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Counterion Diffusion in Bulk Ionomers. 1. Fluorescence Study of the Diffusion of Benzylammonium and *N,N*-Dimethylbenzylammonium in Polymethacrylates Carrying Sulfonic Acid Substituents

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ABSTRACT: The diffusion of benzylammonium (BAH^+) and dimethylbenzylammonium ($DBAH^+$) counterions from films of polymethacrylates with small numbers of partially neutralized sulfonic acid side chains into a pellet of a similar unneutralized polymer containing a fluorescence quencher was monitored by following the decreasing emission intensity. The diffusion coefficients, D, were compared with those of the unprotonated bases BA and DBA in polymers carrying no sulfonic acid groups. The D in the ionomers were much smaller, since the part of the counterions forming ion pairs with polymer-bound sulfonates makes a negligible contribution to the diffusion. $DBAH^+$ diffuses more than twice as fast as BAH^+ since ion pairs formed by the tertiary amine are more highly dissociated. The temperature dependence of D for DBA in poly(ethyl methacrylate) (PEMA) and poly(butyl methacrylate) (PBMA) followed the WLF equation, but that of $DBAH^+$ in the corresponding polymers carrying a small number of sulfonic acid groups was much steeper. This was attributed to the additional activation energy for the diffusion of the protonated bases due to the activation energy for the dissociation of the ion pairs. The degree of ion-pair dissociation inferred from the relative D value of $DBAH^+$ and DBA increased with increasing polarity of the polymer in the order PBMA < PEMA < poly(methyl methacrylate-*co*-methyl acrylate).

Introduction

Ionomers are nonpolar flexible-chain molecules carrying on a small portion of their monomer residues ionized chain substituents. When dissolved in nonpolar solvents, the chain-bound ions and their counterions form stable ion pairs which tend to associate with each other. In dilute solution this association is intramolecular and leads to chain contraction, but at higher concentrations intermolecular ion association is dominant, as reflected in a sharp increase in solution viscosity.[1] In bulk ionomers, the mutual attraction of ion pairs leads to the segregation of an ion-rich microphase as revealed by small-angle X-ray scattering, and this quasi-cross-linking has a profound effect on the rheological behavior of the material.[2,3]

In a previous report from this laboratory we described a study of the kinetics of counterion interchange when dilute solutions of two ionomers carrying different fluorescent counterions were mixed in a stopped-flow apparatus.[4] That work was based on the idea that nonradiative energy transfer will be very small as long as donor and acceptor fluorophores are associated with different macromolecules, but will become efficient when both kinds of counterions are located in the domain of the same polymer molecule. Thus, irradiation of the donor absorption band will lead to increasing acceptor emission as the counterion exchange proceeds. This interchange could, in principle, involve two mechanisms: In the first, the encounter of two ion pairs leads to an exchange of their partners. In the second, a free counterion attacks an ion pair, leading to the exchange. On the basis of the dependence of the first-order rate constant of the process on the ionomer concentration, we concluded that under our experimental conditions the two mechanisms made similar contributions to the counterion exchange.

The present study was designed to explore the nature of the counterion diffusion in bulk ionomers. Here it would be expected that counterions in polymer-bound ion pairs make a negligible contribution to the diffusion compared to free counterions. Specifically, we should expect for the observed diffusion coefficient D of the counterions

$$D = D_{\mathrm{free}}\alpha \qquad (1)$$

where D_{free} characterizes the diffusion of free counterions and α is the degree of dissociation of the ion pairs. In our experiments we determined diffusion coefficients of benzylammonium (BAH^+) and dimethylbenzylammonium ($DBAH^+$) in polymethacrylates carrying a small number of partially neutralized sulfonic acid groups and compared the D values with those for the same low concentrations of the unprotonated bases BA and DBA in polymethacrylates carrying no sulfonic acid groups as a function of temperature and the nature of the polymer matrix.

