Radiation-Induced Cationic Polymerization of α-Methylstyrene Enhanced by Diphenyliodonium Hexafluorophosphate

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ABSTRACT: The addition of diphenyliodonium hexafluorophosphate enhances the radiation-induced cationic polymerization of α-methylstyrene in dichloromethane. The greatest enhancement effect was observed at lower temperature and higher salt concentration. The polymer obtained in the presence of the salt exhibits a bimodal molecular weight distribution, indicating the simultaneous propagation by free ions and ion pairs. From the pulse radiolysis study, it is evident that the enhancement of the polymerization by the salt is attributable not only to the promotion of the formation of propagating cations and monomer radical cations but also to the stabilization of monomer and dimer radical cations toward neutralization by Cl^- and basic impurities through ion-pair formations with PF_6^-.

Introduction

The use of diaryliodonium salts,[1-3] triarylsulfonium salts,[4-7] and triarylselenonium salts[8] having relatively stable nonnucleophilic anions such as PF_6^-, SbF_6^-, BF_4^-, etc. in photoinduced cationic polymerization has been noted by several investigators. On irradiation with ultraviolet light, the salts undergo photodecomposition to yield Brønsted acids capable of initiating the cationic polymerization of a wide variety of monomeric substrates. It has also been reported that the salts can initiate cationic polymerizations by oxidizing free radicals to corresponding carbocations in the thermal and photochemical polymerizations initiated by radical initiators such as azobis(isobutyronitrile) and benzoyl peroxide.[9,10] As is well-known, the radiation-induced cationic polymerization is mainly dependent on the content of basic impurities such as water since the cationic species responsible for the polymerization are in free-ion states, while a relatively small dependence on basic impurities is observed in catalytic cationic polymerization where the cationic species are in ion-paired states.[11] In particular, the radiation-induced polymerization of α-methylstyrene is inhibited unless the samples are rigorously dried. It is reasonable, therefore, to expect that the radiation-induced cationic polymerization may be enhanced in the presence of the salts having nonnucleophilic anions not only due to production of cationic species but also because the counterions may stabilize the cationic species by forming ion pairs.

In earlier papers,[12,13] we have been concerned with the enhancement effects of triphenylsulfonium hexafluorophosphate, $(C_6H_5)_3SPF_6$, and diphenyliodonium hexafluorophosphate, $(C_6H_5)_2IPF_6$, in the radiation-induced cationic polymerization of styrene. In the pulse radiolysis study the increase in the yield and lifetime of styrene dimer radical cations indicates that the enhancement effect is mainly due to increase in the stabilities of monomer and dimer radical cations in the primary processes of initiation by the ion-pair formation with PF_6^-. The present study involves the radiation-induced cationic polymerization of α-methylstyrene in dichloromethane in the presence of $(C_6H_5)_2IPF_6$. The role of the salt in the primary processes of the radiation-induced polymerization was studied by pulse radiolysis. The present study reveals the promotion of the formation of propagating cations by the salt, which was not recognized in the previous study with styrene as a monomer.

Experimental Section

Materials. α-Methylstyrene and dichloromethane, obtained from Wako Pure Chemical Industrial Co., were successively washed three times with 10% aqueous sodium hydroxide solution and with distilled water and then fractionated. The middle fractions were poured into storage vessels containing CaH_2 on a vacuum line and degassed by the freeze–thraw method. $(C_6H_5)_2IPF_6$, provided by 3M Co., and $(C_6H_5)_2ICl$, obtained from Aldrich Chemical Co., were used after drying at about 80 °C for 30 min under vacuum.

Procedures. α-Methylstyrene and dichloromethane were introduced into Pyrex ampules containing the dried salt after their volumes were measured in calibrated tubes. γ-Irradiation of the samples was done by a ^{60}Co source at a dose rate of 2.3×10^5 rd/h. Poly(α-methylstyrene) was precipitated by an excess of methanol, filtered, and dried in a vacuum oven. The conversion was calculated from the dry weight of polymer. The molecular weight distribution was measured by gel permeation chromatography (Toyo Soda HLC-801).

