elucidation of the composition and constitution of sulfuric acid as a solution. Brand[36] and Deno and Taft[38] have proposed that the H_0 values of sulfuric acid between 83% and 99.8% can be derived from the "semitheoretical" eq. 4 (X = mole fraction) if an equilibrium constant of 50 obtains for eq. 5. Below 83% there is a sharp breakdown of eq. 4, rationalized in terms of a changing equilibrium constant or in terms of anomality of activity coefficient behavior.

$$H_0 \text{ (calcd.)} = -8.47 + \log X_{HSO_4^-}/X_{H_2SO_4} \qquad (4)$$

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \qquad (5)$$
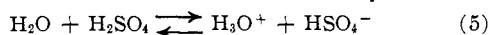
The constancy of the equilibrium constant above 83% is surprising, since it implies ideality of sulfuric acid as a solution. That the latter should actually be true has been doubted[36] and severely criticized.[11,39] It is an unrealistic supposition to assume that the activity coefficients of all the species in solution in this acid region are invariant, since existing evidence supports the fact that the activity coefficients of charged species vary with concentration[8] and that neutral molecules also may show acidity dependent activity behavior.[9-11] Although the free water concentration calculated from eq. 5 closely parallels the measured activity of water,[40] this can be taken to mean that the activity coefficient of water is reasonably constant over this region, but can be shown not to be invariant. No such support exists for the constancy of activity coefficients of the species bisulfate ion, hydronium ion and sulfuric acid.

Wyatt[39] has chosen to rationalize the observed deviation of the activity of water from the actual concentration of free water present in solution at any sulfuric acid

(38) N. C. Deno and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **76**, 244 (1954).
(39) P. A. H. Wyatt, *Discussions Faraday Soc.*, **24**, 162 (1957).
(40) W. F. Giauque, E. W. Hornung, J. E. Kunzler and T. R. Rubin, *J. Am. Chem. Soc.*, **82**, 62 (1960).

concentration as the result of the presence of various equilibria of type 6 involving the hydration of hydronium ions. By assigning equilibrium constants for (6) of appropriate magnitude in various acid regions, and by assuming a much larger equilibrium constant for (5), he manages to derive H_0 values in close agreement with experimental values.

$$H_2O + H_3O^+ \rightleftharpoons H_3O^+ (H_2O) \qquad (6)$$
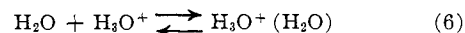
We have attempted to derive correlations similar to those above for our new H_0 values. It can be shown that the empirical eq. 4 holds above 95% sulfuric acid with a changed constant of -9.47. Below this concentration, the calculated values from this equation are too negative and the deviations from the experimental values are of changing magnitude. This implies that no adjustment can be made in eq. 4 by assuming a different constant or by invoking a particular equilibrium constant for eq. 5, in the manner of Deno and Taft. A more complex treatment in the fashion of Wyatt may account for the observed H_0 values, but no simple calculations suffice.

It can be concluded that the success of the treatment by Deno and Taft is the fortuitous result of the errors present in the reported H_0 values. The breakdown of eq. 4 with our new H_0 values is not disturbing and is entirely reasonable, since activity coefficients should not be expected to be constant in the concentrated sulfuric acid region.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND INSTITUTE FOR THE STUDY OF METALS, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

A Chain Model for Polyelectrolytes. VIII. Further Studies of Counterion Activity in Solutions of Polyethyleneimine Hydrochloride

BY SAVO LAPANJE,[1a] PETER F. JONES[1b] AND STUART A. RICE

Measurements are reported of the activity coefficient of the chloride counterion in solutions of polyethyleneimine hydrochloride with various added 1:1 and 1:2 salts. The results are interpreted to demonstrate that the charge configuration of the added small anion is pertinent in determining the distribution of counterions about a polyion.

I. Introduction

Despite the experimental and theoretical advances of the past decade, our ability to predict quantitatively the behavior of polyelectrolyte solutions is severely limited.[2] The reasons for this are easy to ascertain: polyelectrolyte solutions are complex systems containing several components each interacting with all others with a long range coulomb potential; the available mathematical descriptions of the state of the system are incomplete and approximate; and experiment has not yet turned up a convenient expansion parameter about which a theory can be constructed. Given these circumstances it is important to devise experiments which test the physical interpretations as well as the numerical predictions of approximate theories.