Experimental Section

Monomers. Methyl, ethyl, and butyl methacrylates (MMA, EMA, BMA) and methyl acrylate (MA) from Aldrich Chemical Co. were used as received. *n*-Propyl methacrylate (PMA) was made by transesterification of MMA with *n*-propanol in the presence of *p*-toluenesulfonic acid.[5] [(2-Acrylamido)propyl]-methanesulfonic acid (APMS) was obtained from Scientific Polymer Products. To prepare 4-(methacryloylamino)azobenzene (AAB–MA), methacryloyl chloride was added dropwise at 0 °C to a chloroform solution of equimolar 4-aminoazobenzene with sufficient triethylamine to take up the evolving HCl. After being stirred for 1 h at room temperature, the mixture was heated for 1 h under reflux, triethylamine hydrochloride was filtered off, and the mixture was shaken with aqueous sodium bicarbonate and water and dried with anhydrous sodium sulfate. The chloroform was evaporated, and the residue was recrystallized

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from ethanol-water (mp 158–159 °C). NMR and IR spectra agreed with the AAB-MA structure. The UV spectrum had λ_{max} 347 nm, ϵ_{347} 23 500 in methanol and λ_{max} 353 nm, ϵ_{353} 23 270 in dioxane. [(*N*-Dansylamino)ethyl]methacrylamide (DNS-MA), prepared as previously described,[6] had λ_{max} 335 nm, ϵ_{335} 4400 $L\cdot mol^{-1}\cdot cm^{-1}$ in dioxane.

Polymer Preparation. Dioxane solutions containing 25 wt % EMA, BMA, 1:1 EMA/BMA, or MMA/MA (60 wt % MMA) and 0.5 wt % AIBN were heated for 24 h to 60 °C and the polymer (conversion 60–70%) was precipitated into methanol or methanol–water. It was purified by three reprecipitations. Copolymers of DNS-MA with PMA or MMA/MA (60 wt % MMA) and AAB-MA with PMA or MMA/MA (60 wt % MMA) containing 5 mol % in the polymerizing mixture had conversions of 50%, 42%, 60% and 45%, respectively. They were precipitated five times from dioxane into methanol to ensure the absence of any chromophore not attached to the polymer. Copolymers of APMS with EMA, BMA, 1:1 EMA/BMA, or MMA/MA (60 wt % MMA) were prepared in 7:1 2-propanol–methanol containing diisobutylamine equimolar to APMS. After polymerization (conversions 45–55%), the solution was stirred with excess HCl in propanol to remove the amine from the polymer and precipitated into water or methanol–water acidified with 2 mL of concentrated HCl in 1800 mL. The copolymers were purified by two reprecipitations.

Polymer Characterization. The intrinsic viscosities of the EMA and BMA homopolymers were 0.33 and 0.54 dL/g, respectively, in butanone at 23 °C, corresponding to M_v of 136 000 and 403 000.[7] The MMA/MA copolymer was estimated, by comparison of the ratio of the ^{13}C peak heights for CO and the α-CH_3 in the copolymer and a MMA homopolymer, to contain 52% MMA residues. The copolymers containing AAB or DNS residues had compositions similar to the monomer mixture from which they were derived, assuming that the polymer-bound chromophores had the same extinction coefficients as the corresponding monomers. The sulfonic acid content of APMS copolymers was determined by titration of dioxane solutions with methanolic $NaOCH_3$ to the phenolphthalein end point. The APMS content of the copolymers was about half of that in the monomer mixture.

Preparation of Samples for Diffusion Measurements. Diffusion measurements of BAH^+ and $DBAH^+$ in APMS copolymers with various methacrylates were performed using a sandwich assembly consisting of (a) a top film containing the dansyl fluorophore used as an internal fluorescence standard, (b) a film of the APMS–methacrylate copolymers partially neutralized with BA or DBA, and (c) a pellet of the APMS–methacrylate copolymer containing the azobenzene fluorescence quencher. Films were obtained by solution casting on a Teflon sheet, allowed to dry slowly for 48 h, and vacuum-dried to constant weight. Film thicknesses of 0.20–0.25 mm were produced. The top film was a blend of the DNS-MA/PMA copolymer or DNS-MA/MMA/MA terpolymer with the polymethacrylate (no APMS residue) containing 2.9×10^{-4} mmol/g dansyl residues. The pellet was a blend of the APMS–methacrylate copolymer with the corresponding AAB-MA copolymer containing 0.042 mmol/g AAB residues. For diffusion measurements of the unprotonated bases BA and DBA in polymethacrylates carrying no APMS residues, the sandwich assembly had only one film, containing both the diffusing bases and the fluorescence standard.[8] The concentration of the diffusants in the ionomers was given by the APMS content and its degree of neutralization. For instance, in the EMA/BMA/APMS containing 2.7 mol % APMS residues 15% neutralized, the BA concentration was 0.33 wt %, that of DBA 0.42 wt %. The same weight percent concentrations were used in the polymethacrylates containing no APMS.