The pulse radiolysis study was performed with the L-band linear accelerator at Osaka University. The samples were sealed in Pyrex ampules fitted with Suprasil cells of 10-mm optical path length. A beam of approximately 8 A of electrons of 28 MeV with a pulse width of 10 ns was used. The optical measuring system consists of 450-W xenon pulse lamp (OPG-450, Osram), a monochromator (Nikon G-250), a photomultiplier (Hamamatsu TV, R928), and an oscilloscope (Tektronix, 7834).

Results and Discussion

Polymerization. The time–conversion curves for the radiation-induced polymerization of α-methylstyrene in dichloromethane solutions containing $(C_6H_5)_2IPF_6$ are shown in Figure 1. Comparison of the curves shows that the polymerization is enhanced as the salt concentration increases and temperature is lowered. Inhibition periods are observed in all cases. No polymer was obtained in the absence of the salt, probably because of inadequate drying of the samples.[14] When a dichloromethane solution of 3×10^{-2} M salt was first irradiated for 2 h at −78 °C and then the monomer was introduced, no polymer was obtained after 2 h at −78 °C, indicating that the enhancement of the polymerization is not due to the Brønsted acid produced from the salt.

Figures 2 and 3 show the molecular weight distributions of the polymers obtained at 0 and −78 °C, respectively. The polymers obtained at 0 °C have bimodal molecular weight distributions, which indicate the possibility that two different mechanisms of propagation operate simultaneously. Since the radiation-induced polymerization of α-methylstyrene proceeds exclusively by a cationic mechanism, both peaks of the bimodal distribution curve are considered to be of products of different cationic propagating species. From the trend that the height of the lower molecular weight peak increases with increasing salt concentration, it is tentatively assigned to the product of propagating species paired with PF_6^-, and the other peak of higher molecular weight is assigned to the product of

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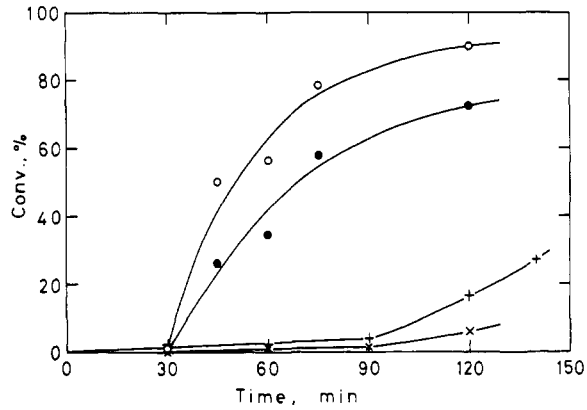

Figure 1. Time–conversion curves for the radiation-induced polymerization of α-methylstyrene in CH_2Cl_2 in the presence of $(C_6H_5)_2IPF_6$: Monomer concentration, 2.0 M. Temperature and salt concentration: (○) −78 °C, 3×10^{-2} M; (●) −78 °C, 6×10^{-3} M; (+) 0 °C, 3×10^{-2} M; (×) 0 °C, 6×10^{-3} M.

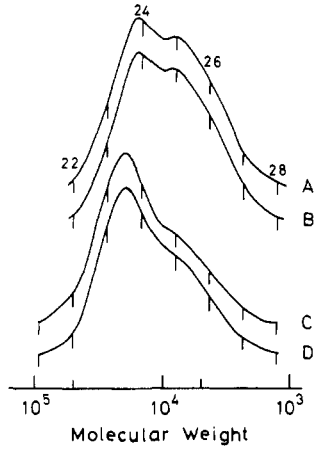

Figure 2. Molecular weight distributions of the polymers obtained at 0 °C. Salt concentration and irradiation time: (A) 3×10^{-2} M, 90 min; (B) 3×10^{-2} M, 60 min; (C) 6×10^{-3} M, 120 min; (D) 6×10^{-3} M, 60 min.

