.025	29	30	42	29	29	41	.0052
	.04	29	31	42	29	30	41	.0017
1.0	0	27	12	30	27	12	29	0.031
	0	27	12	30	27	12	29	.033
	0.0025	27	20	34	27	20	34	.017
	.005	29	30	42	29	29	41	.015
	.01	35	30	46	34	29	46	.0064
	.025	35	30	46	34	29	46	.0043
	.04	37	31	48	36	30	48	.0019

Table 12

Values of K_H and Λ_H in the Polyelectrolyte Solutions

$$\Lambda_H = \frac{10^3 K_H}{C'_H} = \frac{10^3 t_H K}{C'_H}$$

C_P	C_{HBr}	t_H	$10^3 K_H$	Λ_H	Λ'_H	Λ_H/Λ'_H
0.1	0.0025	0.701	0.8001	320.0	344.73	0.928
	.005	.753	1.5952	319.0	342.85	.930
	.01	.7947	3.3447	327.9	340.29	.964
	.025	.8119	8.2570	329.8	336.04	.981
	.04	.8150	13.282	326.7	333.21	.980
0.3	0.0025	0.606	0.8202	328.1	344.73	0.952
	.005	.700	1.6089	321.8	342.85	.939
	.01	.7519	3.2855	322.1	340.29	.947
	.01	.7532	3.2736	320.9	340.29	.943
	.025	.7972	8.1920	327.2	336.04	.974
	.04	.8019	13.117	322.7	333.21	.968
0.5	0	0.121	0.0781	341.0	348.18	0.979(a)
	0	.169	0.1102	481.2	348.18	1.382(a)
	0.0025	.512	0.8213	328.5	344.73	.953
	.005	.631	1.5805	316.1	342.85	.922
	.01	.7185	3.2323	316.9	340.29	.931
	.025	.7783	8.0655	322.1	336.04	.959
	.04	.7943	13.038	320.7	333.21	.962
1.	0	0.125	0.1544	467.9	347.87	1.345(b)
	0	.101	0.1255	380.3	347.87	1.093(b)
	0.0025	.373	0.7799	312.0	344.73	.905
	.005	.528	1.5631	312.6	342.85	.912
	.01	.6463	3.1664	310.4	340.29	.912
	.025	.7452	7.9110	315.9	336.04	.940
	.04	.7687	12.713	312.7	333.21	.938

Values of K and C'_H were obtained from Tables 3 and 4, respectively. Lines marked (a) and (b) were calculated on the basis of $C'_{HBr} = 2.29 \times 10^{-4}$ and 3.30×10^{-4} , respectively.

Fig. 3 — Influence of C_{HBr} on α as calculated by method (i).

Fig. 4: — Influence of C_{HBr} on α as calculated by method (ii).

Fig. 5. — Influence of C_{HBr} on α as calculated by method (iii)

Fig. 6. — Effect of x on the curves of α vs. C_{HBr} as calculated by method (iv) for 0.1% PVPBr.

Fig. 7.— Effect of x on curves of α vs. C_{HBr} as calculated by method (iv) for 0.3% PVPBr.

Fig. 8. - Effect of x on the curves of α vs. C_{HBr} as calculated by method (iv) for 0.5% PVPBr.

Fig. 9. — Effect of x on the curves of α vs. C_{HBr} as calculated by method (iv) for 1% PVPBr.

Fig. 10. — Influence of C_p on α as calculated by method (i).

Fig. 11. — Influence of C_p on α as calculated by method (ii).

Fig. 12. - Influence of C_p on α as calculated by method (iii).

Fig. 13. — Influence of C_p on α as calculated by method (iv) with $x = 1.05$.

Fig 14. — Influence of C_p on α as calculated by method (iv) with $x = 1.10$.

Fig. 15. — Extrapolated values of α as a function of C_p at $C_{HBr} = 0$.

Fig. 16 — Variation of mobility with HBr at constant PVPBr concentration.

Fig. 17. — Variation of mobility with C_p at constant HBr concentration.

Table 13

Comparison of α Values Obtained by Methods
(i), (ii), (iii) and (iv) for Sodium
Polyacrylate in NaCl Solutions (a)

C_{NaCl}	$\alpha(i)$	$\alpha(ii)$	$\alpha(iii)$	$\alpha(iv)$ $x=1.10$
0.00905	0.355	0.367	0.361	0.334
.0302	.328	.346	.341	.300
.0453	.307	.329	.324	.274
.0604	.310	.341	.339(b)	.274

(a) Data taken from F. T. Wall and M. J. Eitel, J. Am. Chem. Soc., 79, 1556 (1957). The values of $\alpha(i)$ were obtained by Wall and Eitel. Other values were calculated from their data. $C_p = 0.07N$ for all the solutions (PAA completely neutralized with NaOH).