Pellets with a 16-mm diameter and a 4-mm thickness were molded under a pressure of 1200 kg/cm^2 for 5 min at $T_g + 50$ °C. Circles of 16-mm diameter were cut from the cast films and an assembly composed of a paper, the pellet, the central and top films (or one film only for experiments involving unprotonated bases), and a Teflon spacer was exposed to a pressure of 800 kg/cm^2 for 3 min at $T_g + 40$ °C. After slow cooling, the assembly was kept under pressure for 1 h before removal from the press.

Fluorescence Measurements. Emission intensities in the reflectance mode (30°/60°) were recorded on a Perkin-Elmer MPF 44B fluorescence spectrometer at room temperature using Perkin-Elmer solid sample accessory 063-0502. The sandwich assemblies were heated in the cavity of a thermostated steel block under a pressure of 5 kg/cm^2 to avoid specimen distortion and were removed at various times for fluorescence measurements. The dansyl chromophore in the top film was excited at 350 nm, and its emission was recorded at 465 nm.[9] The BA, DBA, BAH^+, and $DBAH^+$ diffusants were excited at 260 nm, and their emission intensities were measured at 285 nm. The concentration of the diffusant was kept below a value corresponding to an original optical density of 0.16 for the film, so as to minimize the internal filter effect.

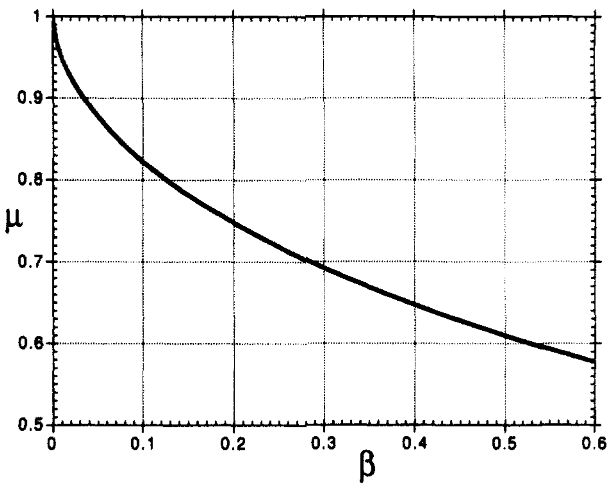

Figure 1. Relation between μ, the fraction of diffusant remaining in the film, and $\beta = Dt/x^2$.

Results and Discussion

Whereas a good deal of work has been reported on the diffusion of various molecular species through polymers,[10] we are unaware of any previous study of the diffusion of counterions through bulk ionomers. In the present study the diffusion of fluorescent species was followed by the change in the reflectance fluorescence of diffusants (relative to the dansyl emission intensity used as an internal standard) as they passed from a film into a pellet containing a similar polymer with a fluorescence quencher. With the emission intensity proportional to the exciting radiation absorbed in a film with an initial optical density A_0, the fraction of the diffusant, μ, remaining in the film is related to the ratio I/I_0 by which the emission intensity has decreased by

$$\frac{I}{I_0} = \frac{1 - \exp(-2.3\mu A_0)}{1 - \exp(-2.3A_0)} \qquad (2)$$

Also, for the diffusion of a solute from a film of thickness x into a pellet of thickness y, it can be shown (see Appendix) that at time t

$$\mu = \gamma\left\{1 + 2\sum_{n=1}^{\infty} \exp[-(\pi n\gamma)^2\beta]\left[\frac{\sin(\pi n\gamma)}{\pi n\gamma}\right]^2\right\} \qquad (3)$$

where $\gamma = x/(x + y)$ and $\beta = Dt/x^2$. For $\gamma < 0.1$ and $\mu > 0.2$, the dependence of μ on γ is negligible. A plot of μ as a function of β under these conditions is shown in Figure 1. After use of Figure 1 to obtain the β corresponding to experimental μ values, a plot of βx^2 against t yields D as the slope.

