Ultrasonic Absorption in Aqueous Polyelectrolyte Solutions. II. Polyethylenimine

Erwin Baumgartner,[1a] **Gordon Atkinson,***[1b,c] **and Mostafa Emara**[1b,d]

Contribution from the Universidad de Buenos Aires,
Facultad de Farmacia y Bioquímica, Departmento de Físico-Química,
Buenos Aires, Argentina, and the Department of Chemistry, University of Maryland,
College Park, Maryland 20742. Received June 28, 1972

Abstract: Ultrasonic absorption has been measured in aqueous solutions of polyethylenimine (PEI) in the frequency range 1–190 MHz. The effects of molecular weight, concentration, degree of neutralization, and nature of the counterion have been investigated. The polyelectrolyte solute shows an excess absorption which can be characterized by a wide absorption band. This behavior is explained by a distribution of relaxation times corresponding to the process of counterion–chain interaction. The distribution of relaxation times is interpreted as due to the flexibility of the polyionic chain. An analysis of the dependence of the ultrasonic absorption on molecular weight shows that unneutralized, low molecular weight PEI (molecular weight 600 and 1200) does not behave, at least from a kinetic point of view, like a polyelectrolyte, but rather like an electrolyte. On the other side, neutralized low molecular weight PEI and high molecular weight PEI at any degree of neutralization present a characteristic polyelectrolytic behavior, that is, no dependence of the ultrasonic absorption on molecular weight.

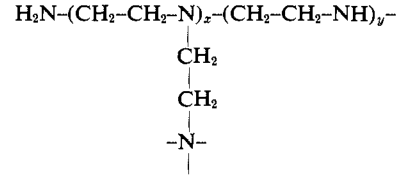
Ultrasonic absorption in aqueous solutions of salts of poly(acrylic acid) (HPA) and carboxymethylcellulose (CMC) has been reported in a previous paper.[2] It has been shown that these polyelectrolytes produce an excess absorption characterized by very wide absorption bands, which were attributed to counterion interaction with the repetitive segments of the polyion chain rather than to processes due to the chain as a whole. The observed absorption bands were related to distributions of relaxation times, rather than one or two single relaxations. This behavior can be explained by the consideration that the repeating segments of the polymeric solute and the counterions, in the case of a polyelectrolyte, find themselves in different environments, due to the disordered and changing structure of the solute.[2]

As a way to study the dynamics of the helix-coil transition, ultrasonic absorption has been measured in synthetic poly(amino acids).[3–5] Since in these systems carboxylate and charged amino groups interact with counterions, the ultrasonic absorption due to conformational changes could be obscured by counterion–polyion interactions. Therefore, it is clear that the effect found in solutions of PA and CMC has to be taken into account when studying conformational transition kinetics for synthetic poly(amino acids) or biopolyelectrolytes.[2]

The present work was undertaken for several reasons. (1) It seemed important to extend the description of very fast kinetic processes taking place in solutions of weak anionic polyelectrolytes, as given in paper I, to weak cationic polyelectrolytes. (2) It was necessary to determine whether the counterion–polycation interaction, as it probably takes place in solutions of poly(amino acids) or biopolymers, has to be taken into account, when using ultrasonic absorption to measure conformational transitions. (3) The chosen polyelectrolyte in this work, polyethylenimine (PEI), allows the study of the transition from simple electrolytes to polyelectrolytes. It is possible to compare observed kinetic properties of the corresponding low molecular weight amines, ethylenediamine (en), diethylenetriamine (den), triethylenetetramine (trien), and tetraethylenepentamine (tetraen),[6] with kinetic properties of PEI of different molecular weights. The availability of PEI of rather low molecular weight (600 and 1200) made it possible to observe an intermediate kinetic behavior between an electrolyte and a polyelectrolyte.

Experimental Procedures

Samples of PEI of different molecular weights were obtained through the courtesy of the Dow Chemical Co. The general formula for this polyelectrolyte is



$$H_2N\text{-}(CH_2\text{-}CH_2\text{-}\underset{\substack{|\\ CH_2\\ |\\ CH_2\\ |\\ \text{-}N\text{-}\\ |}}{N})_x\text{-}(CH_2\text{-}CH_2\text{-}NH)_y\text{-}$$

The ratio of primary, to secondary, to tertiary nitrogen is approximately 1:2:1, according to the manufacturer's specifications.[7] Four samples, PEI 6, PEI 12, PEI 600, and PEI 1000, of molecular weights of 600, 1200, 40–60,000, and 50–100,000, respectively, were used in this study. The PEI solutions of different degrees of neutralization were prepared by weight from a stock PEI solution and adding standardized HCl or H_2SO_4 solution.

The ultrasonic absorption of the solutions was measured in the range 1–190 MHz using pulse techniques. A standard send–receive pulse apparatus[8] was used for the range 10–190 MHz. Due to the availability of rather small quantities of PEI, and since

---

[1] (a) Universidad de Buenos Aires; (b) University of Maryland; (c) presently at the Department of Chemistry, The University of Oklahoma, Norman, Okla. 73069; (d) presently at the Chemistry Department, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt.

