(f) **Mass Spectrum.**—Consolidated Model 21-103 mass spectrometer was used at an ionizing potential of 70 volts. The principal peaks in the spectrum for masses above 65 corresponded to the ions: SOF^+, SF_2^+, SOF_2^+, SF_3^+, SOF_3^+ and SF_5^+. No peaks for masses greater than that of SF_5^+ were observed.

(g) **Nuclear Magnetic Resonance Spectrum.**—The nuclear magnetic resonance spectrum of $S_2O_2F_{10}$ was obtained through the use of a Varian Model 4311 B high resolution spectrometer employing a sixty megacycle oscillator. The spectrum consisted of only one peak with some evidence for fine structure.

(h) **Thermal Decomposition of $S_2O_2F_{10}$.**—A sample of $S_2O_2F_{10}$ was placed in a nickel vessel like one described previously.[2] The temperature of the vessel was slowly increased from 51.2 to 338° with both temperature and pressure being recorded periodically. At about 200° a positive deviation of the pressure from perfect gas behavior was noticed. With increasing temperature beyond this point the pressure initially rose quite rapidly and then slowly approached asymptotically perfect gas behavior. When the reactor was slowly cooled, it was observed that the pressure in the vessel followed the behavior of a perfect gas but at a pressure 2.5 times as great as would be expected from the initial pressure. The products of the above reaction were SF_6, SO_2F_2, SOF_4 and O_2. In another run the temperature of the reaction vessel was maintained near 521° for a period of 12 hr. Only absorption bands for SO_2F_2 and SF_6 were observed in the infrared spectrum of the product.

(i) **Reaction with Hydroxide and Iodide Solutions.**—A sample of $S_2O_2F_{10}$ placed in a sealed bulb with 5 N NaOH was only slightly attacked after a seven day period at 100°; the vast majority of the compound remaining unaffected. A sluggish reaction with a solution of potassium iodide was observed. Reaction was incomplete after a 48 hr. period at 100° but was complete after seven days at 100° producing 2 equivalents of iodine per mole of peroxide.

Discussion

Although none of the preparative methods described above have given high yields of bis(-pentafluorosulfur) peroxide, it appears likely that the yields could be increased by removing the product as it is formed and by continuing the preparative reaction until the reactants have been consumed. This comment applies equally to the method of combining SF_5OF with SOF_2. As things stand, the authors now prefer the method in which SF_5OF combines with SOF_2 under pressure at about 170°.

In some of the preparations described above a "catalyst" was used. It is not clear from the results obtained that the "catalyst" accelerated the formation of bis-(pentafluorosulfur) peroxide or that it increased the yield,

When irradiation of pentafluorosulfur hypofluorite is used as the preparative method, it is probable that the yield of peroxide product can be increased by removing fluorine. Since the reaction

$$2\ SF_5OF = SF_5OOSF_5 + F_2$$

is reversible, the removal of fluorine should favor the formation of the peroxide. This factor has been demonstrated by a run in which SF_5OF was irradiated for 140 hr. by a ultraviolet lamp shining on the end of this run about 70% of the product was SF_5OOSF_5. The flask also contained O_2, SiF_4, SO_2F_2 and a little SF_5OF and SOF_4. Little if any fluorine was present. Apparently it had been consumed by reaction with the quartz flask.

The irradiation of pentafluorosulfur hypofluorite may involve the reaction

$$SF_5O \xrightarrow{\text{u.v.}} SF_5O\cdot + F\cdot$$
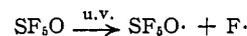
and this may be followed by recombination of the free radicals. The formation of peroxides by the combination of RO· radicals has been reported by Buncel and Davies.[8]

All of the properties of $S_2O_2F_{10}$ observed in this research are consistent with the structure found by Harvey and Bauer.[1] There is no reason to doubt that the substance is bis-(pentafluorosulfur) peroxide, SF_5OOSF_5.

(8) E. Buncel and A. G. Davies, *J. Chem. Soc.*, 1550 (1958).

Expansion of a Polyion in Salt Solutions[1]

BY MITSURU NAGASAWA[1b]

It is known that the existing theories of polyion expansion, such as those of Hermans, Overbeek and Pals, Katchalsky and Lifson, Flory and Nagasawa and Kagawa, predict calculated values of the polyion volume much larger than those found experimentally. In this paper it is shown that the main reason for this discrepancy is the neglect of the electrostatic effect of the polyion on the counterions, *i.e.*, the neglect of the activity coefficient of the counterions. If the activity coefficient of the counterions, determined experimentally, is introduced into these theories, the calculated expansions correspond closely to the experimentally determined ones. Finally, it is demonstrated that the introduction of the counterion activity coefficient is equivalent to the use of an effective charge density and hence to the introduction of the site-binding model.