Comparison of the Diffusion Coefficients of Benzylammonium and Dimethylbenzylammonium Counterions. The diffusion of the fluorescent species was followed in terpolymers containing an equal number of EMA and BMA residues and a variable content of APMS

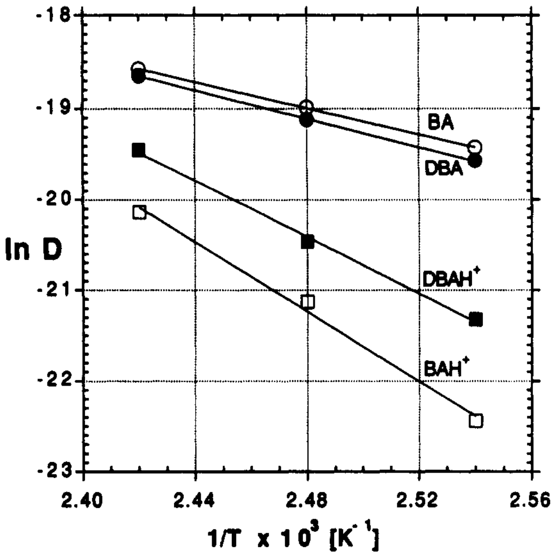

Figure 2. Diffusion coefficients of BA and DBA in the 1:1 copolymer of ethyl and butyl methacrylate and of the counterions BAH^+ and $DBAH^+$ in the terpolymer EMA/BMA/APMS containing 2.7 mol % APMS, neutralized 15%.

Table I
Diffusion of Benzylammonium and *N,N*-Dimethylbenzylammonium in Terpolymers of APMS with 1:1 Ethyl and Butyl Methacrylate and the Unprotonated Bases in the EMA/BMA Copolymer

diffusant	mol % APMS in polymer	% neutralzn of APMS	temp (°C)	$10^{10}D$ (cm²/s)
BAH^+	2.7	15	120	1.8
	2.7	15	130	6.7
	2.7	15	140	18
BA	0	0	120	37
	0	0	130	57
	0	0	140	86
$DBAH^+$	1.7	23	120	8.1
	1.7	23	130	15
	1.7	23	140	44
	2.7	15	120	5.5
	2.7	15	130	13
	2.7	15	140	36
	4.3	9.5	140	15
DBA	0	0	120	32
	0	0	130	50
	0	0	140	80

partially neutralized with BA and DBA and also in EMA/BMA copolymers containing BA or DBA. An equimolar EMA/BMA copolymer may be assumed to have a glass transition temperature similar to that of poly(*n*-propyl methacrylate), which has been reported as 35 °C.[11] The small content of neutralized and unneutralized APMS residues would be expected to lead only to a minor increase of T_g.[12]

Table I lists the *D* values determined for BA and DBA in the EMA/BMA copolymer and the BAH^+ and $DBAH^+$ counterions in the EMA/BMA/APMS terpolymers. As shown in Table I and Figure 2, the *D* values for the unprotonated bases are very similar, with the mobility of the less bulky BA larger. The protonated bases in the ionomer diffuse much more slowly. For instance, in the ionomer containing 2.7 mol % APMS, BAH^+ is retarded at 120 °C by a factor of 20, whereas the retardation of $DBAH^+$ is only by a factor of 6. This difference may be accounted for by the larger dissociation of ion pairs containing the tertiary amine; the larger fraction of $DBAH^+$ free counterions causes this bulkier species to diffuse faster. Also, since ion-pair dissociation would be expected to be reduced by an excess of unneutralized sulfonic acid groups, it is not surprising that in ionomers containing 0.4 ion pairs for 100 monomer residues the diffusion coefficient of $DBAH^+$ at 140 °C decreases as the unneutralized AMPS content is increased.