[2] G. Atkinson, E. Baumgartner, and R. Fernández-Prini, *J. Amer. Chem. Soc.*, **93**, 6436 (1971).

[3] T. K. Saksena, B. Michels, and R. Zana, *J. Chim. Phys. Physicochim. Biol.*, **65**, 597 (1968).

[4] (a) G. G. Hammes and P. B. Roberts, *J. Amer. Chem. Soc.*, **91**, 1812 (1969); (b) J. J. Burke, G. G. Hammes, and T. B. Lewis, *J. Chem. Phys.*, **42**, 3520 (1965).

[5] R. C. Parker, K. Applegate, and L. J. Slutsky, *J. Phys. Chem.*, 70, 3018 (1966).

[6] M. M. Emara, G. Atkinson, and E. Baumgartner, *J. Phys. Chem.*, **76**, 334 (1972).

[7] L. E. Davis in "Water-Soluble Resins," 2nd ed, R. Davidson, Ed., Reinhold, New York, N. Y., 1968, Chapter 11.

[8] R. Garnsey and D. W. Ebdon, *J. Amer. Chem. Soc.*, **91**, 50 (1969).

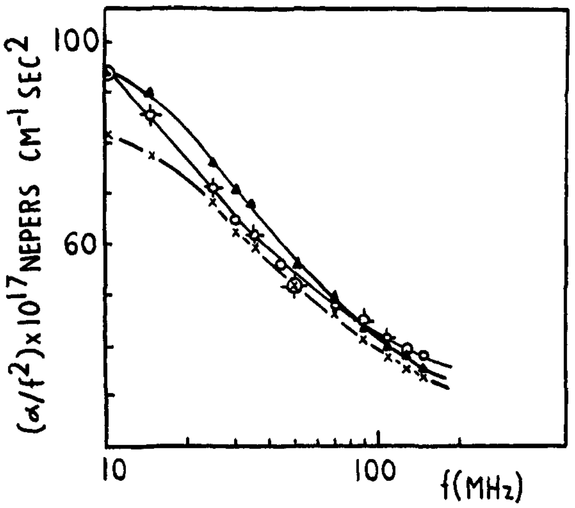


Figure 1. Ultrasonic absorption (α/f^2) *vs.* log f for aqueous solutions of PEI 1.83 N at i = 0.0: (×) PEI 6, (▲) PEI 12, (○) PEI 600, (+) PEI 1000.

the cell for the 1–30 MHz region requires approximately 2 l. of solution, only a few measurements were made in this region. A differential cell[9] using distilled water as a reference was employed for the simultaneous measurement of ultrasonic absorption and velocity. The frequency of measurement was determined by a heterodyne beat method with a Gertsch FM-3 frequency meter. The accuracy of the absorption coefficient, α, was estimated to be on the order of 2% for all solutions, except at frequencies 10 and 15 MHz, at which the error in α was estimated to be higher, 3–5%. The error in frequency measurements is negligible compared with the error in the absorption coefficient measurements. Both cells were thermostatted to 25 ± 0.1° with circulating water.

Analysis of Data

It has been shown conclusively in paper I that a fitting process using eq 1, which corresponds to discrete chemical processes

$$(\alpha/f^2) = \sum_{j=1}^{m} \frac{A_j}{1+(f/f_{rj})^2} + B \qquad (1)$$

where the symbols have their usual significance, is rather meaningless in the case of carboxylic polyelectrolytes. This is so because the determined parameters A_j, f_{rj}, and B are extremely dependent on the experimental frequency range. This fact could have been inferred from the experimental curve of α/f^2 *vs.* log f, which does not level out in the experimentally accessible range of frequencies (see Figure 2 and Table I of paper I).

Besides the unsatisfactory nature of the data fitting process using eq 1, that is, to consider the observed ultrasonic absorption as due to discrete chemical processes, the equation appears unacceptable from more general considerations, as already stated in the introduction. Any dynamic process taking place in solutions of polymeric solutes and involving the solute should have a distribution of relaxation times even assuming the unlikely case of infinitely narrow molecular weight distribution. This is expected because of the different environments in which the various repeating segments of the polymeric solute find themselves. Only dynamic processes involving individual segments in highly ordered structures (perfect helix, for example) could be expected to have a distribution of relaxation times sharp enough to correspond closely to a single relaxation.