(b) This value becomes 0.319 if method (iv) is used with $x = 1.03$, and 0.306 with $x = 1.05$.

Fig. 18. — Influence of C_{NaCl} on α for sodium polyacrylate as calculated by methods (i), (ii), (iii), and (iv).

Discussion of Results

The most important result of this investigation is a comparison of the values of α obtained by the four different methods, and of the influence of added electrolyte on these values. Such a comparison will be facilitated, however, by first considering the mobility data and the values of Λ_H in the polyelectrolyte solution.

Mobility Data

In considering the influence of C_{HBr} and C_P on the mobility of the polyion, two factors are expected to play an important role. One is a decrease in the effective size of the polyion due to a change in shape upon the addition of a simple electrolyte such as HBr, as shown by viscosity studies (45). This decrease in size would tend to increase the mobility with increasing HBr concentration. The second factor is a change in α , and thus the charge on the polyion. By analogy with systems of simple weak electrolytes, one would expect α to decrease as HBr is added, because of the common-ion effect. A decrease in α with added HBr would tend to decrease the mobility of the polyion.

(45) R. M. Fuoss and U. P. Strauss, J. Polymer Sci., 3, 602 (1948).

An examination of Fig. 16 reveals that the polyion mobility does decrease with increasing HBr, and thus the effect of charge on the mobility must be greater than that of shape. Furthermore, since the polyion mobility is obtained directly from experimental quantities with no assumptions involved, the decrease in mobility with HBr concentration is unequivocal evidence that α decreases with increasing HBr concentration.

The decrease in mobility with increasing C_p at constant HBr concentration is just the opposite from what one would expect if the behavior were governed by the common-ion effect on α . The fact that this decrease is more pronounced at low HBr concentrations where the polymer is more extended, than at high HBr concentrations where the polymer is more compact, indicates that it is probably due to polymer-polymer interaction. This emphasizes the fact that the region of greatest interest should be at low polymer concentrations where such interactions are negligible, and it is regrettable that this is precisely the region of greatest experimental error.

Bsharah (46) studied the electrophoretic behavior of PVPBr in HBr solutions, and obtained polyion mobilities by the more accurate moving boundary method. Unfortunately

(46) L. Bsharah, doctoral dissertation, The Ohio State University (1955).

Bsharah was interested in the areas under the peaks in the Schlieren diagrams, and finding the descending boundaries too diffuse to measure the areas, he recorded only the mobilities obtained from the ascending boundaries. It can be shown theoretically (47), that the constituent mobility of the polyion can be obtained directly from the velocity of the descending boundary in a moving boundary experiment, but only indirectly from the ascending boundary, since the conductance in the diluted polymer solution following the boundary is not known in the latter case. The mobilities obtained by Bsharah are thus higher than u_p , the constituent mobility of the polyion. Bsharah estimated that the descending boundaries in his experiments moved only about half as fast as the ascending boundaries. The latter give mobilities which (after correction for a temperature difference) are about twice as large as the values of u_p obtained in the present investigation, so the values of u_p obtained by the two methods are approximately the same.

An interesting thing about the mobilities calculated by Bsharah was their internal consistency. That is, both the u vs. C_{HBr} curves and the u vs. C_p curves had the expected shapes, and the u vs. C_{HBr} curves for various

(47) H. Svensson, Acta. Chem. Scand., 2, 841 (1948).

polymer concentrations never crossed as do the corresponding curves (Fig. 16) obtained in the present investigation.

It would be interesting to obtain u_p from the descending boundaries in a series of moving boundary experiments, and to compare these values with those obtained in the present investigation, since the two should be identical. Although Bsharah found the descending boundaries too diffuse to measure the areas under the peaks, the author believes that the center of these boundaries could be located with sufficient accuracy to enable one to calculate the velocity of the boundary, and thus u_p .