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(2) For a convenient review see S. A. Rice and M. Nagasawa, "Polyelectrolyte Solutions," Academic Press, Inc., New York, N. Y., 1961.

One feature common to all polyelectrolyte theories is the intimate association between counterions and polyion. It is now believed that surrounding a polyion skeleton is a region of very high counterion concentration. In some theories the sheath is likened to a one-dimensional fluid and a cell model is used to calculate the properties of the polyion–counterion distribution.[2] The distribution is usually considered to result from non-specific coulomb interactions, and to be a consequence of only the polyion charge density and the magnitude of the counterion charge. The question of the possible role of specific counterion–polyion interactions has not been settled. Should specific interactions exist, the basic premise that only the linear charge density of the polyion and the magnitude of the counterion charge are of importance in determining the counterion distribution would have to be modified.

In this paper we report some experiments designed to test the specificity of the counterion–polyion interaction. The basic question asked is: does the density of coun-

terions about a given polyion depend only on the charge type or can specific spatial pairing of charges lead to enhanced counterion densities? To answer this question we have studied the activity of the chloride ion as counterion to positively charged protonated polyethyleneimine when in the presence of various other negative ions. The other negative ions were chosen to be non-specific (NO_3^-), species specific (Cl^-) and spacing specific. In the latter category we have grouped together one ionic species with a charge spacing that nearly matches the charge spacing on the polyion and other ions with successively larger charge spacings. If the charge type is the dominant characteristic determining the counterion distribution, the activity of Cl^- would be expected to be independent of the charge spacing of the ions. If specific interactions are important the activity of Cl^- would be expected to vary as the charge spacing of the added ion varies. We find that when the charge spacing of the added counterion matches that of the polyion, the Cl^- is preferentially displaced from the ion atmosphere about the polyion. The experiments do not unambiguously identify the nature of the specific interaction, but they do show the importance of such interactions.

II. Experimental Method

The cell used to obtain the Cl^- activity in our experiment was

Hg, Hg_2Cl_2|satd. KCl||sample solution|AgCl, Ag
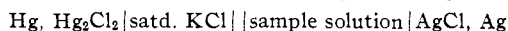
This is a cell with transference. Assuming, however, that the liquid junction potential between a Cl^- solution and a saturated KCl solution has a constant (presumably small) value for different concentrations of the same sample, its electromotive force (e.m.f.) can be expressed as

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

where E^0 is the corrected standard e.m.f. of the above cell. This assumption has been used in earlier work[3] and we apply it herein to the case where a third electrolyte is present. We believe the uncertainty introduced by the neglect of the liquid junction potential to be small at the level of precision we seek.

It should be noted that the term "activity coefficient of the chloride ion" is used herein in the sense of stoichiometric activity coefficient. That is, the activity coefficient is introduced to describe departures from ideality produced both by changes in the number of free ions effectively present and changes from their behavior when assumed to be free. Thus, in every case γ_{Cl^-} refers to an e.m.f. based on the total stoichiometric concentration of chloride ions.

Silver–silver chloride electrodes were prepared from commercial Beckman silver electrodes by the procedure described earlier.[3] The standard potential, also determined by the procedure described earlier, was always within the range (18–25 mv.) quoted by the manufacturer. Most of our measurements were made with one electrode for which $E^0 = -20.22$ mv. The e.m.f. was measured with a Leeds–Northrup K-3 potentiometer and either a Leeds–Northrup stabilized DC microvolt amplifier or a Rubicon high sensitivity box galvanometer. In both cases the sensitivity was about 1 μv. per mm. of scale deflection. All e.m.f. measurements were made at 25°.

The polyethyleneimine (PEI) used was from the same sample as used in our earlier studies. It was a gift from the Chemirad Corporation, East Brunswick, N. J. The hydrochloride was prepared by the method described earlier. The samples of aromatic sulfonates were obtained from commercial vendors. The salts were purified by repetitive recrystallization from water before use in the cell measurements.