Introduction

It is well known that linear polyions have very expanded forms in solution. The origin of the expansion is now accepted to be the electrostatic repulsive force between the fixed charges on the polyion. Many models have been suggested for the purpose of computing the electrostatic expansion; we cite Hermans and Overbeek[2a] and Pals[2b], Katchalsky and Lifson,[3] Flory,[4] Harris and Rice[5,6]

(1) (a) This work was supported by grants from the National Science Foundation and the National Institutes of Health. (b) On leave from Department of Applied Chemistry, Nagoya University, Nagoya, Japan.

(2) (a) J. J. Hermans and J. Th. G. Overbeek, *Rec. trav. chim.*, **67**, 761 (1948). (b) D. T. F. Pals and J. J. Hermans, *ibid.*, **71**, 433 (1952).
(3) A. Katchalsky and S. Lifson, *J. Polymer Sci.*, **11**, 409 (1953).

as representative of the theories. Despite the efforts quoted, no satisfactory theory has been developed.

It has often been reported that the theory of Hermans, Overbeek[2a] and Pals[2b] is in good qualitative agreement with experiment, but quantitatively it gives calculated volumes which are too large, particularly for vinyl compounds.[7] The theories of Katchalsky and Lifson and Flory also predict marked over expansion.[6,8,9] Although some interesting rationalizations[10-12] have been given for the quantitative discrepancies, it is almost certain that the (electrostatic) repulsive forces calculated in the above cited theories are too large. The computed repulsion is in fact far beyond the adjustable range of the configurational entropy force. It has also often been reported that the assumption of site-binding, that is, a decrease of the effective charge density, is very useful in explaining the discrepancy between the theory and experiment. In a similar vein it has been shown that the failure of the Debye–Hückel approximation is not the reason for the discrepancy.[13]

The concept of site-binding was first introduced into a precise calculation by Harris and Rice.[5,6] The expansions calculated from their theory by using the data of Huizenga, Grieger and Wall[14] seems to be fairly close to the experimental values. However, a weak point of the theory is that it is somewhat inconvenient for numerical calculations. Therefore, it is interesting to see how the introduction of site-binding idea will improve the agreement with experiment in the case of the theories not taking account of site-binding.

To complete the theory in a self-consistent manner, it is desirable to calculate the fraction of bound ions theoretically. Unfortunately, there is no really satisfactory theory of site-binding to a polyion, though a relationship between the amount of site-binding and the pH of the solution was given by Harris and Rice[5] and by Lifson.[15] In view of this situation, we shall use the binding determined from other independent experiments. In this paper, the activity coefficient of the counterions will be used for this purpose.

The electrostatic free energy of an electrolyte solution is due to the mutual interaction among the ions in the solution. Therefore, the free energy must be computed as the work of creating the ionic atmospheres around both positive and negative ions. In polyelectrolyte solutions, it may be difficult to visualize an ionic atmosphere about a counterion but a counterion close to a polyion not

(4) P. J. Flory, J. Chem. Phys., **21**, 162 (1953).

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

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

(7) H. Fujita, K. Mitsubachi and T. Homma, J. Colloid Sci., **9**, 466 (1954).

(8) P. J. Flory and J. E. Osterheld, J. Phys. Chem., **53**, 653 (1953).

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

(10) S. Lifson, ibid., **23**, 431 (1957).

(11) S. Lifson, J. Chem. Phys., **29**, 89 (1958).

(12) H. Inagaki and T. Oda, Makromol. Chem., **21**, 1 (1956); H. Inagaki, S. Hotta and M. Hirami, iibd., **23**, 1 (1957).

(13) M. Nagasawa and I. Kagawa, Bull. Chem. Soc. Japan, **30**, 961 (1957).

(14) J. R. Huizenga, P. F. Grieger and F. T. Wall, THIS JOURNAL, **72**, 2636, 4228 (1950).

(15) S. Lifson, J. Chem. Phys., **26**, 727 (1957).