Values of Λ_H in the Polyelectrolyte Solutions

Values of Λ_H obtained from the equation

$$\Lambda_H = \frac{10^3 K_H}{C'_H} = \frac{10^3 t_{HK}}{C'_H}$$

are tabulated in Table 11. The quantity C'_H in the above equation should represent the total concentration of free H^+ ions. It was stated earlier that there was partial quaternization of the polymer with HBr rather than butyl bromide and that some of this HBr would be hydrolyzed in solution. For solutions of PVPBr in water the degree of hydrolysis was calculated from the expression

$$\% \text{ hydrolysis} = \frac{a_H}{C_H} \times 100 \quad (33)$$

where a_H is the activity of H^+ as determined by pH measurements and C_H is the total H^+ concentration as determined by titration with OH^- . C'_H was then calculated from the degree of hydrolysis (page 25). For solutions in HBr, it was assumed that hydrolysis was negligible and thus the concentration of H^+ in the HBr solution (C'_H) was used to calculate Λ_H .

The data can best be discussed by examining the values of Λ_H / Λ'_H , the ratio of the H^+ equivalent conductance in the polyelectrolyte solution to that in the HBr solution in which the polymer was dissolved. In general, this ratio increases with C_{HBr} at constant C_P , and decreases with C_P at constant C_{HBr} . This is the tendency which is expected, since the decrease in Λ_H is attributed to the presence of the polymeric ions, and should depend on the C_{HBr}/C_P ratio.

There are a few exceptions to the decrease of Λ_H / Λ'_H at low HBr concentrations (below 0.005N). This is probably due to the neglect of hydrolysis of the HBr with which the polymer is partially quaternized. If some hydrolysis occurs in these solutions, then C'_H should be larger, which would decrease Λ_H and the ratio Λ_H / Λ'_H .

For solutions of PVPBr in water, the ratio Λ_H / Λ'_H is greater than unity, which is obviously incorrect. The discrepancy probably arises from the use of too small a value for C'_H in these solutions. As stated previously,

values of C'_H for solutions of PVPBr in water were obtained from an estimate of the degree of hydrolysis (35% in a 1% solution and 48% in a 0.5% solution) as calculated from equation 33. The assumption was made that the activity coefficient of H^+ was unity, the correct expression being

$$\% \text{ hydrolysis} = \frac{(C_H)_{\text{free}}}{(C_H)_{\text{total}}} = \frac{a_H / \gamma_H}{C_H} \quad (34)$$

Since the activity coefficient γ_H should be less than one, the degree of hydrolysis calculated from equation 33 will be too low, which will lead to low values of C'_H .

Values of γ_H in a polyelectrolyte solution are not known, but an estimate can be made by determining what values of γ_H will give reasonable values for the ratio Λ_H / Λ'_H . This is complicated by the fact that there is considerable experimental error in t_H and thus in Λ_H for these solutions, with the result that there is considerable variation in Λ_H obtained for duplicate measurements on the same solution.

Assuming that $\gamma_H = 0.75$, the per cent hydrolysis calculated from equation 34 becomes 46.6 for a 1% solution and 64.0 for a 0.5% solution. The resulting values of Λ_H become 255.2 and 360.1 (duplicate runs) for 0.5% PVPBr, and 351.7 and 285.9 for 1% PVPBr.

Certainly one would expect γ_H to be less for a 1% polymer solution than for a 0.5% solution, but the data are

not accurate enough to estimate the effect of C_P on γ_H . The only criterion used to estimate γ_H was that it give values of Λ_H for solutions of PVPBr in water which are less than the values of Λ_H obtained in 0.0025 N HBr solutions. It can be seen that the discrepancy between data for duplicate runs is so great that even this estimate is extremely rough. Nevertheless, it is felt that the data does indicate that the activity coefficient of H^+ in PVPBr solutions, for which C_P is in the neighborhood of 0.5-1.0%, is no greater than 0.75.

In conclusion, it should be noted that the data in Table 11 indicate that in the PVPBr solutions studied, Λ_H is only 92-98% of its value in the HBr solution in which the polymer is dissolved. Thus the assumption made by Wall and co-workers (10-12, 22) that Λ_i for the by-ions can be obtained from data on simple electrolytes leads to values of α which are too low. For the same fractional decrease in Λ_i , the error in α is greater for H^+ than for other ions, however, because Λ_H is greater than Λ_i for other ions.

Comparison of the Values of α Calculated by the Four Methods

Influence of HBr.--By analogy with simple weak electrolyte systems, one would expect a plot of α vs. C_{HBr} to decrease sharply at first, and then more gradually, because

of the common-ion effect. This trend should be more pronounced for low polymer concentrations, i.e., at a given HBr concentration one would expect lower values of α at lower polymer concentrations.