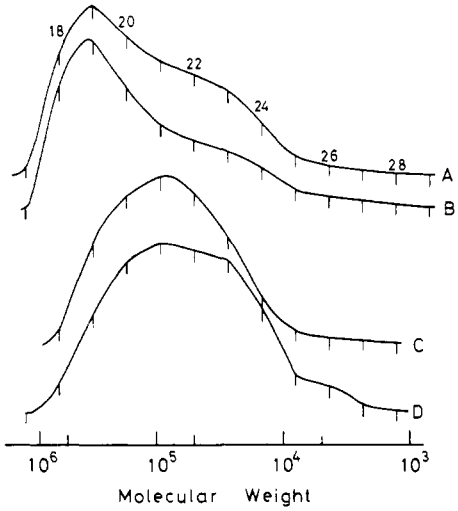

Figure 3. Molecular weight distributions of the polymers obtained at −78 °C. Salt concentrations and irradiation time: (A) 3×10^{-2} M, 75 min; (B) 3×10^{-2} M, 45 min; (C) 6×10^{-3} M, 120 min; (D) 6×10^{-3} M, 60 min.

propagating species in free-ion states. The molecular weight distributions of the polymers obtained at −78 °C show that the products contain higher molecular weight polymers than those obtained at 0 °C. The formation of the higher molecular weight polymers is more significant

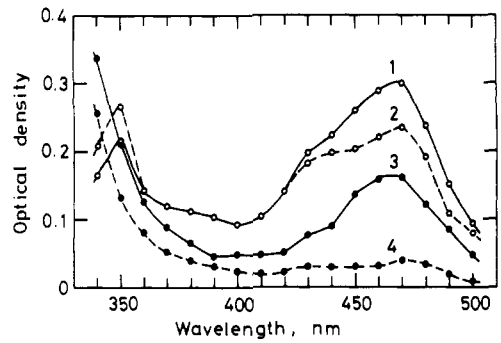

Figure 4. Transient absorption spectra at a monomer concentation of 0.77 M in CH_2Cl_2. (1) at the end of the pulse, $[(C_6H_5)_2IPF_6] = 3 \times 10^{-2}$ M; (2) 500 ns after the pulse, $[(C_6H_5)_2IPF_6] = 3 \times 10^{-2}$ M; (3) at the end of the pulse, in the absence of additive; (4) 500 ns after the pulse, in the absence of additive.

at the higher salt concentration. It is known that the molecular weight is increased by lowering temperature in the catalytic polymerization of α-methylstyrene, where propagation by ion pairs is important; polymers having average molecular weights as high as 8×10^4 are produced at low temperatures.[15] On the other hand, the molecular weight of the polymer obtained by γ-irradiation in dichloromethane at −78 °C under rigorously dry conditions is rather low, $\bar{M}_n = 3.5 \times 10^3$, as shown in our earlier paper.[14] On this basis, the formation of the higher molecular weight polymers at −78 °C can be accounted for by the contribution of propagation by ion pairs, which increases with increasing salt concentration. Thus it is considered that the added salt contributes to the propagation processes because of its anion, PF_6^-, forming the ion pair with the propagating cation.

Pulse Radiolysis. The effect of the salt on the initiation processes of the polymerization was studied by the pulse radiolysis at a monomer concentration of 0.77 M in dichloromethane at room temperature. Figure 4 shows the transient absorption spectra in the presence and absence of the salt. Comparison of the spectra reveals that the addition of the salt results in an increase in absorption at around 470 nm and an appearance of an absorption peak at 350 nm. According to the literature,[16,17] the absorption band at around 470 nm is assigned to α-methylstyrene dimer radical cations, which further react with monomer to give propagating cations having an absorption band at around 340 nm. The absorption bands assigned to monomer radical cations are observed at around 690 and 350 nm only at low temperatures and/or at low monomer concentrations because they have a quite short lifetime. In the present study no absorption band was observed from 500 to 800 nm. It is reasonable to consider that the formation of the dimer radical cations is completed within the pulse duration, 10 ns, under the present conditions, at room temperature and at the relatively high monomer concentration.

Figure 5 shows the decay of light absorption at 350 nm in the presence of various additives. The decay curve in the absence of additive (curve C) involves two distinct parts, i.e., the rapid decay in the beginning and the subsequent slow decay. This indicates that absorption at 350 nm is due to two species having different lifetimes. The species responsible are considered to be propagating cations and benzyl-type radicals, which have been reported to have a strong absorption band at around 320 nm.[18,19] The rapid decay in the beginning is accelerated by the addition of a basic substance such as methanol (curve D) and hence assigned to cationic species, probably the propagating cations. Absorption at 350 nm is slowly in-