Fig. 1.

only has an electrostatic effect on the polyion as a member of the ionic atmosphere but also is itself affected by the polyion. Due to this effect the counterions collected near the polyion will have lower activity coefficients than the ions far from the polyion. This effect has been discussed in a few papers. In a paper of Harris and Rice,[16] consideration of this effect is given through a parameter χ. They expressed the average force between a mobile ion at the point r and a fixed polyion by the equation

$$W_\alpha (r) = Z_\alpha e\psi(r) + \chi(r)$$

where $\psi(r)$, the average electrostatic potential at the point r in the presence of the fixed polyion, is computed from a Poisson–Boltzmann equation as in the Debye–Hückel theory and $\chi(r)$ is the work required to destroy an ion atmosphere in the external solution and to build one at the point r. Marcus[17] and Lifson[15] also have pointed out that the activity coefficient of a mobile ion can be related with the electrostatic potential around the polyion.

The introduction of the activity coefficient of the counterions inside the polymer domain has the same effect as the assumption that some ions are site bound or that there is an effective charge, as was pointed out previously.[13] The depression in the activity coefficient of the counterion most probably corresponds to the non-uniform distribution of counterions inside the polymer domain, as shown in Fig. 1. In this paper, however, it is unnecessary to discuss the origin of the low activity coefficient of the counterion in detail. The introduction of the activity coefficient of the counterion is sufficient to supplement the part neglected in the theories of the expansion of polyions, though it is not satisfactory from the viewpoint of statistical thermodynamics. The purpose of this paper is to see how the introduction of the activity coefficient of

(16) F. E. Harris and S. A. Rice, ibid., **25**, 955 (1956).

(17) R. A. Marcus, ibid., **24**, 636 (1956).

counterions improves the agreement of the theories with experiment. The discussion in this paper is limited to solutions with salt added since the interactions between polyions are still not properly understood.

Calculation of Expansion of a Polyion.—To show that the introduction of the activity coefficient into theoretical equations is reasonable, it is convenient to briefly summarize the calculation of the electrostatic free energy reported by Nagasawa and Kagawa. That is, it is assumed that a polyion having a radius of R_s and Z ionized negative groups is in an infinitely large volume of a simple electrolyte solution of 1–1 type. If the charged groups are uniformly distributed inside the sphere, the charge density $(- \rho_i)$ is given by

$$\rho_0 = Ze \Big/ \frac{4}{3} \pi R_s{}^3 \tag{1}$$

where e is the absolute value of the electronic charge. The electrostatic potential around the polymer is obtained from the Poisson–Boltzmann equation. A solution given by Lifson,[18] Nagasawa and Kagawa[13] is quoted here for the purpose of illustrating the role of activity coefficient terms in the electrostatic potential. Their result is

$$\psi_1 = E_D \Big[1 -$$
$$\frac{1 + KR_s}{K' \cosh (K'R_s) + K \sinh (KR_s)} \frac{\sinh (K'r)}{K'r} \Big] (r < R_s)$$
$$\psi_2 = \tag{2}$$
$$E_D \Big[\frac{(1 + K'R_s)e^{-K'R_s} - (1 - K'R_s)e^{-K'R_s}}{K'(e^{-K'R_s} + e^{K'R_s}) - K(e^{-K'R_s} e^{K'R_s})} \Big] \frac{e^{-Kr}}{r} (r > R_s)$$

where

$$E_D = - \frac{kT}{e} \ln \frac{1 + \sqrt{1 + \left(\frac{8\pi}{3} \frac{1}{Z} R_s{}^3 n_c\right)^2}}{\left(\frac{8\pi}{3} \frac{1}{Z} R_s{}^3 n_c\right)} \tag{3}$$

$$(K')^2 = K^2 \cosh (eE_D/kT) \tag{4}$$

$$K^2 = \frac{8\pi e^2}{DkT} n_c \tag{5}$$

Here E_D is the Donnan potential between the inside and outside of the polymer sphere, as first discussed by Kimball, Cutler and Samielson.[18a] n_c is the number concentration of the added salt per unit volume of the solvent and r is the radial distance from the center of the sphere. The reason for the appearance of the Donnan potential in eq. 2 was fully discussed in ref. 13. If it is assumed that a thermodynamic discussion of this microscopic Donnan membrane potential is valid, then we must replace both analytical concentrations, $Z/^4/_3 \pi R_s{}^3$ and n_c, by the thermodynamically appropriate expressions, $\gamma_K{}^P(Z/^4/_3 \pi R_s{}^3)$ and $\gamma_K{}^S n_c$. Since $\gamma_K{}^P$ is much smaller than $\gamma_K{}^S$ as discussed in the Introduction, it can be seen that the result of replacing Z and n_c by their effective values is to make the true values of E_D smaller than that given by eq. 3. This is analogous to the phenomena observed with a macroscopic Donnan membrane equilibrium involving a polyelectrolyte.[19]

(18) S. Lifson, *J. Chem. Phys.* **27**, 700 (1957).