An examination of Figs. 3, 4 and 5 reveals that method (i) gives the expected decrease in α with C_{HBr} , but methods (ii) and (iii) give an increase in α with increasing HBr concentration, which is indeed surprising. The slopes of the α (i) vs. C_{HBr} curves are steeper than one would expect, and do not level off as expected at higher HBr concentrations.

Figs. 6-9 show the influence of C_{HBr} on α as calculated by method (iv). For low values of x the curves go through a minimum, i.e., they decrease with increasing C_{HBr} at first, but as the HBr concentration is increased further, the curves begin to rise. The increase in α at higher HBr concentrations can be removed by increasing the value of x , and the curves approach the expected shape at sufficiently high values of x . Figs. 6-9 show that as C_p is increased, higher values of x are required to prevent the curves from rising in more concentrated HBr solutions, values of $x = 1.05, 1.12, 1.15$ and 1.20 being necessary to prevent the rise in solutions for which $C_p = 0.1, 0.3, 0.5$ and 1% .

The general expression for α , free of all assumptions, may be written from equation 7 as

$$\alpha = \frac{1 - \frac{C'_H \Lambda_H}{10^3 K} - \frac{C'_H \Lambda_{Br}}{10^3 K}}{\frac{10^3 Q_{PK}}{n} + C_P \Lambda_{Br}} \quad (35)$$

This equation is perfectly valid as long as Λ_H and Λ_{Br} are determined in the polymer solution. In method (i) the conductance of H^+ in the HBr solution, Λ'_H , was used in place of Λ_H . An examination of Table 12 shows that $\Lambda_H < \Lambda'_H$, and the difference is greater at lower HBr concentrations. Therefore method (i) will give values of α which are too low. One might expect that the error introduced by the assumption $\Lambda'_H = \Lambda_H$ would be greater at lower HBr concentrations, since the difference $\Lambda'_H - \Lambda_H$ is greater in this region. An examination of Table 5 shows that the numerator of equation 35 (or its equivalent, equation 24) becomes smaller with increasing HBr concentration, with the result that while $\Lambda'_H - \Lambda_H$ decreases in magnitude, the fractional error in α increases with C_{HBr} .

A comparison of Figs. 4 and 5 reveals that the results of method (iii) are no better than those of method (ii) as

far as the influence of HBr on α is concerned (48), although the approximation in (iii) is better than that in (ii).

Method (iv), which takes into account the fact that Λ_{Br} in the polyelectrolyte solution is less than in an HBr solution, gives the expected shape to the curves if the proper value of the parameter x is used. Unfortunately the quantity x is too complex a function to evaluate. Figs. 6-9 show that x is dependent on C_p , and it can be shown that x also depends on C_{HBr} . An examination of equation 35 shows that if x is independent of C_{HBr} , then a decrease in Λ_{Br} will tend to make the α vs. C_{HBr} curves rise with increasing HBr, as did a decrease in Λ_{H} (cf. Figs. 3 and 4). In order to prevent this rise, x must increase with increasing HBr concentration. This same conclusion follows from equation 11 which gives the relationship between Λ_1 in an arbitrary mixture of ions and its value Λ'_1 in a simple binary electrolyte solution. Equation 11 predicts that this "mixture effect" will become greater as the ionic strength of the solution is increased.

Since the "mixture effect" should disappear at zero HBr concentration, all four methods should give the same

(48) Lest the author be criticized for trying to fit the data to preconceived ideas, it should be pointed out that the mobility data, which are free from assumptions, indicate that α does decrease with increasing HBr concentration.

values of α at $C_{\text{HBr}} = 0$. Although there is considerable error in the extrapolations, Figs. 3-9 indicate that this prediction is correct within the experimental error.

Influence of C_p .--At sufficiently high concentrations of HBr, where the ionic atmosphere of the polyion is saturated with HBr, one would expect α to be independent of C_p . At lower HBr concentrations, where the atmosphere around the polyion is unsaturated, one would expect an increase in α with increasing C_p , because as more polymer is added, some of the HBr must leave the atmosphere of the polyions already present in order to form an atmosphere around the added polyions.

An examination of Fig. 10 reveals that the expected trend is observed for method (i) except that the curves are probably too steep at low polymer concentrations. This is the region for which the α (i) vs. C_{HBr} curves were also too steep.