It has been shown in paper I that the symmetric Cole–Cole distribution (SCC),[10] originally used in dielectric relaxation studies, could be employed to analyze ultrasonic absorption in solutions of polyelectrolytes. The expressions for α/f^2 and the ultrasonic energy dissipated in the process responsible for the absorption per wavelength, $(\alpha\lambda)_r$,[11] are

$$\alpha/f^2 = \frac{A \sin\frac{n\pi}{2}(\tan\phi)^{n-1}}{1 + 2(\tan\phi)^n \cos\frac{n\pi}{2} + (\tan\phi)^{2n}} + B \qquad (2)$$

$$(\alpha\lambda) = \frac{A' \sin\frac{n\pi}{2}(\tan\phi)^{n}}{1 + 2(\tan\phi)^n \cos\frac{n\pi}{2} + (\tan\phi)^{2n}} + B'f \qquad (3)$$

where A is an amplitude factor (*cf.* eq 1) dependent only on the equilibrium properties that characterize the process and $\tan\phi = (f/f_r)$. The exponent n is such that $0 \leq n \leq 1$ and gives the width of the distribution. When n is unity, eq 2 and 3 describe a single relaxation.

In the present case of solutions of PEI, almost all the experimental curves of α/f^2 *vs.* log f, over the accessible range of frequencies, display the characteristic shape corresponding to a distribution of relaxation times. That is, no leveling out of the data at lower frequencies is observed (see below for exceptions). The experimental curves are well represented by the SCC distribution over the whole frequency range. The analysis was done by a least-squares method, using eq 2. The values of n are in almost all cases between 0.40 and 0.70, which clearly indicates that the processes responsible for the ultrasonic absorption correspond to a distribution of relaxation times.

Effect of Molecular Weight and Concentration. The ultrasonic absorption of 1.83 monomolar (1.83 N) PEI solutions was the same for the samples 600 and 1000 (molecular weight 40–60,000 and 50–100,000) at any frequency in the 10–190 MHz range and at any degree of neutralization i. The same kind of behavior has been observed for NaPA solutions and for HPA and poly(methacrylic acid) (HPMA) by Michels and Zana.[12] The obvious conclusion is that the dynamic processes taking place in this range of frequencies involve the repetitive segments of the polymer chains and not the chains as a whole.

On the other hand, PEI 6 and PEI 12 (molecular weight 600 and 1200) exhibit a different behavior. When i = 0.0, a 1.83 monomolar solution of PEI 12 gives a higher absorption at any frequency than a solution of the same concentration of PEI 6, whereas solutions of PEI 600 and 1000 of the same concentration show an absorption curve (Figure 1) intermediate between the curves corresponding to PEI 6 and PEI 12. At any other i, PEI 6 and PEI 12 show the same absorption curve, but the absolute value of α/f^2 is

---

[9] R. Corsaro, G. Atkinson, and B. R. Perlis, *Chem. Instrum.*, **2**, 389 (1970).

[10] K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

[11] M. Eigen and L. de Maeyer in "Techniques of Organic Chemistry," Vol. VIII, 2nd ed, A. Weissberger, Ed., Interscience, New York, N. Y., 1963, Part 2.

[12] B. Michels and R. Zana, *Kolloid Z.*, **234**, 1008 (1969).

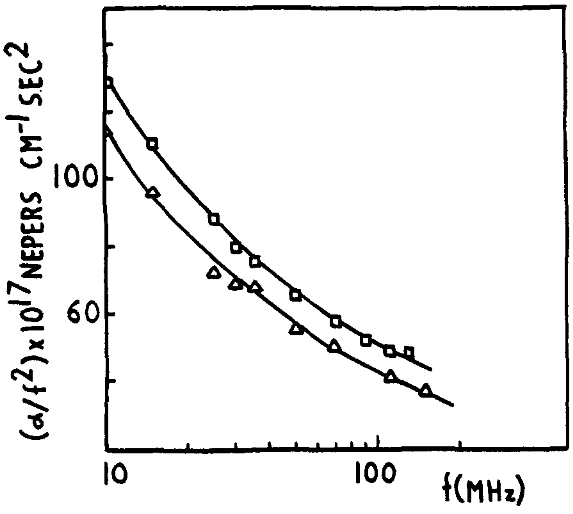


Figure 2. Ultrasonic absorption (α/f^2) *vs.* log f for aqueous solutions of PEI 6 1.83 *N*: (△) $i = 0.448$, (□) $i = 0.672$.

smaller than for PEI 600 and PEI 1000. There is another fact which distinguishes the kinetic behavior of PEI 6 and PEI 12 at $i = 0.0$ from the corresponding ones for PEI 600 and PEI 1000. The analysis of the data by a SCC distribution gives a value of $n = 0.90$ for both low molecular weights, whereas the high molecular weights have a value close to 0.60. This means that the distribution corresponds almost to a single relaxation ($n = 1.0$) in the case of the low molecular weight PEI. This would imply that PEI 6 and PEI 12 at $i = 0.0$ behave, at least from a kinetic point of view, not like an "actual" polyelectrolyte. This is understandable when taking into consideration that molecular weights of 600 and 1200 correspond to approximately 14 and 28 nitrogenated groups. The number of charged groups is much smaller than those indicated before, and this means that the picture of the counterion interacting with a distribution of different environments is certainly not applicable in this case. In other words, in the case of unneutralized PEI 6 and PEI 12, we have something intermediate between an electrolyte and a polyelectrolyte.

