Molecular Structure of Ion Pairs from Electric Dipole Moments. III. Substituted Anilinium Chlorides and *p*-Toluenesulfonates in Octanoic Acid[1]

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Abstract: In spite of the hydrogen-bonded solvent structure of octanoic acid, dielectric measurements on dilute solutions of control substances show that dipole moments of useful accuracy can be obtained. The following dipole moments (μ) were obtained for substituted anilinium chloride and *p*-toluenesulfonate (Ts) ion pairs (substituent, anion, μ (D)); *N*-Me, Cl, 6.25; *N*-Me$_2$, Cl, 7.02; *N*-Me$_3$, Cl, 8.70; 4-F, Ts, 5.55; *N*-Me, Ts, 6.26; *N*-Me$_2$, Ts, 7.27; *N*-Me$_2$-4-Br, Ts, 6.85; *N*-Me$_3$, Ts, 6.85. The data for ion pairs with hydrogen-bonding cations are consistent with a "corner structure" in which cation and anion are bound by a single hydrogen bond, with relatively free rotation about the N-H- - -X hydrogen-bond axis. Analysis by the method of model compounds indicates that in the Ts ion pairs, the angle C$_1$-S- - -N is nearly tetrahedral in *N*-Me, Ts and *N*-Me$_2$, Ts, but near 128° in *N*-Me$_3$, Ts. (C$_1$ is the α-phenyl carbon atom.) Analysis by Böttcher's model indicates that electrostatic forces favor C$_1$-S- - -N angles of 100-106° in all cases. At the given concentrations (0.001-0.01 F), association to ion pair dimers was slight except for *N*-Me$_3$, Cl. Dissociation to un-ionized acid and base ($BH^+X^- \rightleftarrows B + HX$), when possible, amounted only to 1-6%.

Salts formed from the reaction of strong acids (HX) with strong bases (B) exist in dilute solution in solvents of low dielectric constant largely in the form of hydrogen-bonded ion pairs.[2] The structure of such ion pairs is of interest because it has a marked effect on the chemical properties and the acidity of the solutions. In previous papers[3,4] we showed that electric dipole moments can give quantitative information about the structure of ion pairs, especially about the distance between the ionic electrical centers and the sites and mode of attachment. In this paper we report electric dipole moments for a series of *N*-methyl-substituted anilinium *p*-toluenesulfonates and chlorides. Analysis of these dipole moments on the basis of approximate models leads to consistent conclusions concerning the structure of the ion pairs.

As in the previous work,[3,4] dielectric measurements were made on dilute (0.001-0.01) solutions in octanoic acid. This solvent is suitable because of its low dielectric constant (ϵ 2.46 at 25 °C), coupled with a relatively good ability to dissolve electrolytes. The conductivity of the solutions was uniformly low ($\sim 10^{-9}\ \Omega^{-1}$ cm), showing that free-ion concentrations are negligible both stoichiometrically and in affecting the measured solution capacitance.[5,6] Newly measured equilibrium constants for the dissociation of ion pairs to un-ionized acid and base in octanoic acid (eq 1) were small enough, in agreement with previously established patterns,[7-9] so that this potential complication could also be neglected.

$$BH^+X^- \overset{K_1}{\rightleftharpoons} B + HX \tag{1}$$

On the other hand, the association of ion pairs to ion pair dimers (eq 2) was not entirely negligible, but was too slight to have a serious effect on the accuracy of ion pair dipole moments.

$$2BH^+X^- \overset{K_2}{\rightleftharpoons} (BH^+X^-)_2 \tag{2}$$

Effect of Hydrogen-Bonded Solvent Structure. Octanoic acid owes its relatively good solvent power for electrolytes to the presence in the molecules of polar carboxyl groups. However, the contribution of these groups to the polarization of the pure solvent is greatly reduced by the formation of nonpolar dimers. When a solute is introduced, the dimer structure may be disturbed, with a resultant change in the polarization of the *solvent* in the solution. We shall call this phenomenon a solute-induced medium effect. If it were important, then the measured molar dielectric increment ($d\epsilon/dc_2$) for the solute would be a composite quantity, comprising both the polarization of the solute and the solute-induced medium effect. Although the latter effect is important in acetic acid,[10] it appears to be unimportant in octanoic acid.