For the cases where KNO_3 and NaCl were the added electrolytes, only small changes in γ_{Cl^-} were expected and therefore great care was exercised in solution preparation. For the cases when Na_2SO_4 and the other 1:2 electrolytes studied were added, large changes in γ_{Cl^-} were expected. In these latter cases, solutions were made by dilution using standard laboratory ware. The accuracy of concentration determination by this method is about 1%. The activity coefficients reported when the added electrolyte is KNO_3 or NaCl are estimated to be accurate to 0.2%, whereas for the cases when Na_2SO_4, etc., are the added electrolytes the estimated accuracy is 1%. For this reason we report in Table II only two figures for γ_{Cl^-}. The reproducibility of γ_{Cl^-} measured on different solutions prepared independently was within the quoted figures. It should be noted that the precision

of measurement of the e.m.f. was much greater, usually better than 0.1%.

III. Experimental Results and Discussion

The results obtained in this investigation are displayed in Tables I and II.[4] It is immediately evident that the addition of 1:2 electrolyte serves to raise γ_{Cl^-} substantially. For the case where NaCl or KNO_3 is the added electrolyte, at low polyelectrolyte concentration γ_{Cl^-} tends to the values found in the pure salt,[5] e.g., γ_{Cl^-} ($m = 0.1$) = 0.780, γ_{Cl^-} ($m = 0.01$) = 0.903, γ_{Cl^-} ($m = 0.005$) = 0.928. This is the behavior expected. On the other hand, when a 1:2 salt is added γ_{Cl^-} exceeds unity over a substantial range of polyion concentration. Also, the difference in γ_{Cl^-} between any pair of solutions containing 1:2 salts greatly exceeds the difference in γ_{Cl^-} between solutions containing NaCl and KNO_3. Unfortunately, salting out of the polymer by the various aromatic disulfonates prevented measurements of γ_{Cl^-} at the higher concentrations. Under some conditions salting in occurred and measurements could then be obtained.

TABLE I

ACTIVITY COEFFICIENT OF Cl^- IN THE PRESENCE OF EXTRA 1:1 SALT

PEI· HCl	KNO₃ added			NaCl added			No added salt
	$m =$ 0.005	$m =$ 0.01	$m =$ 0.10	$m =$ 0.005	$m =$ 0.01	$m =$ 0.1	
0.001	0.900	0.887		0.890	0.866		0.562
.002	.856	.856	0.710	.823	.833		.516
.004	.747	.782	.703	.741	.767		.479
.005				.710	.756	0.744	.467
.006	.713	.758	.697	.672	.747		.457
.008	.689	.713	.693	.636	.715		.440
.010	.607	.680	.690	.614	.664	.735	.428
.020	.500	.564	.673	.504	.564	.685	.391
.030	.483						
.040		.473	.638	.434	.466	.634	.360
.050	.415			.416	.440	.610	.351
.060		.420	.602	.393	.421	.594	.343
.080			.582	.376	.403	.562	.339
.100	.373	.383	.566	.358	.386	.537	.337
.200			.461		.349	.415	.321

The absences in Table II are primarily due to these solubility effects. The data recorded in Table II are sufficient to show: (a) At a given concentration of 1:2 salt, and for low concentrations of the polyelectrolyte, the more closely the charge spacing matches the charge spacing of the polyion, the higher is γ_{Cl^-}. (b) When the ratio of 1:2 salt to polyelectrolyte concentration is close to unity or exceeds unity, γ_{Cl^-} is greater than unity. Indeed, when this ratio is greater than unity over a range of concentrations, γ_{Cl^-} exceeds unity over the same range. These statements are valid only when the total ionic concentration is not too large. (c) At high concentrations of PEI·HCl, the differences between the various 1:2 salts tend to diminish. However, under all conditions studied, the values of γ_{Cl^-} in solution with a 1:1 salt were smaller than the values of γ_{Cl^-} in solution with a 1:2 salt.

(3) S. Lapanje, J. Haebig, H. T. Davis and S. A. Rice, *J. Am. Chem. Soc.*, **83**, 1590 (1961).