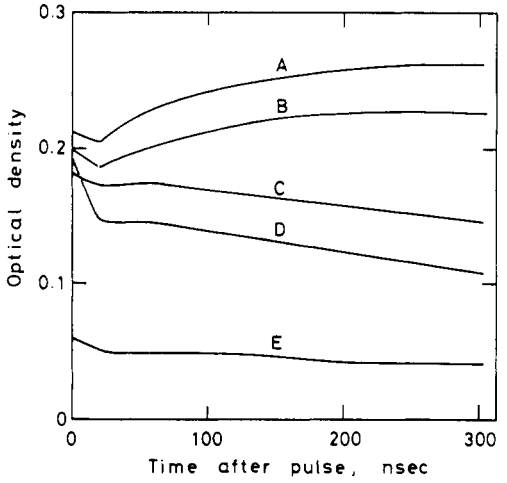

Figure 5. Decay of light absorption at 350 nm. Additives: (A) 3×10^{-2} M $(C_6H_5)_2IPF_6$; (B) 6×10^{-3} M $(C_6H_5)_2IPF_6$; (C) none; (D) 3×10^{-2} M CH_3OH; (E) 1×10^{-2} M $(C_6H_5)_2IPF_6$ and 3×10^{-2} M CH_3OH.

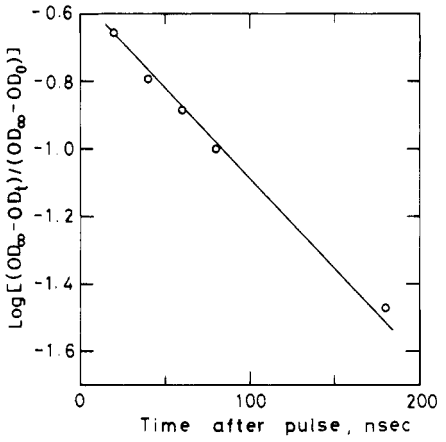

Figure 6. First-order kinetic plot for the slow increase in absorption at 350 nm in the presence of 3×10^{-2} M $(C_6H_5)_2IPF_6$; $(OD)_\infty$ is the optical density at 180 ns after the pulse, which is constant up to about 3 μs.

creased after the pulse when $(C_6H_5)_2IPF_6$ is added (curves A and B). It is appreciably decreased by the addition of methanol to the solution containing the salt (curve E). The results indicate that the addition of the salt results in a slow formation of cationic species and that the both species, the cationic and radical species, are consumed when the salt and methanol are simultaneously added. On this basis, it is reasonable to consider that the salt reacts with the radical to yield the propagating cation, as previously proposed in the thermal and photochemical polymerizations.[9,10]

$$P\cdot + (C_6H_5)_2IPF_6 \rightarrow P^+ + PF_6^- + C_6H_5I + C_6H_5\cdot \quad (1)$$

where P· should be a low molecular weight radical species, having a structure of substituted benzyl, since α-methylstyrene does not polymerize by a radical mechanism. The slow increase in absorption at 350 nm in the solution containing the salt obeys first-order kinetics as shown in Figure 6.

Figure 7 shows the decay behavior of the dimer radical cations obtained by following absorption at 470 nm in the presence of various additives. Both the yield and lifetime are increased by the addition of $(C_6H_5)_2IPF_6$ (curves A and B). The decay curves exhibit maximum absorption at around 70 ns after the pulse, whereas only a rapid decay is observed in the absence of the salt (curve C). This

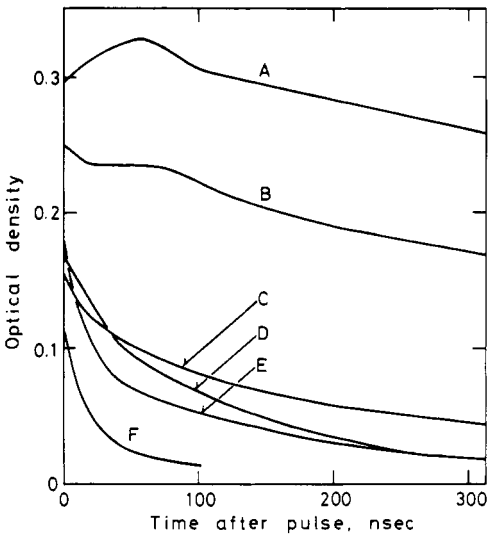

Figure 7. Decay of light absorption at 470 nm. Additives: (A) 3×10^{-2} M $(C_6H_5)_2IPF_6$; (B) 6×10^{-3} M $(C_6H_5)_2IPF_6$; (C) none; (D) 1×10^{-2} M $(C_6H_5)_2IPF_6$ and 3×10^{-2} M CH_3OH; (E) 3×10^{-2} M CH_3OH; (F) saturated with $(C_6H_5)_2ICl$ (about 3×10^{-3} M).