Table II
Diffusion of *N,N*-Dimethylbenzylammonium in the MMA/MA/APMS Terpolymer and of the Unprotonated Base in MMA/MA

diffusant	mol % APMS in polymer	% neutralzn of APMS	temp (°C)	$10^{10}D$ (cm²/s)
$DBAH^+$	2.0	15	110	0.68
	2.0	15	120	2.0
	2.0	15	130	6.0
	2.0	15	140	15
DBA	0	0	110	3.0
	0	0	120	7.4
	0	0	130	15
	0	0	140	28

Table III
Diffusion of *N,N*-Dimethylbenzylammonium in EMA/APMS Copolymer and the Unprotonated Base in Poly(ethyl methacrylate)

diffusant	mol % APMS in polymer	% neutralzn of APMS	temp (°C)	$10^{10}D^a$ (cm²/s)
$DBAH^+$	2.6	15	125	1.6
	2.6	15	135	5.6
	2.6	15	145	15
	2.6	15	155	29
	2.6	15	165	43
DBA	0	0	105	0.99 (0.97)
	0	0	115	2.7 (2.9)
	0	0	125	7.9 (7.1)
	0	0	135	13 (15)
	0	0	145	31 (29)
	0	0	155	53 (50)
	0	0	165	75 (80)

[a] The values in parentheses were computed from eq 3 using parameters given in the text.

Another significant observation is the much steeper temperature dependence of *D* values characterizing the BAH^+ and $DBAH^+$ counterions as compared to that of the unprotonated bases in the copolymer free of sulfonic acid groups. In the case of the counterions, an increasing temperature not only increases the mobility of the free counterions but also increases the fraction of counterions which are dissociated and contribute to the diffusion. In the temperature range of 120–140 °C, the apparent activation energy ΔE_0^* for the diffusion of BA and BAH^+ is 58 and 160 kJ/mol, respectively, and for DBA and $DBAH^+$ 63 and 130 KJ/mol, respectively. The difference between the ΔE_0^* for a protonated and unprotonated base may be ascribed to the activation energy for the dissociation of the ion pair, and it is striking that this difference, 102 kJ/mol for the benzylammonium sulfonate, is much higher than the 67 kJ/mol for dimethylbenzylammonium, which would be expected to form a less stable ion pair.

Dependence on the Polarity of the Polymer Matrix. Since the stability of ion pairs should decrease with increasing polarity of the medium, it was of interest to study the *D* values in ionomers containing varying concentrations of polar ester groups. We determined, therefore, *D* for the $DBAH^+$ counterion in EMA/APMS, BMA/APMS, and the MMA/MA/APMS terpolymer and compared the behavior of the $DBAH^+$ in the ionomers with that of the unprotonated DBA in corresponding polymers containing no sulfonic acids.

The results are given in Tables II–IV. Plots of ln *D* against $1/T$ in the MMA/MA copolymer, poly(ethyl

Table IV
Diffusion of *N,N*-Dimethylbenzylammonium in BMA/APMS Copolymer and the Unprotonated Base in Poly(butyl methacrylate)

diffusant	mol % APMS in polymer	% neutralzn of APMS	temp (°C)	$10^{10}D^a$ (cm^2/s)
DBAH$^+$	2.5	16	112	1.6
	2.5	16	122	8.3
	2.5	16	132	18
	2.5	16	142	58
DBA	0	0	62	1.2 (1.4)
	0	0	72	4.1 (3.5)
	0	0	82	7.6 (7.6)
	0	0	92	13 (15)
	0	0	102	31 (27)
	0	0	112	46 (46)
	0	0	122	68 (74)
	0	0	132	120 (112)
	0	0	142	160 (164)

[a] The values in parentheses were computed from eq 3 using parameters given in the text.