(4) In principle γ_{Cl^-} might be elevated by addition of SO_4^- in the absence of polyion. However, examination of the published data on the activity of HCl in solution with various 1:2 electrolytes shows that at low ionic strength $\gamma_\pm$(HCl) always decreases on addition of 1:2 salt or on increasing the concentration of 1:2 salt. (See, for example, H. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold Publ. Co., New York, N. Y., 1958, p. 594.) We therefore conclude that in the presence of Na_2SO_4 and absence of polyion, γ_{Cl^-} will decrease as the concentration of Na_2SO_4 increases.

(5) See, for example, H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 2nd. ed., Reinhold Publ. Corp., New York, N. Y., 1950.

TABLE II
ACTIVITY COEFFICIENT OF Cl⁻ IN THE PRESENCE OF EXTRA 1:2 SALT

PEI·HCl m	Na₂SO₄ $N =$ 0.00192	$N =$ 0.0096	$N =$ 0.096	Na₂ m-benzenedisulfonate $N =$ 0.00192	$N =$ 0.0096	$N =$ 0.096	Na₂ 1,5-naphthalenedisulfonate $N =$ 0.00192	$N =$ 0.0096	Na₂ 4,4'-diphenyldisulfonate $N =$ 0.00192	$N =$ 0.0096
0.001	1.35	1.19		1.21		0.91				
0.003	1.27	1.11		1.19	1.19	0.90	1.18			
0.005	1.10	1.10		1.14	1.13	0.89	1.10			
0.007	0.93	1.09		1.00	1.12		0.93		1.00	
0.010	0.84	1.08		0.90	1.11	0.86	0.84		0.84	
0.030	0.57	0.89		0.62	0.80	0.82	0.59	0.75	0.61	
0.050	0.53	0.67		0.53	0.63	0.80	0.53	0.63	0.54	0.65
0.070		0.64	0.82	0.50	0.57	0.78	0.48	0.58	0.49	0.57
0.100	0.52	0.58	0.78	0.43	0.50	0.74	0.46	0.51	0.45	0.52

If we regard the distance between two oxygens as the important length parameter describing the tetrahedral $SO_4^=$ ion, we find this distance to be approximately 2.42×10^{-8} cm. It is difficult to know what to take for the pertinent length parameter in the case of the aromatic disulfonates. The distances between sulfur atoms are 4.10×10^{-8} cm., 6.71×10^{-8} cm. and 10.42×10^{-8} cm. for the m-benzenedisulfonate, 1,5-naphthalenedisulfonate and 4,4'-biphenyldisulfonate ions, respectively. If the appropriate parameter is the distance between oxygen atoms, the above distances are slightly increased. The distance between charged nitrogen atoms on the polyethyleneimine skeleton depends upon the local chain configuration. If the nitrogens are *trans* to the C–C bond, and all atoms lie in one plane, the distance is about 3.47×10^{-8} cm. If the nitrogens are *cis* to the C–C bond and all atoms lie in one plane, the distance is about 2.50×10^{-8} cm. It is clear that the charge spacing of $SO_4^=$ most nearly matches that of the polyion, especially in the *trans* configuration. The aromatic disulfonates are mismatched by varying amounts, although the charge spacing in m-benzenedisulfonate is not grossly different from that in PEI·HCl.

The data reported herein suggest to the authors that the distribution of counterions about a polyion depends upon the spatial configuration of charges on the counterion. It should be pointed out, however, that the data we have been able to obtain are insufficient to establish unambiguously the suggested mechanism. At the lowest concentrations of polyion, two out of three measurements support our suggestion. Unfortunately, experimental difficulties prevented the measurements at $m = 0.001$ in all cases except that of added sodium sulfate and sodium m-benzenedisulfonate. The fact that the activity coefficient is large (and even exceeds unity) over a large concentration range is, however, a significant confirmation of the idea that the divalent ions preferentially displace monovalent ions about a polyion. It is therefore tempting to make a simple extrapolation and suggest that the pertinent configurational parameter is the matching of the polyion local charge distribution to the charge distribution of the counterion. The reader should note that *we are not suggesting that undissociated ion pairs form*, but only that charge-spacing specificity plays a role in determining the behavior of polyelectrolyte solutions.