Upon increasing the degree of neutralization, the curves (α/f^2) *vs.* log f for PEI of low molecular weight assume the characteristic shape for a distribution of relaxation times (see a typical example in Figure 2). n of eq 2 is now around 0.50, indicating a distribution of the processes responsible for the absorption.

Analyzing the effect of concentration on the absorption of ultrasound one gets a picture very similar to the one described in the introduction. An increase in polyelectrolyte concentration was observed to give an increase in α/f^2 in the case of HPA and CMC.[2] To evaluate the concentration dependence of the relaxational part of the absorption, $(\alpha/f^2)_r$, the background absorption B was subtracted from the observed $(\alpha/f^2)_r/c$ for NaPa, NaCMC, and CaCMC and was plotted against log f, assuming $B = 23.0 \times 10^{-17}$ neper sec^2 cm^{-1}. It was found to be independent of concentration (Figure 4 of paper I); this means that the time scale and amplitude of the processes occurring in these solutions show no experimentally detectable changes when the concentration of polyelectrolyte is varied.

This result and the molecular weight independence of (α/f^2) were employed to support the validity of the use of the model of polyonic domains[2,13,14] to describe the dynamic processes occurring over the concentration and frequency range of that study.

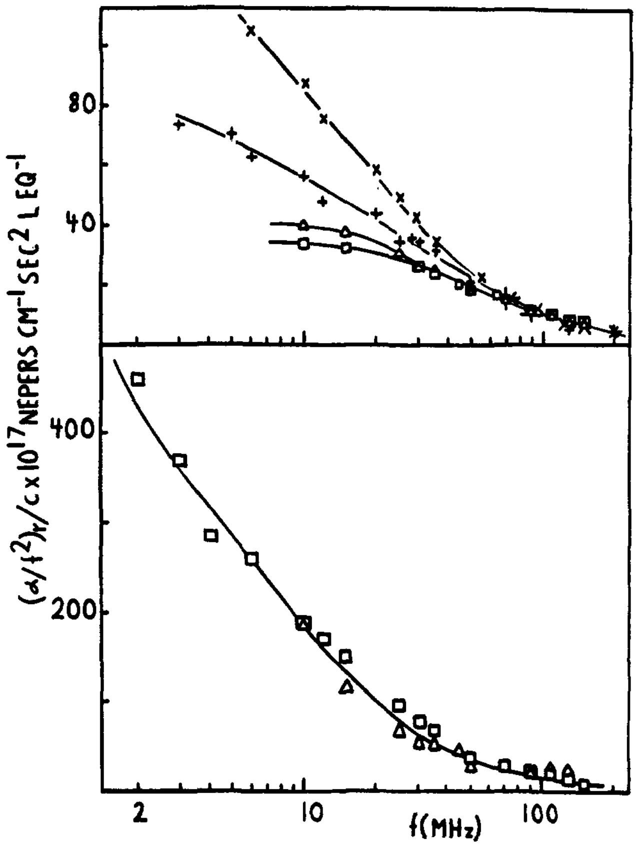


Figure 3. Upper part, effect of concentration on $(\alpha/f^2)_r/c$ for PEI 12 at $i = 0.0$: (□) $c = 2.0$ *N*; (△) $c = 1.83$ *N*; (+) $c = 0.863$ *N*; (×) $c = 0.549$ *N*. Lower part, effect of concentration on $(\alpha/f^2)_r/c$ for PEI 12 at $i = 1.0$ ($B = B_{H_2O}^0 = 23 \times 10^{-17}$ neper sec^2 cm^{-1}): (□) $c = 1.83$ *N*; (△) $c = 0.863$ *N*.

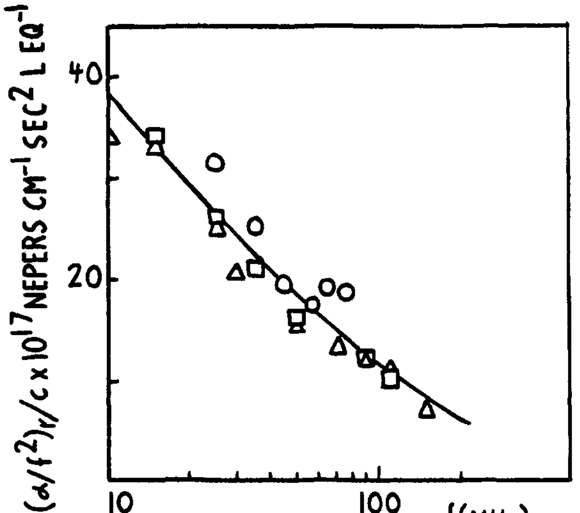


Figure 4. Effect of concentration on $(\alpha/f^2)_r/c$ for PEI 1000 at $i = 0.0$ ($B = B_{H_2O}^0 = 23 \times 10^{-17}$ neper sec^2 cm^{-1}): (□) $c = 1.83$ *N*; (△) $c = 0.91$ *N*; (○) $c = 0.5$ *N*.