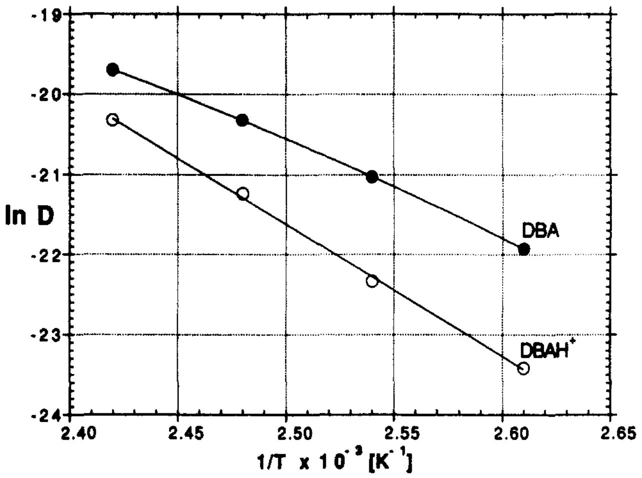

Figure 3. Diffusion coefficients of DBA in the MMA/MA copolymer and of the DBAH$^+$ counterion in the MMA/MA/APMS terpolymer containing 2.0 mol % APMS, neutralized 15%.

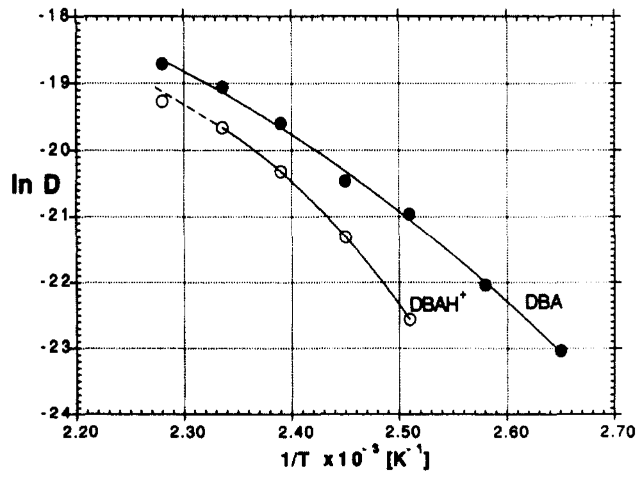

Figure 4. Diffusion coefficients of DBA in poly(ethyl methacrylate) and of DBAH$^+$ counterions in EMA/APMS containing 2.6 mol % APMS, neutralized 15%.

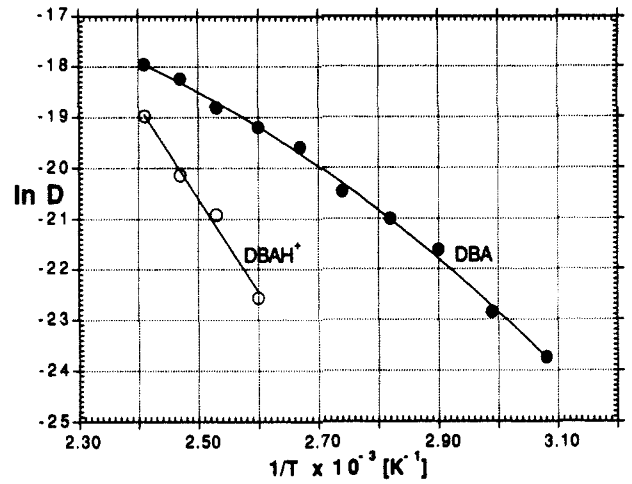

Figure 5. Diffusion coefficients of DBA in poly(butyl methacrylate and of DBAH$^+$ counterions in BMA/AMPS containing 2.5 mol % APMS, neutralized 16%.