It is important to note that no specificity could be found for univalent counterions in the experiments of Nagasawa and Rice.[6] These investigators studied counterion association to copolymeric polyions in which the skeletal distribution of charges was inhomogeneous. It was found that the extent of univalent counterion association depended only on the over-all linear charge density and not on the distribu-

tion of skeletal charges. This observation is in excellent agreement with the theory of Kotin and Nagasawa.[7] The class of 1:2 electrolytes studied in the present work therefore differs markedly in behavior from that of univalent counterions and this should be remembered throughout the following discussion.

The experiments reported herein are somewhat akin to ion-exchange experiments. Thus, we may say that the $SO_4^=$ ion displaces Cl⁻ from the polyion core. It is interesting that the displacement has the gross features of an equilibrium. That is, for a selected concentration of added electrolyte the displacement of Cl⁻ is greatest when the ratio of sulfate to chloride concentrations is greatest. When the concentration of Cl⁻ (and hence of PEI·H⁺) is much larger than that of the 1:2 salt, the activity of Cl⁻ is approximately constant over a range of concentration of both PEI·HCl and 1:2 salt. Both of these observations are in qualitative accord with the behavior expected of a maintained ionic equilibrium. Indeed, such exchange equilibria have been used to describe the properties of ion exchange resins. In this language it is then easy to explain why, say for the case where Na₂SO₄ is the added electrolyte, when the concentration of PEI·HCl is low enough $(m = 0.001)$ γ_{Cl^-} $(0.00192) > \gamma_{Cl^-}$ (0.0096) but when the concentration of PEI·HCl is higher $(m = 0.010)$ the opposite is observed, γ_{Cl^-} $(0.00192) < \gamma_{Cl^-}$ (0.0096).

The recent elegant calculations of Kotin and Nagasawa have shown how the counterions distributed about a polyion may be conveniently divided into two groups. These investigators show that it is possible to find a boundary surrounding a rod-shaped polyion such that

$$f = 1 - \frac{DkTL}{2Nq^2} \qquad (1)$$

where f is the degree of ion binding, q the unit charge, L and N the length and number of charges on the polyion and D the dielectric constant. Their calculations make no allowance for specific effects and are limited, at present, to the case where the added electrolyte is of the 1:1 type. Kotin and Nagasawa note that the value of $(1 - f)$ is in very close agreement with experimental values of the counterion activity coefficient for the case of pure aqueous polyelectrolyte solutions. Now, when the concentration of PEI·HCl is much larger than that of the added 1:1 electrolyte, the activity coefficient of Cl⁻ tends toward that observed in the absence of 1:1 electrolyte (see Table I). The principal effect of the added electrolyte in this region seems to be to provide extra shielding of the charges on the polyion, thereby causing γ_{Cl^-} to increase toward unity. The increased shielding effect outweighs the reduction expected in γ_{Cl^-} due to increased ionic strength. The shielding effect is most noticeable when the concentra-

(6) M. Nagasawa and S. A. Rice, *J. Am. Chem. Soc.*, **82**, 5070 (1960).

(7) L. Kotin and M. Nagasawa, *J. Chem. Phys.*, **36**, 873 (1962).

tion of polyion is much less than that of the added electrolyte.

Examination of Tables I and II shows clearly that the effect on γ_{Cl^-} of added 1:2 electrolyte exceeds that expected from just shielding or ionic strength effects. It appears, then, that the Kotin–Nagasawa calculations are applicable to the case of added 1:1 electrolyte and are probably extendable only to the case of a point charge 1:2 electrolyte: for the purposes of this discussion, the principal result of the Kotin–Nagasawa analysis is that f depends only on properties of the polyion. Of course, a polyion model with continuous charge distribution can never display specificity effects. Moreover, the results of our experiments clearly indicate that the structure of the counterion is also of importance, and the Kotin–Nagasawa theory cannot deal

with such specific features of ionic structure. However, to the extent that it is valid to identify the minimum in the counterion distribution function (with distance away from the polyion) with the boundary between free and associated counterions, and to the extent that it is valid to use the Bjerrum approximation of relating the densities of associated and free ions in terms of an equilibrium constant, the discussion of γ_{Cl^-} given above is useful. Examination of the data and the arguments used then further reinforces the observation that specific interactions may exist between counterion and polyion and may be of importance in determining the counterion distribution.