Figures 3 and 4 show the effect of concentration on

---

(13) R. Fernández-Prini, E. Baumgartner, S. Liberman, and A. E. Lagos, *J. Phys. Chem.*, 73, 1420 (1969).

(14) G. Manning, *J. Chem. Phys.*, 51, 924, 934, 3249 (1969).

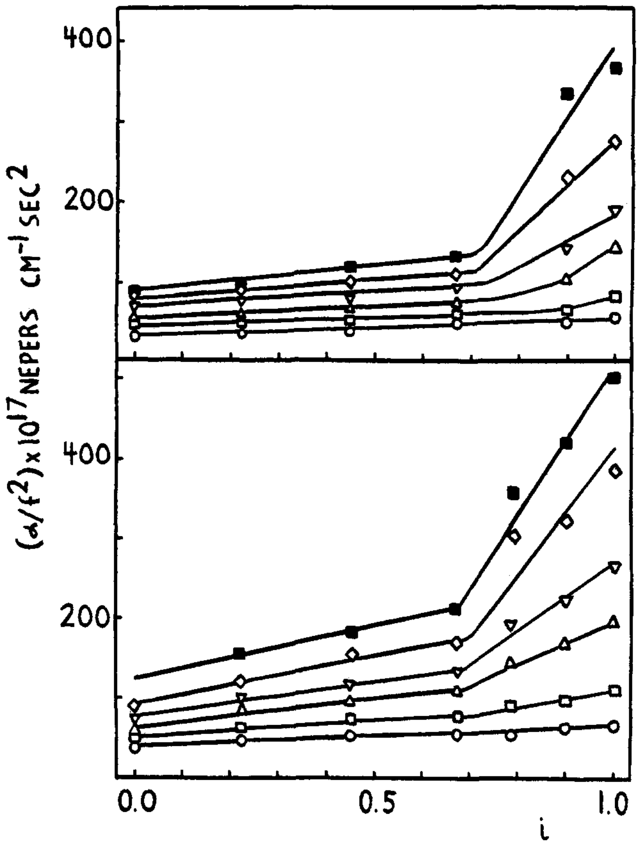


Figure 5. Ultrasonic absorption (α/f^2) *vs.* degree of neutralization for PEI 1.83 *N* at different frequencies: upper part, PEI 6; lower part, PEI 1000. (□) 10 MHz; (◇) 15 MHz; (▽) 25 MHz; (△) 35 MHz; (□) 70 MHz; (○) 130 MHz.

$(\alpha/f^2)_r/c$ for PEI 12 at $i = 0.0$ and 1.0 and for PEI 1000 at $i = 0.0$. It can be seen in these examples that for low molecular weight PEI at $i = 0.0$, $(\alpha/f^2)_r/c$ is not independent of concentration. On the contrary, the observed behavior is similar to the one corresponding to nonpolymeric solutes with discrete relaxations. On the other hand, for high molecular weight PEI $(\alpha/f^2)_r/c$ is independent of concentration. The same behavior is found for PEI of low molecular weight when $i > 0.0$. All this evidence is consistent with the ideal that there is a transition from an almost electrolyte to an actual polyelectrolyte.

Effect of Degree of Neutralization. Figure 5 shows the effect of degree of neutralization on (α/f^2) at different frequencies for PEI 6 and PEI 1000. Up to a degree of neutralization approximately 0.7, the behavior is completely analogous to the one reported in paper I, for HPA. Between $i = 0.7$ and 0.8 there is an inflection of the curve and at higher degrees of neutralization the slope is much higher. We advance as a possible explanation of this behavior the following. Solutions of different degrees of neutralization were obtained by adding standardized HCl to the PEI solutions in an amount calculated by assuming that all the nitrogenated groups in the PEI molecule can be titrated. Recent evidence made available to us[15,16] shows that this is not so. Actually, only approximately 80% of the amino groups can be titrated. This failure to neutralize all of the amino groups was suggested as due to the reduced basicity of specific amino groups as adjacent amino groups become neutralized.[15] This fact would imply that in the abscissa axis of Figure 5 the point $i = 1.0$ should be where the point $i = 0.8$ lies. If this were the case, the behavior of the PEI system, as far as fast dynamic processes are concerned, is similar to the HPA system. The ultrasonic absorption observed at $i > 0.8$ could be attributed to the presence of concentrated HCl in excess (up to ~0.5 *M*). A fact that supports this interpretation is that adding excess NaCl (0.5 *M*) to PEI 1000 1.83 *N* at $i = 1.0$ does not increase the absorption of ultrasound (see below), but an addition of HCl (0.5 *N*) increases α/f^2 in such a way that the point falls on the straight line obtained by extrapolating the experimental points above $i = 0.8$ in Figure 5. A more thorough investigation of this possibility is now under way.