methacrylate), and poly(butyl methacrylate) (PBMA) as well as in the corresponding polymers containing APMS are plotted in Figures 3–5. It may be seen that the plots for the diffusion of the unprotonated base in PEMA and PBMA are curved, and we found that they follow the WLF equation, as observed by others who studied the diffusion of probes through polymers.[10,13] A least-squares fit of the experimental data to the formulation used by Xia et al.[10c]

$$\log [D(T)/T] = \log [D(T_g)/T_g] + BC_1^g(T - T_g)/(C_2^g + T - T_g) \quad (4)$$

where C_1^g and C_2^g are the WLF parameters and the factor B depends on the dimensions of the diffusing particle, yielded for PEMA (T_g = 338 K[12]), $D(T_g) = 2.03 \times 10^{-14}$ cm^2/s, $BC_1^g = 8.31$, $C_2^g = 51.5$ K; and for PBMA (T_g = 293 K[12]) $D(T_g) = 2.10 \times 10^{-13}$ cm^2/s, $BC_1^g = 7.59$, $C_2^g = 73.4$ K. Tables III and IV show that the experimental data closely fit eq 4. The temperature dependence of the DBAH$^+$ diffusion coefficient in APMS copolymers was again much steeper than that of the DBA in polymers containing no sulfonic acid groups, the difference in ΔE_0^* in the temperature range 120–140 °C being 101 kJ/mol between BMA/APMS and PBMA, 60 kJ/mol between EMA/APMS and PEMA, and 47 kJ/mol between MMA/MA/APMS and MMA/MA. It can be seen that the additional activation energy required for the dissociation of the DBAH$^+$ sulfonate ion pair decreases sharply with an increasing polarity of the polymer matrix.

If we assume that the mobility of the *free* counterions BAH$^+$ and DBAH$^+$ is the same as that of the unprotonated species, then the ratio of the D values of a base in an ionomer and a similar polymer containing no AMPS should yield the degree of ion-pair dissociation α. The temperature dependence of α in ionomers of varying polarity computed in this manner, as represented in Figure 6, exhibits the expected increase in ion-pair dissociation with an increasing polarity of the polymer matrix.

Concluding Remarks. Our results demonstrate that the diffusion of counterions in bulk ionomers depends on the dissociation of the ion pairs. Many years ago, Fuoss[14] derived, on the basis of electrostatic considerations, the association constant K_A for ion-pair formation as

$$K_A = (4\pi N_A/3000)a^3 \exp(e^2/a\kappa kT) \quad (5)$$

where N_A is Avogadro's number, a is the distance between the centers of ions in an ion pair, e is the charge of an electron, κ is the dielectric constant, and kT has the usual significance. Later, it was found that the extent of ion association cannot be fully accounted for by electrostatics, since it is also sensitive to specific solvent effects.[15] For instance, the experimental value for the dissociation constant for benzylammonium chloride in acetonitrile at 25 °C was 5.3×10^{-5}, much smaller than the value of 0.089 predicted by the Fuoss relation.[15]

Whereas the present study dealt with ionomers containing bulky organic counterions, the diffusion of alkali

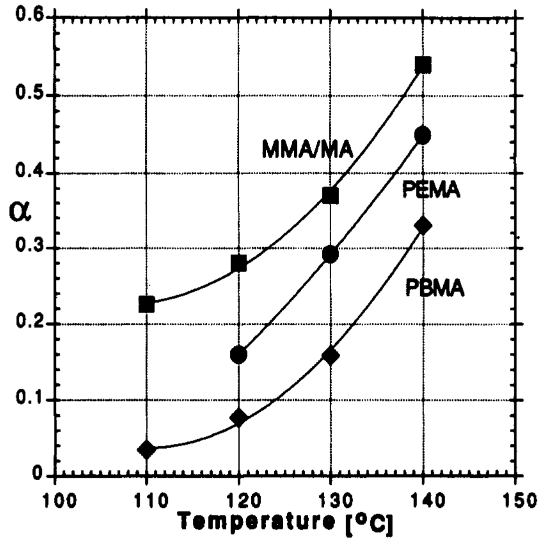

Figure 6. Degree of dissociation, α, of DBAH$^+$ sulfonate ion pairs in BMA/APMS, EMA/APMS, and MMA/MA/APMS. (Smoothed curves drawn through the experimental D values in Figures 3–5 were used to estimate α.)

counterions would be of much greater interest, particularly since it might reflect the influence of ion-pair aggregation. We have found that 3-acetamido-2-naphthoic acid has its fluorescence quenched on neutralization, and we plan to exploit this phenomenon in a study of alkali ion counterion diffusion in ionomers based on copolymers of methacrylates with 3-(methacrylamido)-2-naphthoic acid using techniques similar to those employed in this investigation.