(18a) G. E. Kimball, M. Cutler and H. Samelson, *ibid.*, **56**, 57 (1952).

(19) M. Nagasawa, A. Takahashi, M. Izumi and I. Kagawa, *J. Polymer Sci.*, **38**, 213 (1959).

In comparison with experiments, we will find that in most experiments E_D does not exceed kT/e if we take into account the activity coefficient of the counterions inside the polymer domain. Then, eq. 3 can be simplified

$$E_D{}^0 = - \frac{kT}{e} \frac{\gamma_K{}^{'P}}{\frac{8\pi}{3} \frac{1}{Z} R_s{}^3 n_c \gamma_K{}^S} = \frac{4\pi\rho_0}{DK^2} \frac{\gamma_K{}^{'P}}{\gamma_K{}^{'S}} \tag{6}$$

$$(K')^2 = K^2 = \frac{8\pi e^2}{DkT} n_c \tag{7}$$

by which eq. 2 becomes the same as the equation of Hermans and Overbeek[2a] except for the presence of $\gamma_K{}^P$, $\gamma_K{}^S$ in ρ_0 term. Thus, the introduction of the activity coefficient of the counterion inside the polymer domain is completely equivalent to the assumption of an effective charge density $(\rho_0)_{eff}$ of the polymer sphere.

The electrical free energy of this system, which is defined as the difference between the free energy of systems in the real state and in the imaginary non-charged state having the same configuration of polymer, is calculated as the work done when all particles in the solution are charged up simultaneously from the imaginary non-charged state to the real state, keeping the interior and the exterior of the polyion sphere at equilibrium. The integration was carried out by Nagasawa and Kagawa[13] to give eq. 27 in ref. 13. The work to charge up the simple ions against their ionic atmosphere should be added to this value, but as stated in the Introduction, this work will be taken into account in terms of activity coefficients in the final equation. If the activity coefficient of the counter ion is introduced, KR_s is generally larger than 3. For such large values of KR_s, $\sigma(a)$ defined by eq. 29 in ref. 13, can be simplified as

$$\sigma(a) = 2.303 \log (2a) - 1.4223 +$$
$$\frac{\frac{3}{2} - \left(\frac{3}{2} + 3a + a^2\right) e^{-2a}}{a^2} - E_1 (-2a) \tag{8}$$

where $\simeq 2.303 \log (2a) + \frac{3}{2a^2} + 1.42$ for $a \gtrsim 3$

$$-E_1 (-2a) = \int_{2a}^{\infty} \frac{e^{-y}}{y} dy \tag{9}$$

Therefore, if the activity coefficients of simple ions are taken into account, the final equation for calculating R_s is

$$kT \Big[\frac{3}{R_s{}^2 - \frac{5}{36} NA^2} - \frac{108}{5} \frac{NA^2}{l} \Big] R_s$$
$$= - D(KR_s)[E_D{}^0]^2 \Big[2.303 \log (KR_s) +$$
$$\frac{9}{4} \frac{1}{(KR_s)^2} - 0.98 \Big] \text{ for } KR_s \gtrsim 3 \tag{10}$$

where A is the length of a segment and N is the number of segments in a molecule. The end-to-end distance, h, is related with R_s by[2a]

$$R_s{}^2 = \frac{5}{36} NA^2 \left(1 + \frac{h^2}{NA^2}\right) \tag{11}$$

Since the activity coefficient of the counterions can be determined experimentally, the length of a segment A is the only parameter in eq. 10.