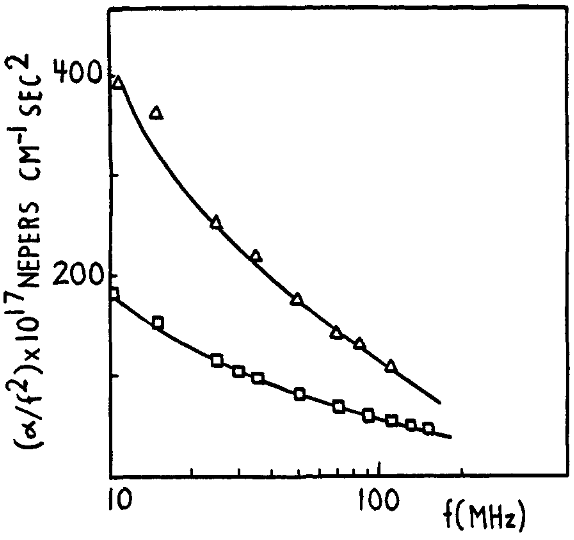


Figure 6. Ultrasonic absorption (α/f^2) *vs.* log *f* for aqueous solutions of PEI 1000 1.83 *N* at $i = 0.45$: (□) titrated with HCl, (△) titrated with H_2SO_4.

Effect of Counterions and Excess Salts. When titrating PEI with H_2SO_4 instead of HCl a sharp increase in absorption is observed at any *i*. Figure 6 shows the variation of (α/f^2) with log *f* for a 1.83 monomolar solution of PEI 1000 at $i = 0.45$, titrated with HCl and H_2SO_4. The same behavior has been observed for other molecular weights and degrees of neutralization. Although it is much more difficult to explain the behavior of anions than that of cations, and although there are no measurements done of the volume change ΔV accompanying the binding of counterions as have been done for countercations,[17] it can be assumed that ΔV (per mole of bound ion) for sulfate is greater than for chloride, which explains the higher absorption observed experimentally.

The addition of NaCl 0.5 and 1.0 *N* to PEI 6 and PEI 1000 at $i = 1.0$ does not produce any increase in absorption. The same result has been observed when dealing with HPA and CMC.

Discussion

We shall now discuss the possible sources of the excess ultrasonic absorption found in solutions of PEI.

(15) C. R. Dick and G. E. Ham, *J. Macromol. Sci., Chem.*, 4 (6), 1301 (1970).

(16) D. Turyn and R. Fernández-Prini, submitted for publication.

(17) U. P. Strauss and Y. P. Lueng, *J. Amer. Chem. Soc.*, 87, 1476 (1965).

Since the reported absorption is not affected by the addition of excess 1–1 salts and is increased by the presence of bivalent ions, it is possible to rule out viscous losses as the responsible process for the excess absorption. This should be decreased by the addition of excess simple salts or polyvalent counterions. The fact that solutions of PEI 600 and PEI 1200 of equal concentration had the same ultrasonic absorption sustains this conclusion, because a change in molecular weight should change the viscosity. The fact that the absorption is not independent of molecular weight for PEI 6 and PEI 12 at $i = 0.0$ is explained by a different reason (see below).

Another possible source of absorption could be the dynamic viscoelastic behavior of polymer solutions. The equations corresponding to this effect, derived by Rouse[18] and applied by Dunn[19] to ultrasonic absorption, predict a dependence of $(\alpha/f^2)_r$ on solute molecular weight and on the shear viscosity of the solution. Hence, viscoelasticity does not seem to be an important effect in these polycationic solutions.

Dielectric dispersion in polyelectrolyte solutions ($f > 1$ MHz) has been attributed[20] to ion atmosphere relaxation. Excess salt should increase the ion atmosphere relaxation frequency, but no such effect is observed in our case.

We therefore interpret the observed ultrasonic absorption in the case of PEI solutions in the same way as done for carboxylic poyelectrolyte solutions in paper I. It is due to counterion interaction with the repetitive segments of the polyion chain.

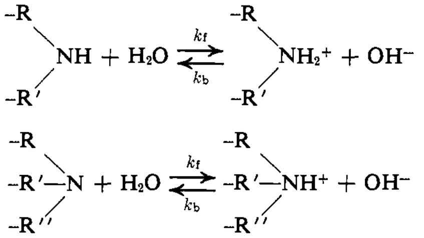
It would be unrealistic and oversimplified to describe this interaction as taking place between isolated charged groups on the chain and single counterions, particularly for a correct description of the dynamics of the process, because of the flexibility of the polyionic chain. A more correct description of the process is that each counterion "sees" a different environment, which leads to a distribution of the process of counterion–chain interaction, which in turn gives a distribution of relaxation times.

The effect found in this work will have to be taken into account, together with the one reported in paper I, when using ultrasonic absorption in an attempt to measure conformational transition kinetics for biopolyelectrolytes. It is clear that this type of counterion interaction can lead to absorption effects large in comparison to those expected from conformational changes.