indicates that a slow formation of the dimer radical cations is occurring. Methanol as a basic additive accelerates the decay (curve E). It also inhibits the slow formation of the dimer radical cations when added to the solution containing the salt (curve D). Both the yield and lifetime are appreciably decreased by the addition of the diphenyliodonium salt having nucleophilic Cl^-, $(C_6H_5)_2ICl$, suggesting that the monomer and dimer radical cations are neutralized with Cl^- (curve F).

The slow formation of the dimer radical cations in the presence of the salt can be explained by the oxidation of radical apecies such as $CH_2Cl\cdot$ and $C_6H_5\cdot$ having ionization potentials higher than that of monomer followed by exothermic charge transfer from the resulting cations to monomer, as proposed in an earlier paper.[13] Thus in the presence of the salt, the monomer radical cations are produced by slow and rapid formation processes subsequently resulting in those of the dimer radical cations.

$$CH_2Cl_2 \rightsquigarrow CH_2Cl_2^{+}\cdot + e^- \quad (2)$$

$$e^- + CH_2Cl_2 \rightarrow Cl^- + CH_2Cl\cdot \quad (3)$$

$$CH_2Cl_2^{+}\cdot + M \rightarrow CH_2Cl_2 + M^{+}\cdot \quad \text{(rapid formation)} \quad (4)$$

$$R\cdot + (C_6H_5)_2IPF_6 \rightarrow R^+ + PF_6^- + C_6H_5I + C_6H_5\cdot \quad (5)$$

$$R^+ + M \rightarrow R\cdot + M^{+}\cdot \quad \text{(slow formation)} \quad (6)$$

$$M^{+}\cdot + M \rightarrow D^{+}\cdot \quad (7)$$

where $M^{+}\cdot$ and $D^{+}\cdot$ denote the monomer and dimer radical cations, respectively, and R·, $CH_2Cl\cdot$, and/or $C_6H_5\cdot$ are produced by reactions 3 and 5.

Figure 8 shows the first- and second-order kinetic plots for the decay in the absorption band at 470 nm in the absence of additive, demonstrating that the decay obeys second-order kinetics rather than first-order kinetics. This means that the decay of the dimer radical cations is mainly due to the neutralization with Cl^-, the product of dissociative electron capture by the solvent (reaction 3). Therefore, the retarded decay of the dimer radical cations in the presence of the salt shown in Figure 7 is attributable to the stabilization toward the neutralization by the ion-pair formation with PF_6^-. The increase in the yield of the dimer radical cations at the end of the pulse suggests that

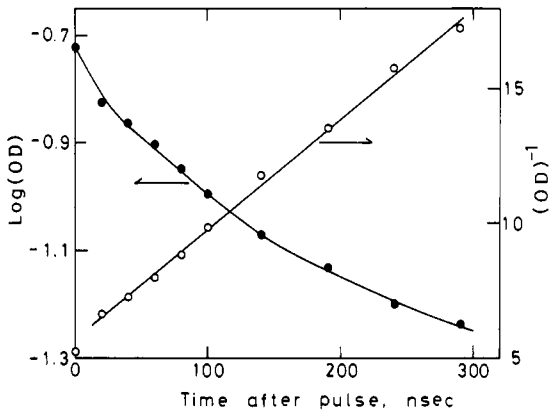

Figure 8. First- and second-order kinetic plots for the decay of absorption at 470 nm in the absence of additive.