Comparison with Experiment.—To calculate R_s from eq. 10, we must know the activity coefficient of the counterions inside and outside the polymer domain. Fortunately, it has been shown[9,20] that additivity holds for the activity of the counterion. That is, the activity of the counterion is expressible as the sum of the activity of the counterion in the polyelectrolyte solution without added salt and that of the same ion in the simple salt solution without polyelectrolyte, as

$$(\gamma_K)_{obsd.} = \frac{\bar{\gamma}_K{}^P C_{KP} + \bar{\gamma}_K{}^S C_{KA}}{C_{KP} + C_{KA}} \qquad (12)$$

where $\bar{\gamma}_K{}^P$, $\bar{\gamma}_K{}^S$ are the activity coefficients of the counterion in the pure water solution of the polyelectrolyte and in the solvent, respectively, and C_{KP} and C_{KA} are the equivalent concentrations of the polyelectrolyte and the simple salt in the solution. The additivity of the counterion activity means that we may divide the activity of the counterion between the activity originating from the polyelectrolyte and that of the simple salt in the solvent. That is, $\gamma_K{}^P$, $\gamma_K{}^S$ in eq. 6 can be considered to be equal to the value in the polyelectrolyte solution without added salt, $\bar{\gamma}_K{}^P$, and in the solvent without polyelectrolyte, $\bar{\gamma}_K{}^S$, respectively.

Measurements of the activity coefficient of the counterion are available for sodium polyvinylalcohol sulfates.[9,21] The values of R_s calculated for some samples of polyvinylalcohol sulfate in sodium chloride solutions are shown in the column, $R_{calcd.}$ of Tables I and II. The values of $\gamma_K{}^P$ used for the calculation are shown in these tables. These values are obtained by the extrapolation of the curves in Fig. 6 of ref. 21.

TABLE I

EXPANSION OF Na-POLYVINYL SULFATE IN SODIUM CHLORIDE SOLUTIONS (I)

Sample A[24]: deg of polym. = 1600; Z = 976, deg. of est. = 0.61; $(\gamma_{Na}{}^P)_{Cp \to 0}$ = 0.14

NaCl concn. (N)	[η] 100 ml./g.	R_exp. in Å. from viscosity		
		R_F (A = 20 Å.)	R_F (A = 40 Å.)	R_{DB}
2.00 × 10⁻¹	1.52	213	238	187
1.00 × 10⁻¹	1.97	228	251	205
5.00 × 10⁻²	2.64	260	280	232
2.00 × 10⁻²	3.80	273	292	265
1.00 × 10⁻²	5.05	296	314	295
5.00 × 10⁻³	7.26	327	343	335
2.00 × 10⁻³	11.46	379	393	398

R_calcd. in Å. from eq. 19		R_calcd. in Å. from Hermans-Overbeek		R_calcd. in Å. from Katchalsky-Lifson
(A = 20 Å.)	(A = 40 Å.)	(A = 20 Å.)	(A = 40 Å.)	(A = 25 Å.)
168	218	178	227	168
180	226	193	241	199
202	238	216	260	276
228	270	246	294	372
255	300	276	328	420
288	336	310	366	453
337	394	361	427	510

To determine the expanded volume of the polyion experimentally, light scattering experiments are most suitable. Unfortunately, however, we have

TABLE II

EXPANSION OF Na-POLYVINYL SULFATE IN SODIUM CHLORIDE SOLUTIONS (II)

Sample B[13]: deg. of polym. = 1470, Z = 1070; deg. of est. = 0.73; $(\gamma_{Na}{}^P)_{Cp \to 0}$ = 0.11

NaCl concn. (N)	[η] 100 ml./g.	R_exp. in Å. from [η]		R_calcd. in Å. from eq. 19	
		R_{Flory} (A = 20 Å.)	R_{Flory} (A = 40 Å.)	(A = 40 Å.)	(A = 40 Å.)
1.00		173	200	148	204
5.00 × 10⁻¹		189	206	150	205
1.00 × 10⁻¹		225	246	169	217
5.02 × 10⁻²		241	261	184	229
2.01 × 10⁻²		276	294	212	253
1.00 × 10⁻²		299	317	237	283
5.04 × 10⁻³		331	346	268	313
2.02 × 10⁻³		369	381	317	370

Sample C[9]: deg. of polym. = 1570; Z = 1021; deg. of est. = 0.65; $(\gamma_{Na}{}^P)_{Cp \to 0}$ = 0.12

1.00	0.8	158	193	150	210
5.00 × 10⁻¹	1.14	200	225	154	214
1.00 × 10⁻¹	2.07	231	253	172	227
5.00 × 10⁻²	2.71	248	269	188	234
2.00 × 10⁻²	4.30	283	302	214	260
1.00 × 10⁻²	6.10	313	330	237	286
5.00 × 10⁻³	8.6	345	362	277	320
1.00 × 10⁻³	17	426	439	366	430

no light scattering data for polyelectrolyte solutions in which the counterion activity was measured. The calculated values from viscosity data are probably less reliable than those from light scattering since all theories of viscosity have been developed for non-ionic polymers which have a more or less Gaussian distribution of segments. However, the ambiguity arising from the usage of viscosity data is much smaller than the discrepancy observed between the H–O or K–L theories and experiment.