Appendix

The dependence of the mass fraction, μ, of the diffusant remaining in a film of thickness x attached to a pellet of thickness y as a function of time t is obtained as a solution of a one-dimensional diffusion equation:

$$\frac{\partial C(s,t)}{\partial t} = D\frac{\partial^2 C(s,t)}{\partial s^2} \tag{6a}$$

where $C(s,t)$ is the concentration of the diffusant and s is the distance from the surface of the film, with the initial and boundary conditions:

$$C(s,0) = C_0 U(s) U(x-s) \tag{6b}$$

$$\left\{\begin{aligned} &\left.\frac{\partial C(s,t)}{\partial s}\right|_{s=0} = 0 \\ &\left.\frac{\partial c(s,t)}{\partial s}\right|_{s=x+y} = 0 \end{aligned}\right. \tag{6c}$$

where $U(s)$ is the step function.[16] The initial condition (5b) reflects the uniform distribution of the diffusant in the film at $t = 0$.

Using a technique similar to those presented in ref 16, we can represent the solution for the concentration, which will satisfy boundary conditions (6c) in the form of the cosine Fourier series:[17]

$$C(s,t) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \exp\left[-\frac{Dt}{(x+y)^2}(\pi n)^2\right] \cos\left(\frac{\pi n s}{x+y}\right) \tag{7}$$

where the coefficients a_n have to be determined by the initial condition (6b). Omitting intermediate calculations and introducing the dimensionless time parameters $\beta = Dt/x^2$ and $\gamma = x/(x+y)$, we obtain a solution satisfying initial and boundary conditions:

$$C(s,\beta) = \gamma C_0 \left\{1 + 2\sum_{n=1}^{\infty} \exp[-(\pi n\gamma)^2\beta] \frac{\sin(\pi n\gamma)}{\pi n\gamma} \times \cos\left(\pi n\gamma\frac{s}{x}\right)\right\} \tag{8a}$$

Integrating eq 8a over the thickness of the film, we obtain the fraction of the diffusant μ:

$$\mu = \frac{\int_0^x C(s,\beta)\,\mathrm{d}s}{C_0 x} = \gamma\left\{1 + 2\sum_{n=1}^{\infty} \exp[-(\pi n\gamma)^2\beta] \times \left[\frac{\sin(\pi n\gamma)}{\pi n\gamma}\right]^2\right\} \tag{8b}$$

In the limiting case of a diffusion from a film into an infinite medium ($y \gg x$, $\gamma \rightarrow 0$) eqs 8a and 8b become the well-known expressions

$$C(s,\beta) = \frac{C_0}{2}\left[\mathrm{erf}\left(\frac{x-s}{2x\sqrt{\beta}}\right) + \mathrm{erf}\left(\frac{x+s}{2x\sqrt{\beta}}\right)\right] \tag{8c}$$

$$\mu = \mathrm{erf}\left(\frac{1}{\sqrt{\beta}}\right) + \left[\exp\left(-\frac{1}{\beta}\right) - 1\right]\sqrt{\frac{\beta}{\pi}} \tag{8d}$$

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(8) When BAH$^+$ and DBAH$^+$ diffusion was studied, the dansyl chromophore was placed in a separate phase into which the cation could not diffuse. However, the uncharged BA and DBA could have diffused into the dansyl-labeled film, complicating the data analysis and it was, therefore, preferable to have the dansyl label in the film containing the diffusants.

(9) It should be noted that the emission maximum of the dansyl chromophore in the polymer (465 nm) was strongly blue-shifted from the maximum observed in mobile organic solvents (for the polymer in ethyl methacrylate this maximum was at 495 nm). This shift is due to the suppression of the formation of twisted intramolecular charge-transfer (TICT) state in the rigid medium (Kosower; et al. *J. Am. Chem. Soc.* **1975**, *97*, 2167).

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