The relevant data are listed in Table I. Here, *apparent* dipole moments (μ_{app}) for a series of solutes in octanoic acid, obtained by applying Onsager's theory[11,12] to experimental measurements of $d\epsilon/dc_2$, are compared with "true" molecular dipole moments (μ) in the gas phase or in benzene solution. If solute-induced medium effects were important, the two sets of values would be distinctly different.[10] In fact, the two sets are in very reasonable agreement over a wide range of polarity, even for LiCl ion pairs. Experience with acetic acid[10] suggests that the agreement is especially significant for the nonpolar solutes, CCl$_4$ and C$_6$H$_6$. For these solutes, μ_{app}^2 is -0.15 and $+0.20$, respectively (Table I), which is close enough to zero for the present purpose.

Dipole Moments of Ion Pairs. The electrolytes for which data were obtained are listed in Table II. We were especially interested in the effect of the number of N-H hydrogen atoms on ion pair structure and therefore set out to study the entire series of *N*-methyl-substituted anilinium salts. Unfortunately, anilinium *p*-toluenesulfonate and its 4-Br and 4-Cl substituted derivatives are quite insoluble in octanoic acid. Fortunately, the 4-F substituted derivative is just soluble enough for study.

In most cases, ϵ varied linearly with c_2, and the molar dielectric increment $S_2 = d\epsilon/dc_2$ could be obtained without difficulty. When slight curvature was found, it was negative and could be ascribed to the formation of nonpolar ion-pair dimers.[2,13] The data were actually fitted to the equation, $\epsilon = \epsilon_0 + S_2\alpha c_2$, where α is the ion-pair fraction, i.e., $(1 - \alpha)/\alpha^2 c_2 = K_2$; see eq 2. This treatment assumes that the molar dielectric increment S' for the ion-pair dimers is zero, and the values obtained for K_2 (Table II) thus are semiquantitative at best. In particular, if $S' = 2S_2$, one would fail entirely to detect ion pair dimer formation.[14] In fact, most of the values obtained for K_2 are quite small. The relatively high value obtained for the quaternary ammonium

Table I. Apparent Dipole Moments in Octanoic Acid Compared with Dipole Moments in Gas Phase or Benzene

Substrate	μ_{app}, D (HOct)[a]	μ, D (G or B)[b]
CCl_4	0.39[a]	0.00 (G); <0.1 (B)
C_6H_6	j0.45[a,c]	0.00 (G); <0.1 (CCl_4, H_x)
C_6H_5Cl	1.69[a]	1.72 (G); 1.57 (B)
C_6H_5CN	4.17[a]	4.14 (G); 3.93 (B)
LiCl	6.79[d]	7.12 (G)[e]

[a] Unpublished results obtained by Dr. Stephen E. Gould in this laboratory. [b] Based on A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, Calif., 1963. [c] $j = (-1)^{1/2}$; i.e., $\mu_{app}^2 = -0.20$. [d] Reference 3. [e] A. J. Hebert, F. J. Lovas, C. A. Melendres, C. D. Hollowell, T. L. Story, Jr., and K. Street, Jr., *J. Chem. Phys.*, **48**, 2824 (1969).

Table II. Molar Dielectric Increments and Other Properties for Ion Pairs in Octanoic Acid at 25 °C

Substituents in cation	Anion	S_2, l. mol^{-1}	K_2,[a] l. mol^{-1}	10^6K_1,[b] mol l.$^{-1}$	V_2,[c] ml mol^{-1}	R_2,[d] ml mol^{-1}
4-F	Ts^-	3.6	3	(2.7)	211	73.0
N-Me	Cl^-	4.6	5	(3.4)	126	45.1
N-Me	Ts^-	4.6	<1	(1.7)	222	77.8
N-Me_2	Cl^-	5.8	<1	2.4	142	49.7
N-Me_2	Ts^-	6.2	<1	1.1	238	82.4
N-Me_2, 4-Br	Ts^-	5.5	2	(6.7)	255	90.0
N-Me_3	Cl^-	8.9	35		158	54.2
N-Me_3	Ts^-	5.5	<1		254	86.9

[a] Equation 2; for method of calculation, see text. [b] Equation 1; values in parentheses are estimated by linear free energy relationships and data reported in ref 7 and 9. [c] V_2 was measured for N-Me_2, Ts^- in octanoic acid. ΔV_2 = 16 ml for each Me substituent, 5 ml for 4-F, 17 ml for 4-Br, −96 ml for Cl^- instead of Ts^-. The latter increment was measured directly by Lydia E. Mayer in acetic acid. [d] Based on measurements by Charles D. Brown and Lydia E. Mayer in acetic acid, and group refractions reported by A. I. Vogel, *J. Chem. Soc.*, 607–674 (1948).