Flory's theory[22] is often used to calculate the end-to-end distance of a polymer, $\sqrt{\bar{h}^2}$

$$[\eta] = \Phi \frac{(\sqrt{\bar{h}^2})^3}{M} \qquad (13)$$

where M is the molecular weight of the polymer and Φ is 2.1×10^{21} when $[\eta]$ is expressed by 100 ml./g. The application of Flory's theory to expanded polyions is based on the assumption that the distribution of the segments in the polymer sphere is Gaussian independently of the degree of expansion. The values of $\sqrt{\bar{h}^2}$ thus calculated must be transformed into the radius of the equivalent sphere R_s by the relationship of Hermans and Overbeek,[2a] eq. 11. The values of R_s thus calculated are shown as R_F in the tables.

Since the calculation of the electrostatic free energy is based on a uniform sphere model similar to that used by Debye and Bueche,[23] it is reasonable to calculate R_s from the Debye–Bueche theory. To do so, however, we must know the hydrodynamic resistance of a segment. It is known that the hydrodynamic resistance of a segment determined so as to make the Debye–Bueche theory agree with experimental $[\eta]$ *versus* molecular weight data is

(20) R. A. Mock and C. A. Marshall, *J. Polymer. Sci.*, **13**, 263 (1954).

(21) M. Nagasawa and I. Kagawa, *ibid.*, **25**, 61 (1957).

(22) P. J. Flory, "The Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, New York, 1953, p. 616.

(23) P. Debye and A. M. Bueche, *J. Chem. Phys.*, **16**, 573 (1948).

much smaller than the value determined from the actual dimensions of the segment. There is some uncertainty, then, in the values determined by the Debye–Bueche theory. Nevertheless, it is interesting to see that there is good agreement between the values from Flory's theory and the values calculated from Debye and Bueche's theory if we use the hydrodynamic resistance of a segment which was determined from electrophoresis measurements and was found to be reasonable compared with the actual dimensions of a unit acid[24] (see Table I).

As can be seen the agreement between values calculated from eq. 10 and those obtained from viscosity experiments is satisfactory.

Discussion

The accuracy of the calculated values of eq. 12 depends upon the selection of A and γ_{Na}^{P} used. A is often determined from the limiting value of the intrinsic viscosity in an infinitely concentrated solution of the added salt, by using Flory's equation 13. The value thus determined is about 25 Å. for Na–PVS(I). However, as the viscosity in higher concentrated solutions of added salts show abnormal behavior,[7,25] it is better to select the value so as to make the theory fit the experimental values, if it is not far from the value determined from $\lim_{C_{salt} \to \infty} [\eta]$.

The determination of γ_{Na}^{P} is not so easy. In this paper the value extrapolated to the infinitely dilute solution is used, but it may be better to use a kind of average value, for the curve of γ_{Na}^{P} vs. C_{p} is not linear. Therefore, the value used in this paper may be a lower limit to γ_{Na}^{P} and probably a little larger value, i.e., a value between 0.14 and 0.2 for Na–PVS(I) is a better choice. The increase in γ_{Na}^{P} results in a decrease of the value of A to be used and therefore in slightly better agreement with experiment.

The main part of the ambiguity in $R_{exp.}$ comes from the value of Φ in Flory's equation. $\Phi = 2.1 \times 10^{21}$ is used for ordinary vinyl compounds, but recently Orofino and Flory[26] reported that $\Phi = 0.9 \times 10^{21}$ is suitable for polyelectrolytes. The uncertainty in Φ causes an error of 30% in $R_{exp.}$. However, there is a sentence in the paper of Orofino and Flory which merits attention: "With $\Phi = 2.2 \times 10^{21}$ as usually found for non-ionic polymers, the values of the parameter p (which corresponds to $\gamma_{K}^{P}/\gamma_{K}^{S}$ in this paper) obtained from viscosity data and the data of the second virial coefficients would be in even better agreement. In particular, the dependence of the parameter p on the salt concentration at fixed degree of ionization would virtually disappear." The independence of γ_{K}^{P} of the concentration of added salt was demonstrated by the experiments of Mock and Marshall,[20] Nagasawa, Izumi and Kagawa[9] and was implicitly assumed in the papers of Inagaki and others.[12] Moreover, if a change in Φ is caused by the charge of polymers, the Φ of non-ionized polymer (i.e. polyacrylic acid) should not be equal to the new value for polyions. In view of these problems, the ordinary value for Φ was used in this paper. However, an error of