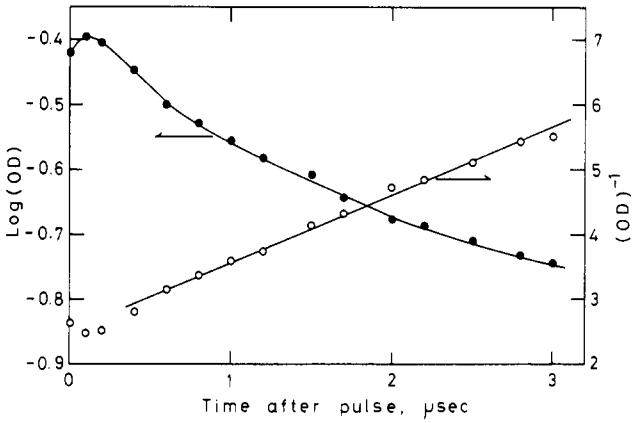

Figure 9. First- and second-order kinetic plots for the decay of absorption at 470 nm in the presence of 3×10^{-2} M $(C_6H_5)_2IPF_6$.

the monomer radical cations are also stabilized toward the neutralization with Cl^- and/or basic impurities when the salt is added.

Figures 9 and 10 show the decay kinetics for absorption at 470 nm in the solutions containing $(C_6H_5)_2IPF_6$ and $(C_6H_5)_2ICl$, respectively. Obedience to second-order kinetics in the system containing $(C_6H_5)_2IPF_6$ is recognized regardless of the retardation of the decay rate. On the other hand, the decay in the presence of $(C_6H_5)_2ICl$ is of first order rather than of second order, which is due to the neutralization with excess Cl^-. The first- and second-order kinetics were also tested for the solutions containing methanol. The decays fitted neither first- nor second-order kinetics, indicating that the neutralization with Cl^- and the reactions with methanol are occurring simultaneouly.[20]

The kinetic plots tested for the decay of absorption at 470 nm show that the decay of the dimer radical cations is mainly due to the neutralization with Cl^-. However, it should be noted that in the pulse radiolysis experiment the concentrations of the dimer radical cations and Cl^- are rather high and the decay due to the neutralization dominates. On the other hand, in the polymerization experiment with γ-rays at relatively low dose rates the decay due to the reactions with monomer and basic impurities is believed to be important. In practice, no polymer was obtained from the solutions containing $(C_6H_5)_2IPF_6$ after irradiation by the electron beams up to doses comparable to that of the polymerization experiment. The slopes of the second-order kinetic plots for the decay of absorption at 470 nm in the presence and absence of $(C_6H_5)_2IPF_6$ are 1.0×10^6 and 4.1×10^7 s^{-1}, respectively. The smaller value of the slope for the system containing the salt demonstrates the stabilization by the ion-pair formation with PF_6^-.

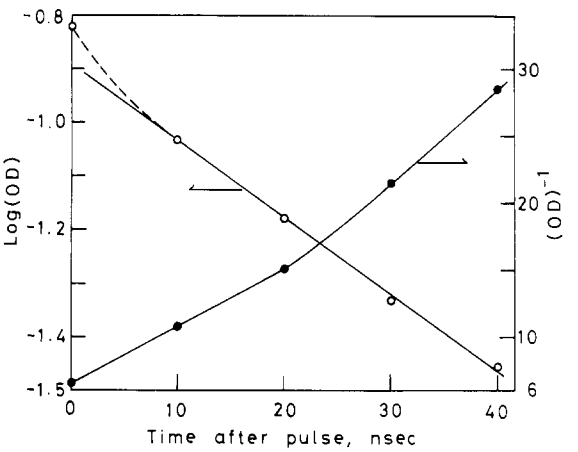

Figure 10. First- and second-order kinetic plots for the decay of absorption at 470 nm in the presence of saturated $(C_6H_5)_2ICl$ (about 3×10^{-3} M).

However, the slow formation of the dimer radical cations should also be responsible for the smaller value of the slope. Furthermore, it has been shown that the monomer radical cations are highly reactive with monomer to give the dimer radical cations, which react with Cl^- or a basic substance in preference to monomer. The low reactivity of the dimer radical cations with monomer is believed to be responsible for the high sensitivity of the radiation-induced cationic polymerization to basic impurites.

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Registry No. $(C_6H_5)_2IPF_6$, 58109-40-3; CH_3OH, 67-56-1; $(C_6H_5)_2ICl$, 1483-72-3; α-methylstyrene, 98-83-9.