Let us now consider the kinetic behavior as a function of molecular weight. It has been found that the low molecular weight analogs of PEI, en, den, trien, and tetraen present an excess absorption, which is due to the proton-transfer reaction at a terminal amine group.[6]

$$\text{-R-NH}_2 + \text{H}_2\text{O} \underset{k_b}{\overset{k_f}{\rightleftarrows}} \text{-R-NH}_3^+ + \text{OH}^- \qquad (4)$$

When increasing the number of nitrogenated groups in the molecule to 14 (PEI 6) and 28 (PEI 12), at $i = 0.0$, a quasi-discrete relaxation seems to be responsible for the observed absorption. This can be deduced from an inspection of the (α/f^2) *vs.* $\log f$ (Figure 1) and from the value of n (width of the SCC distribution) around 0.90. The possible proton-transfer reactions occurring when the solute is PEI are represented in eq 4 and 5. But Shepherd and Kitchener,[21] studying titration curves of PEI of relatively low molecular weight (35–40 monomer units), arrived at the conclusion that at very low degrees of neutralization ($i = 0.0$–0.06) only a few NH_2 end groups are dissociated in aqueous solutions and that therefore no interaction of the polyelectrolyte type is present in this region of degree of neutralization. This interaction is present only at higher i. These conclusions are completely in accordance with our findings, studying kinetic properties. Assuming that there is no distribution of relaxation times at all, and that only $-NH_2$ terminal groups are dissociated, we have calculated k_f and k_b corresponding to the reaction represented in eq 4 for PEI 6 and PEI 12 at $i = 0.0$. They were calculated through eq 6


(5)

$$1/\tau = 2\pi f_r = 2k_b[\text{OH}^-] + k_f \qquad (6)$$

where τ is the relaxation time. f_r was obtained using eq 1 with $m = 1$. $[OH^-]$ was obtained employing an apparent pK of 9.0.[21] The values are $k_f = 9 \times 10^6$ sec^{-1} and $k_b = 3 \times 10^{10}$ sec^{-1} M^{-1} for PEI 6 and $k_f = 2 \times 10^7$ sec^{-1} and $k_b = 2 \times 10^{10}$ sec^{-1} M^{-1} for PEI 12. These values are very reasonable, when compared with values obtained for simple amines,[11] confirming, therefore, the preceding conclusions.

At higher degrees of neutralization, PEI 6 and PEI 12 present absorption curves with no leveling out at low frequencies and analyzing them through the SCC distribution, values of n around 0.50 have been obtained. This behavior corresponds clearly to a polyelectrolyte. When titrating, more and more amino groups, including secondary and tertiary, become charged, and the process we are now looking at ultrasonically is the association between the polyion and the counterions, chloride in our case. The ultrasonic absorption observed in this case (see Figure 5) is clearly different from the corresponding ones for low molecular weight analogs, where a sharp decrease of (α/f^2) has been observed when increasing or decreasing the pH around the equilibrium value of the amine (see Figure 4 in ref 6). Again, our observed kinetic behavior is in accordance with Shepherd and Kitchener's observations.[21]

The high molecular weight PEI (600 and 1000) present polyelectrolytic behavior at any i. This is understandable, because even at $i = 0.0$ the number of nitrogenated groups which are dissociated must be high at these molecular weights, leading, therefore, to

---

(18) P. E. Rouse, *J. Chem. Phys.*, **21**, 1272 (1953).

(19) L. W. Kessler, W. D. O'Brien, and F. Dunn, *J. Phys. Chem.*, **74**, 4096 (1970).

(20) S. B. Sachs, A. Raziel, H. Eisenberg, and A. Katchalsky, *Trans. Faraday Soc.*, **65**, 77 (1969).

(21) E. J. Shepherd and J. A. Kitchener, *J. Chem. Soc.*, 2448 (1956).

a distribution of relaxation processes, corresponding to the reactions represented in eq 4 and 5.

Acknowledgments. We are indebted to Professor R. Fernández-Prini for valuable discussions. The support of the Center of Materials Research of the University of Maryland and the Office of Saline Water, U. S. Department of Interior, is acknowledged. Computing time was supported by the University of Maryland Computer Science Center under National Aeronautics and Space Administration Grant NsG-398.

Direct Spectroscopic Evidence for a Deuterium Solvent Effect on the Lifetime of Singlet Oxygen in Water

Takashi Kajiwara and David R. Kearns*

Contribution from the Department of Chemistry, University of California, Riverside, California 92502. *Received March 20, 1973*

Abstract: The $^1\Delta_g$ oxygen dimol emission produced from the decomposition of hydrogen peroxide has been studied in H_2O and in D_2O. These studies provide direct spectroscopic proof that there is a solvent deuterium effect on the lifetime of singlet oxygen and thus confirm our earlier results which were based on indirect laser photolysis measurements. The pH dependence of the H_2O_2 decomposition and the chemiluminescence have also been studied to provide more information about the nature of the reaction.