(24) M. Nagasawa, A. Soda and I. Kagawa, *J. Polymer Sci.*, **31**, 439 (1958).

(25) I. Kagawa and R. M. Fuoss, *ibid.*, **18**, 535 (1955).

(26) T. A. Orofino and P. J. Flory, *J. Phys. Chem.*, **63**, 283 (1959).

30% in Φ as well as those in A and γ_{Na}^{P} would not change the conclusions of this paper.

Finally, it is interesting to see how the other theories (Hermans and Overbeek,[2] Katchalsky and Lifson,[3] Flory[4]) are modified by introducing the activity coefficient of the counterion or the effective charge density. It has often been reported that the Hermans, Overbeek and Pals' theory is in good qualitative agreement with experiment but quantitatively the calculated values of viscosity are higher than the experimental ones. According to Hermans and Overbeek, the radius of a polyion is determined by

$$y^3 \frac{y^2 - 2}{y^2 - 1} \frac{(1 + 0.6p + 0.4p^2)^2}{1 + 1.2p + 1.2p^2} = \frac{\beta}{3} \quad (14)$$

where

$$y^2 = \frac{36}{5} \frac{R_s^2}{NA^2}$$

$$p = KR_s$$

$$\beta = \frac{18}{5\sqrt{5}} \frac{1}{A\sqrt{N}} \frac{Z^2 e^2}{DkT} \quad (15)$$

If we use the effective charge $Z_{eff.}$ ($= Z \gamma_{Na}^{P}/\gamma_{Na}^{S}$) instead of Z, the calculated radius, R_s, becomes much lower than the original one. The calculated values for Na–PVS–A are shown in Table I. The calculated radii of Hermans and Overbeek are slightly larger than those of eq. 10, but they are also very near to the observed values. Therefore, it can be concluded that the neglect of the activity coefficient of the counterions is the main weak point of the Hermans–Overbeek theory.

According to Katchalsky and Lifson, the end-to-end distance h is calculated from the equation

$$\frac{3hkT}{h_0^2} \lambda = \frac{Z^2 e^2}{Dh^2} \left[\ln\left(1 + \frac{6h}{Kh_0^2}\right) - \frac{6h/Kh_0^2}{1 + 6h/Kh_0^2} \right]$$

$$\lambda = 1 + 0.6 \left[(h/h_\infty)^2/1 - (h/h_\infty)^2 \right] \quad (16)$$

It has often been reported that this equation gives almost fully stretched values to the end-to-end distance of the polyion.[5,9] The use of the effective charge ($Z_{eff.}$) greatly decreases this discrepancy between experimental and calculated coil dimensions, though the calculated values are still larger than the observed ones (see Table I).

Although the calculations of Flory's theory look much different from the calculations in this paper, both must give the same result, if activity coefficients are introduced into the Flory theory. The reference state and the final state are almost the same in both theories. While the work to charge the polymer from the reference state to the actual state was calculated by a charging process herein and by a mixing process in Flory's theory, the results are equivalent. The minor differences are that in this calculation no consideration is given to polymer–solvent interactions while the charge distribution at the boundary of the polymer sphere is neglected in Flory's theory. Orofino and Flory used a parameter p, which corresponds to the activity coefficient term $\gamma_{K}^{P}/\gamma_{K}^{S}$, to explain the discrepancy between the calculated results of Flory's theory and experiments. The values of p are reasonable compared with the experimental activity coefficient data of Nagasawa and Kagawa.[21]

Thus, it can be concluded that all these calculations of the free energy of expansion give almost the same results if the activity coefficient of the counter-

ions inside the polyion or the effective charge is introduced. Therefore, the site-binding model, as proposed by Harris and Rice, may be the proper model for explaining the behavior of linear polyelectrolyte solutions.