Figs. 11 and 12 show just the opposite of the expected effect for methods (ii) and (iii). The deviation is larger at high values of C_{HBr} , but this is the region where the α vs. C_{HBr} curves also deviated from the expected behavior. Figs. 13 and 14 show that for method (iv) the expected behavior can be obtained at higher HBr concentrations if a sufficiently large value of x is chosen.

In general, when the α vs. C_{HBr} curves show the expected trend, the α vs. C_p curves do likewise.

Comparison of α Values with
Those Obtained by EMF
Measurements

Ritchey (49) determined the degree of association of Br^- with PVP⁺ in the absence of HBr from EMF measurements on concentration cells. He used two Ag-AgBr electrodes, one in an HBr solution and the other in a PVPBr solution which was connected to the HBr solution by means of a salt bridge. The EMF of the cell was related to the activities of the Br^- ion in the two solutions by means of equation 36,

$$E = -\frac{RT}{F} \ln \frac{a_{\text{Br}}}{a'_{\text{Br}}} = -\frac{RT}{F} \ln \frac{a_{\text{Br}}}{m'_{\text{Br}} \gamma'_{\text{Br}}} \quad (36)$$

where a_{Br} is the activity of Br^- ion in the polymer solution and a'_{Br} is that in the reference HBr solution.

The PVPBr was dialyzed against distilled water to remove all HBr, and therefore α could be calculated from

$$\alpha = \frac{a_{\text{Br}} / \gamma_{\text{Br}}}{C_{\text{Br}}} \quad (37)$$

where C_{Br} is the total Br^- concentration from the polymer. Assuming a value of unity for γ_{Br} , values of α were

(49) W. Ritchey, Master's thesis, The Ohio State University (1953).

calculated from equation 37 for several PVPBr concentrations. Values of α obtained in this way will be referred to as Ritchey's method I.

In a second series of experiments, Ritchey added small amounts of concentrated HBr to the solutions used in method I, and plotted a_{Br} vs. amount of HBr added. The results were then extrapolated back to $C_{HBr} = 0$, and the extrapolated values of a_{Br} were used to calculate α by means of equation 37. Values of α obtained in this method will be referred to as Ritchey's method II.

The α vs. C_{HBr} curves of the present investigation must be extrapolated to $C_{HBr} = 0$ before a comparison with Ritchey's results can be made. An examination of Figs. 3-9 shows that the extrapolation can best be made by using the curves obtained from method (iv) (Figs. 6-9). The extrapolated values of α depend slightly on the value used for x , and therefore an average value was taken, with the curves having the correct shape being weighted more heavily than those which curved upward at high HBr concentrations.

There is considerable error introduced in the extrapolations, as there was in Ritchey's method II. The extrapolated values of α are plotted as a function of Q_p in Fig. 15, however, and it may be seen that there is good agreement between these values and Ritchey's values which are plotted on the same graph.

Application to Other Poly-electrolyte Systems

Wall and Eitel (50) neutralized polyacrylic acid (PAA) with NaOH, and studied the association of Na^+ with the PAA^- ion in the presence of NaCl by the transference method. They used only one polymer concentration, and measured α as a function of NaCl concentration for different degrees of neutralization, α being calculated by method (i).

For the case of complete neutralization of the PAA with NaOH, Wall's data have been used to calculate α by means of methods (ii), (iii) and (iv). The results of these calculations are presented in Table 13, and are shown graphically in Fig. 18.

It may be seen that the values of α obtained by the four different methods show much better agreement for this system than for PVPBr in HBr solutions. This is not surprising, because the "mixture effect" on the values of Λ_1 becomes zero as the mobilities of the various ions of like charge approach each other (51). Both Wall's sodium polyacrylate and the PVPBr used in the present investigation had mobilities of about $3 \times 10^{-4} \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$. The mobilities of H^+ and Cl^- are about 3.6×10^{-3} and $7.9 \times 10^{-4} \text{ cm}^2$

(50) F. T. Wall and M. J. Eitel, J. Am. Chem. Soc., 79, 1556 (1957).

(51) H. S. Harned and B. B. Owen, loc. cit., p. 142.

volt⁻¹ sec⁻¹, respectively, so it is evident that the mixture effect will be much greater in the PVPBr-HBr system than in the NaPAA-NaCl system. As a matter of fact, if any monovalent cation except H⁺ had been used as a by-ion in the present investigation, the mixture effect would have been much smaller, since most monovalent cations have mobilities of about $5-8 \times 10^{-4}$ cm² volt⁻¹ sec⁻¹.