In 1971 Merkel and Kearns developed a laser flash photolysis method for determining the lifetime of singlet oxygen in solution in which the decay of singlet oxygen was followed indirectly by its reaction with a colored acceptor (DBBF).[1,2] One of the interesting results of their measurements is that there is a considerable isotope effect on the lifetime of $^1\Delta_g$ (2 μsec in H_2O and 20 μsec in D_2O). The isotope effect as well as the variation of the lifetime in different solvents was well accounted for in terms of an energy transfer mechanism in which $^1\Delta_g$ transfers its electronic excitation energy to the vibrational energy levels of the solvent molecules.[3] These initial results have now been confirmed independently,[4,5] and while there is no reason to doubt they are correct, it was realized that lifetime measurements were indirect. Because of the important role which solvent isotope effects are beginning to play in elucidating the role of singlet oxygen in other photochemical and photobiological processes,[6-10] we believed it was desirable to have an alternative, and, if possible, direct, method for checking the solvent isotope effect on the lifetime of singlet oxygen. In the present study we have accomplished this by measuring the chemiluminescence arising directly from singlet oxygen generated by decomposition of hydrogen peroxide and sodium hypochlorite.

It is well established that singlet oxygen molecules are produced by mixing H_2O_2 aqueous solution and NaOCl aqueous solution, and $^1\Delta_g$ oxygen molecules show a characteristic dimol chemiluminescence at 6334 and 7032 Å and emission from $^1\Sigma$ at 7620 Å.[11-13] From an analysis of rotational structure Khan and Kasha were able to establish that $^1\Sigma$ emission only occurs from the bubbles,[11] and no emission has ever been observed from oxygen molecules dissolved in solution.[11] Since the concentration of excited oxygen in the bubbles depends strongly on the rate at which they decay in the solvent before reaching a bubble, we had hoped that it might be possible to obtain a quantitative estimate of the lifetime of singlet oxygen in H_2O and D_2O. While this turned out not to be possible, we were able to obtain direct spectroscopic evidence that the lifetime of singlet oxygen is longer in D_2O than in H_2O. We have also investigated the pH dependence of the chemiluminescence and the rate of evolution of molecular oxygen and in this way obtained additional information regarding the mechanism of the reaction.

Experimental Section

Materials and Methods. Commercial bleaching reagent "Chlorox" was used as sodium hypochlorite solution and titration with a 0.1 *N* standard As_2O_3 solution[14] showed that it contained 1.55 *N* (or 0.78 *M*) NaOCl. Hydrogen peroxide (30% Mallinckrodt Analytical Reagent) and deuterium oxide (Diaper Inc. 99.7% D_2O) were used without further purification. A D_2O solution of sodium hypochlorite was made as follows. About 30 g of calcium hypochlorite, $Ca(OCl)_2$ (B & A Technical Grade), was dissolved into 300 ml of D_2O. After about 1 hr the undissolved material was removed and the solution was combined with a D_2O solution of Na_2CO_3 (20 g in 89 ml). After precipitation of the white $CaCO_3$ more of the Na_2CO_3 solution was added until no further precipitation of $CaCO_3$ was observed. After about 1 hr the precipitated

---

(1) P. B. Merkel and D. R. Kearns, *Chem. Phys. Lett.*, **12**, 120 (1971).

(2) P. B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, **94**, 1029 (1972).

(3) P. B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, **94**, 7244 (1972).

(4) D. R. Adams and F. Wilkinson, *J. Chem. Soc., Faraday Trans. 2*, 586 (1972).

(5) R. H. Young, D. Brewer, and R. A. Keller, *J. Amer. Chem. Soc.*, **95**, 375 (1973).

(6) P. B. Merkel, R. Nilsson, and D. R. Kearns, *J. Amer. Chem. Soc.*, **94**, 1030 (1972).

(7) R. Nilsson, P. B. Merkel, and D. R. Kearns, *Photochem. Photobiol.*, **16**, 117 (1972).

(8) R. Nilsson and D. R. Kearns, *Photochem. Photobiol.*, **17**, 65 (1973).

(9) H. Schmidt and P. Rosenkranz, *Z. Naturforsch.*, **27b**, 1436 (1972).

(10) A. G. Kepka and L. I. Grossweiner, *Photochem. Photobiol.*, in press.

(11) A. U. Khan and M. Kasha, *J. Chem. Phys.*, **39**, 2105 (1963); 40, 605 (1964).

(12) A. U. Khan and M. Kasha, *Nature (London)*, **204**, 241 (1964).

(13) A. U. Khan and M. Kasha, *J. Amer. Chem. Soc.*, **92**, 3293 (1970).

(14) A. I. Vogel, "A Textbook of Quantitative Inorganic Chemistry," 3rd ed, Longmans, London, 1962, p 395.