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Hydrogenation under Hydroformylation Conditions: Observations, Kinetics, and Mechanism

BY CLYDE L. ALDRIDGE[1] AND HANS B. JONASSEN

Reduction of aldehyde to alcohol under hydroformylation conditions (cobalt catalyst, 160°, hydrogen and carbon monoxide pressures) appears to comprise a two step sequence (a) a heterogeneous hydrogenolysis in which dicobalt octacarbonyl is cleaved to yield cobalt hydrocarbonyl and for which metallic cobalt is the catalyst, followed by (b) a homogeneous hydrogen exchange in which cobalt hydrocarbonyl acts as a reducing agent for the aldehyde. Thiophene and traces of moisture act as poisons. These effects, together with residual surface effects of lead compounds and the concentration dependence of poisoning by lead compounds, are consistent with metallic cobalt catalysis of the hydrogenolysis. The kinetic dependence of the unpoisoned reaction on the variables was determined and a mechanism for the homogeneous hydrogen transfer is proposed.

Introduction

During hydroformylation of an olefin in the presence of a cobalt-containing catalyst some reduction of aldehyde to alcohol and even of the olefin to paraffin occurs, and at temperatures approaching 200° these reductions become major reactions.[2-5] The homogeneous aspects of this reduction of aldehyde have been emphasized in the literature[2-4,6,7] and the reaction interpreted as occurring by a homogeneous free radical chain,[2] by an ionic addition of cobalt hydrocarbonyl to the aldehyde and abstraction of a hydrogen from another molecule of cobalt hydrocarbonyl[6] and by a homogeneous reaction of molecular hydrogen with an aldehyde-cobalt hydrotricarbonyl adduct.[7]

The evidence for homogeneous catalysis of this reaction consists of two experiments: (a) reduction of aldehyde in a hydroformylation reaction mixture still occurs in the presence of certain sulfur-containing compounds, e.g., thiophene,[2-4] and (b) reduced cobalt catalyzes reduction of aldehyde when no carbon monoxide is present, fails to do so when a small amount of carbon monoxide is in the system and regains its activity at higher carbon monoxide pressures.[3]

Recently we have reported that this reaction has a heterogeneous character in that it is subject to poisoning by heavy metal ions which are reducible to the *metal* by the metallic cobalt present in the system and we

have pointed out that consideration must be given to the dynamic equilibrium between cobalt metal and cobalt carbonyls.[8]

This paper reports the results of experiments designed to answer the following questions concerning reduction of aldehyde under hydroformylation conditions. (1) Is a free radical process occurring in this system? (2) Is this catalysis subject to partial poisoning by a sulfur compound, such as thiophene, to a degree that is consistent with a metallic catalyst that is constantly being regenerated? (3) What are the precise kinetic dependences of this reaction on the concentration of the several components—H_2, CO, aldehyde, and cobalt—and can a mechanism be deduced therefrom which is consistent with these and other experimental facts? (4) What is the mode of poisoning by heavy metals and other poisons?

Discussion

Evidence against a Free Radical Process.—Because of the extremely low energy of the carbonyl–hydrogen bond (<78 kcal./mole),[9] the easiest reaction an aldehyde can undergo with a free radical is loss of this hydrogen atom to yield an acyl radical. With branched aldehydes this radical readily loses carbon monoxide to give large yields of the corresponding paraffin.[10,11]

It was demonstrated that 2-ethylhexanal when treated under hydroformylation temperature and pressure conditions with di-t-butyl peroxide (6.5 mole %) yielded the decarbonylation product, n-heptane (30 mole %) (Table I). However, when this aldehyde was reduced under these temperature and pressure conditions via cobalt carbonyl catalysis no n-heptane was

(1) Esso Research Laboratories, P. O. Box 551, Baton Rouge, Louisiana. Robert A. Welch Visiting Scholar to A. and M. College of Texas, 1961-1962.

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