Acid–Base Equilibria in Solvent Mixtures of Deuterium Oxide and Water[1a]

BY E. A. HALEVI,[1b] F. A. LONG AND M. A. PAUL

The dependence of the relative ionization constant of a weak acid on the atom fraction n of deuterium in a mixed deuterium oxide–water solvent is treated from a general point of view, with particular consideration of medium effects caused by the change in solvent. Various limiting formulations for comparison with experiment can be derived from the general equations, depending on the particular simplifying assumptions that are made. The Gross-Butler formulation, characterized by a cubic term in the denominator, results from assuming monohydrated protons and deuterons and additionally ignoring all medium effects, i.e., neglecting free energies of transfer of the relevant species from one medium to another. A "linear" formulation (with a first order term in the denominator) results if one postulates non-specific solvation for the protons and deuterons and again neglects free energy of transfer. Finally a "medium effect" formulation can be derived by assuming that the entire effect is due to free energy of transfer, i.e., that exchange fractionation is negligible. Comparison of these limiting formulations with experimental data for both ionization constants and rate coefficients of acid catalyzed reactions reveals that quite respectable fits may be obtained with each of them. However, for reactions that have K_H/K_D or k_D/k_H values close to unity the Gross–Butler formulation fits considerably less well than the other two. Since the most likely actual situation is some superposition of contributions from medium effects and exchange fractionation, it seems highly doubtful that acid-base studies in mixed solvents will permit unambiguous conclusions about the state of solvation of the protons. Furthermore, in view of the likelihood that medium effects are of consequence, it is doubtful whether rate studies in the mixed solvents will permit choices to be made among kinetic mechanisms, a conclusion which was recently also reached by Gold from a different line of reasoning.

The theory of the solvent isotope effect for water–deuterium oxide mixtures which was developed some time ago by Gross, Butler and their co-workers[2–7] permits a prediction of the variation with solvent deuterium content both of ionization constants of weak acids and of rate coefficients of acid-catalyzed reactions which involve a pre-equilibrium proton transfer. Recently Purlee[8] has re-examined and up-dated this theory, especially in its parametric aspects. He introduced the now firmly established value of $K = 4.0$ for the equilibrium

$$H_2O + D_2O = 2HDO \qquad (1)$$

and also arrived at a new value of $L = 11$ for a second needed equilibrium constant, that for the exchange reaction

$$2D_3O^+ + 3H_2O = 2H_3O^+ + 3D_2O \qquad (2)$$

Purlee then utilized several sets of experimental data, both kinetic and equilibrium, to arrive at relevant values for a function $Q'(n)$ (see equation 3). To do this last he established best values for a pair of parameters, k_2^{+H} and k_3^{+H}, which enter in this function. However, Purlee also showed that the rule of the geometric mean[9] would have sufficed to establish these latter and that in this sense $Q'(n)$ is really

only a function of the constant L and the atom fraction n of deuterium in the solvent. Purlee then gave a detailed comparison of the fit of the up-dated theory with the available data. Among other points he noted that the theory fails to agree with the experimental work for some well known acid catalyzed reactions, among them the mutarotation of glucose and the hydrolysis of methyl acetate.

Still more recently Gold[10] has given further consideration to the Gross–Butler theory. He notes that the function $Q'(n)$ which appears to be rather complex in the Nelson and Butler formulation reduces, with the assumption of the rule of the geometric mean, to

$$Q'(n) = (1 - n + nl)^3 \qquad (3)$$

where for this case $l = L^{-1/3}$. The resulting expressions for relative rates and ionization constants are

$$\frac{k_n}{k_H} = \frac{1 - n + nl^3(k_D/k_H)}{(1 - n + nl)^3} = \frac{1 - n + nL^{-1/3}(k_D/k_H)}{Q'(n)} \qquad (4)$$

and

$$\frac{K_H}{K_n} = \frac{1 - n + nl \, (K_H/K_D)}{(1 - n + nl)^3} \qquad (5)$$

where k refers to rate coefficients, K to ionization constants and the subscripts H, D and n to the solvents water, deuterium oxide and a mixed aqueous solvent with the atom fraction n of deuterium.

One point made by Gold was that the calculated values of k_n/k_H or K_H/K_n are rather insensitive to the value of L and he tabulates data to illustrate

(1) (a) Work supported in part by a grant from the Atomic Energy Commission. (b) On leave from Israel Institute of Technology, Haifa, Israel (1959–1960).

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