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Spherical Macroions in Strong Fields†

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ABSTRACT: The steady-state response of a dilute salt solution of spherical macroions to strong electrical fields has been calculated on the basis of the nonlinear diffusion equations, the Navier–Stokes equation, and Poisson's equation. The electrophoretic mobility shows essentially no nonlinear response at the field strengths considered, but the effective charge and dipole moment, the latter proportional to the conductivity change, show a strongly nonlinear response. At moderate field strengths part of the ion atmosphere is stripped away, but at still larger fields the macroion traps counterions. A positively charged macroion together with its ion atmosphere then has a net negative charge. If the Debye length κ^{-1} and radius a are such that $\kappa a > 1$, as holds for the numerical illustrations, nonlinearity in the polarization or nonquadratic response of the effective charge sets in at field strengths that scale inversely with particle radius. The field strength can therefore be quite low compared to what is required for Wien effects in strong electrolyte solutions, where the required field scales as κ.

I. Introduction

A considerable amount of experimental and theoretical work has been done on nonlinear phenomena in simple electrolytes, especially concerning the Wien effects[1] (increasing conductivity with field strength). No comparable body of theory, or experiments designed to advance theory, seems to exist for macroions or polyelectrolytes. Strong electrical fields are often used for the orientation of anisotropic macroions, and it is sometimes found that molecules not believed to have a permanent moment behave as if they did.[2] So it may be that the polarization of the ion atmosphere is exhibiting a saturation. The main motivation for this work is the exploration of nonlinear effects in the polarization of the ion atmosphere. Incidental results are gathered on the electrophoretic velocity, on the apparent charge that arises from destruction of the ion atmosphere, and on the complex conductivity.

The problem is somewhat more difficult than the corresponding one for simple electrolytes. The electrostatic potentials are usually large compared to k_BT and essentially nothing can be linearized. Electrophoretic effects and convective transport of salt ions are large, and the Navier–Stokes equation is fully coupled with the diffusion equations for the salt ions. It has therefore seemed sensible to start the work with spheres rather than with anisotropic bodies, for which interesting experiments may be easier.

Except for one generalization of great interest but uncertain merit, our basic equations are those used for electrophoresis by Overbeek et al.[3] However, we have followed the notation and formulation of our previous work.[4] Advances in computers and numerical analysis have now brought those equations to the point of fairly routine solubility for linear problems involving spheres. See the work of O'Brien and White[5] on electrophoresis and DeLacey and White[6] on the complex conductivity. Nonlinear problems and the study of anisotropic bodies[7–9] have not yet reached that stage.

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The generalization we mentioned consists in allowance for a coefficient of sliding friction at the surface of the macroion. The velocity gradients near the surface of a macroion can be quite enormous by usual standards. Due to the force exerted on high charge densities by the applied electric field, the solvent is accelerated to the electrophoretic velocity over distances comparable to the Debye length. This length may of course be much smaller than the dimensions of the macroion, which would ordinarily characterize the length scale. Consequently one anticipates that the usual sticking boundary condition may be inadequate. (The suggestion has been made that electrophoretic mobilities may show nonlinear effects originating in breakup of the boundary layer at a few volts/cm.[10] Some scepticism may be warranted in regard to the explanation, but the observation is intriguing.) Our intent here is limited to a comparison between the effects of slippage on a macroion in an electric field, and the sedimentation of an uncharged object. The nature and characterization of slippage between a liquid and solid boundary have received some attention for simple systems,[11] but none that we know of for electrolyte solutions.

In outline our work is as follows. In section II the basic equations are reviewed. The only novelty here is the use of the Stokes "stream function", which considerably simplifies problems of "axisymmetric" flow.[12] There is no special advantage to it for linear problems, and indeed it cannot be used for some interesting linear problems involving rotation or shear. However, this work is restricted to a constant vector applied field, either electrical or centrifugal (or both if they are parallel), of arbitrary amplitude. The symmetry is sufficient that the flow must remain axisymmetric no matter how large the applied force. A preliminary discussion of boundary conditions is given for the purpose of relating the quantities of direct physical interest to the asymptotic behavior of the solutions. The quantities of direct physical interest are assumed to be restricted to the electrophoretic velocity, the apparent dipole moment, and perhaps the apparent charge of the macroion system. The dipole determines the conductivity increment. The theory is confined in all respects

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