Table III. Dipole Moment and Structure of Substituted Anilinium *p*-Toluenesulfonates and Chlorides

Substituents in cation	Anion	μ, D	Θ, deg (Figure 1)[a]	Böttcher's model[b]		
				Θ, deg	R, Å	W, kcal/mol
N-Me	Cl^-	6.25			3.53	−125.9
N-Me_2	Cl^-	7.02			3.67	−119.8
N-Me_3	Cl^-	8.70			3.81[c]	−110.0
					3.85[d]	−110.2
4-F	Ts^-	5.55				
H	Ts^-	6.05[e]		100	3.58	−134.5
N-Me	Ts^-	6.26	114.5	100	3.71	−129.5
N-Me_2	Ts^-	7.27	108.8	104	3.94	−120.4
N-Me_2, 4-Br	Ts^-	6.85	108.8[f]			
N-Me_3	Ts^-	6.85	128.1	106	3.95	−119.8

[a] $\mu_+ + \mu_{q,\alpha}$ is approximated by μ for the chloride ion pair. [b] Parameters used: $10^{24}\alpha_+/cm^3$, 14.00 (N-Me), 15.82 (N-Me_2), 17.60 (N-Me_3), 12.20 (H); $10^{24}\alpha_-/cm^3$, 3.88 (Cl^-), 5.80 (at electrical center of Ts^-) +11.04 (4.58 Å from electrical center on axis of Ts^-). In computing μ_+, we assumed free rotation about the N–H- - -O hydrogen bond and the following bond dipole moments: N-H, 1.3 D; N-CH_3, 0.62 D; N-C_6H_5, 0.2 D. In each case, the vector bond moment points from N to the substituent. Thus in the ion pairs, μ_+ = 0.59 D for N-Me, 0.68 D for N-Me_2, and 0.37 D for H. μ_+ = 0.0 D for N-Me_3^+, Ts^-, and either 0.0 D or 0.42 D for N-Me_3^+, Cl^-. μ_- = 0 for Cl^- and 5.2 D for Ts^-, along the axis in the direction from O_3S to C. [c] μ_+ = 0.0 D. [d] μ_+ = 0.42 D. [e] Predicted from μ for 4-F, Ts^- assuming free rotation about the N–H- - -O bond axis. [f] Assuming free rotation about the N–H···O bond axis.

chloride is in agreement with precedent.[14]

The dissociation of the ion pairs according to eq 1 ranged from 1 to 6% and could be neglected. Values of the equilibrium constant K_1 are included in Table II. The table also lists apparent molar volumes (V_2) and refractions (R_2) for the ion pairs. Although many of the values are reasonable estimates only, they are adequate for the calculation of apparent dipole moments. All told, the accuracy of the molar dielectric increments S_2 is about ±0.2 and that of the derived values of μ_{app} accordingly is about ±2%.

In the calculation of μ from the data in Table II, we used a modification of Onsager's original equation,[11] suggested by Kirkwood,[15] and described as method A in previous work.[12] In this modification, the effect of the reaction field is estimated on the assumption that the polarizability of the cavity occupied by the solute dipole is the same as that of the bulk solution. In practice, this model gives good results for substances of known dipole moment (μ_{app} in Table I, and ref 12). It is particularly appropriate for ion pairs because it obviates the need to estimate the real molar volume of the ion pairs, that is, to correct the apparent molar volume for electrostriction of the solvent.[16] In octanoic acid, the effect is large. For instance, Eustace[17] estimates −52 ml mol^{-1} for the electrostriction of octanoic acid by dimethylbenzylammonium octanoate ion pairs.

Dipole moments calculated in this way from the present data are listed in Table III.