Comparing the values of α as obtained by the four different methods on the NaPAA-NaCl system, several points should be noted. First of all it should be recalled that the values obtained by method (i) are too low, due to the nature of the approximations involved. Fig. 18 shows that the results obtained by methods (ii) and (iii) are only slightly higher than those obtained by (i), while the values obtained by method (iv) with $x = 1.10$ are less than those obtained by method (i). Since the values obtained by method (iv) decrease with increasing x , it is evident that 1.10 is too large a value for x , since the correct value of α must be greater than $\alpha(i)$. As was pointed out previously, the upward trend of the α vs. C_{NaCl} curve at higher NaCl concentrations can be removed by increasing x , yet this trend has not been completely removed for $x = 1.10$, a value which is obviously too large. This again emphasizes the fact that x is not a constant, but must increase with increasing NaCl concentration.

Summary and Conclusions

A critical study of the transference method for determining the extent of counterion association in polyelectrolyte systems has revealed that the method cannot be used without some assumption concerning the values of the ionic conductivities in the polyelectrolyte solution.

In the method as originally used by Wall and associates (10-14), it is assumed that the ionic conductivities of both counterions and by-ions are the same as in a simple binary electrolyte solution, and that these conductivities are additive, together with the conductivity of the polyion, to give the observed conductance of the solution. The validity of this assumption was questioned, since it has been shown both theoretically and experimentally that the observed conductance in an arbitrary mixture of ions is less than the value obtained by adding the individual ionic conductivities as measured in simple binary solutions.

It was shown that if sufficient analytical data are available, the conductivity of the by-ion can be determined in the polyelectrolyte solution, but the counterion conductivity cannot be measured. Several methods were then developed for approximating the counterion conductivity.

The methods developed were applied to a study of Br^- association with PVP^+ in HBr solutions, and to some of Wall's data on NaPAA in NaCl solutions. It was shown that all the methods give essentially the same result at low concentrations of added electrolyte, but that differences occur at higher electrolyte concentrations. Thus Wall's approximations are good at low concentrations of added electrolyte.

It was further shown that as the mobilities of the polyion and the by-ion approach equality, the several methods for calculating the degree of association give the same result, but when the mobilities differ by a factor of approximately 10, as in the case of H^+ and PVP^+ , large differences occur at higher concentrations of added electrolyte. In the latter case, Wall's method gives values of α (degree of dissociation) which are too low, while methods (ii) and (iii) give values which are too high. Method (iv) involves the use of a variable parameter which cannot be evaluated.

In conclusion, the transference method has been found to give reasonably accurate values of ion association in polyelectrolyte systems for which the following conditions are met:

- (1) The polyion and counterion mobilities are of the same order of magnitude.
- (2) The concentration of added salt is less than $0.05N$.

- (3) The system contains only two ion species in addition to the polyion, and both of these are monovalent.

Systems containing more than three ion species or multivalent counterions and by-ions were not investigated. The transference method is not satisfactory for systems in which condition (1) is not met, nor in solutions in which the concentration of added salt is much greater than that specified by condition (2).

In addition, it should be noted that the results are more accurate if sufficient analytical data are obtained to enable one to calculate the transference number (and hence the conductivity) of the by-ion in the polyelectrolyte solution. The analyses are usually quite tedious, however, and the difference between results obtained by this method and those obtained by calculating the by-ion conductivity from data on simple binary electrolytes is not large when the three conditions specified above are met.

For PVPBr in HBr, the results indicate that about 70-80% of the counterions are associated with the polyion. There is a decrease in α (degree of dissociation) with increasing HBr concentration, but for this system the method is not accurate enough to determine α in very concentrated HBr solutions. At zero HBr concentration, α decreases from a value of 0.57 at $C_P = 0$ to a constant value of 0.25 when C_P is greater than 0.5%.

Autobiography

I, Wayne H. Martin, was born in Manchester, Ohio, March 15, 1931. I received my secondary school education in the public schools of Loveland, Ohio, and my undergraduate training at The Ohio State University, from which I received the Bachelor of Science degree in 1952. In September 1952 I enrolled in the Graduate School of The Ohio State University where I specialized in the Department of Chemistry. During my graduate residence I have held the positions of Assistant, Assistant Instructor, Allied Chemical and Dye Corporation Fellow, Instructor, and Research Fellow.