Analysis of Dipole Moments. Method of Model Compounds. In this section we shall compare the dipole moments of the chloride and *p*-toluenesulfonate ion pairs in order to deduce an approximate interionic structure for the latter. The approach to be used has been described in part I.[3]

For ion pairs consisting of noncentric ions, it is convenient to represent the dipole moment according to (3),

$$\mu = \mu_{q,\alpha} + \mu_+ + \mu_- \tag{3}$$

where $\mu_{q,\alpha}$ is a vector sum consisting of the vector $q\mathbf{r}$ due to the ionic charges (r is the displacement from the electrical center of the anion to that of the cation)[18] plus induced moments resulting from the mutual polarization of the ions. In the first approximation, the electrical centers of cation and anion coincide with the centroids of formal positive and formal negative charge, respectively.[3] $\mu_{q,\alpha}$ tends to be parallel to r because the vector $q\mathbf{r}$ is relatively large and the contributing induced moments, which are smaller, tend to be antiparallel. Thus, in first approximation, $\mu_{q,\alpha}$ is directed from Cl^- to N^+ in the anilinium chloride ion pairs, and from the center of the triangle defined by the SO_3 oxygen atoms to N^+ in the Ts^- ion pairs.

μ_+ and μ_- are dipole vectors assignable to cation and anion whose values can be estimated from dipole moments of uncharged model compounds.[3] In the present case, μ_+ is relatively small (Table III, footnote b). μ_- is zero for Cl^-. For Ts^-, μ_- has the large value of 5.2 D (estimated from μ for *p*-toluenesulfonyl chloride) and is directed from O_3S to C_1 along the ionic axis.[18]

For definiteness, consider the model structures for BH^+Ts^- ion pairs shown in Figure 1. In the axial model (c), $\mu_{q,\alpha}$ and μ_- are antiparallel so that the overall dipole moment is relatively small; in the corner model (a) and edge model (b), assuming tetrahedral C_1-S···HB^+ directions as shown, the angle between $\mu_{q,\alpha}$ and μ_- will be slightly greater than the complement of the tetrahedral angle.

In previous work on K^+Ts we found that $\mu_{K^+Ts^-}$ is much smaller than μ for either K^+Cl^- or K^+Br^-, the difference $\mu_{K^+X^-} - \mu_{K^+Ts^-}$ being 5.5 D for X = Cl and 5.6 D for X = Br.[3] Recalling that μ_- = 5.2 D, the results suggested an axial structure for K^+Ts^- such that $\mu_{q,\alpha} \approx \mu$ for KCl. In the present case, by analogy, one would expect that for an axial structure (Figure 1c), $\mu_{BH^+Cl^-} - \mu_{BH^+Ts^-} \approx 5\text{-}6$ D, whereas in fact the differences are −0.01 D for *N*-Me, −0.25 D for *N*-Me_2, and 1.85 D for *N*-Me_3 (Table III). It seems safe to conclude that the axial structure represents at most a minor subspecies. On the other hand, either the corner structure (Figure 1a) or the edge structure (Figure 1b) can represent the majority of the ion pairs. The dipole moments cannot prove this, but the following calculation is instructive. We shall assume again that $\mu_{BH^+Ts^-} = \mu_{BH^+Cl^-} + \mu_-$, that the direction of $\mu_{BH^+Cl^-}$ is that of $\mu_{q,\alpha}$, and that $\mu_- = 5.2$ D. On substituting experimental results from Table III, we can thus estimate the angle between $\mu_{q,\alpha}$ and μ_-. The complement of this angle, which will be denoted by Θ, should be a semiquantitative index of the C_1-S- - -HB^+ angle in the ion pair. (See Figure 1.)

Results obtained for Θ on this basis are listed in Table III. For *N*-methyl and *N*-dimethylanilinium Θ is close to the tetrahedral angle, indicating that structures resembling the corner structure or (less probably, as will be shown) the edge structure of Figure 1 represent the majority of the ion pairs.

The "corner structure" of Figure 1a permits essentially free rotation about the single hydrogen bond joining cation and anion. That rotation is indeed essentially free is suggested by the dipole moment of 4-bromo-*N*-dimethylanilinium *p*-toluenesulfonate. Assuming that Θ has the same value (108.8°) as in the parent ion pair, vector analysis leads to the following predicted values for the resultant dipole moment of the 4-bromo ion pair: for free rotation about the N-H- - -O hydrogen-bond axis, 6.90 D; for restricted rotation, with the two benzene rings trans 8.02 D, cis 5.94 D, perpendicular 7.05 D. The experimental dipole moment is 6.85 D, in almost perfect agreement with the free-rotation model, although a model of restricted rotation with nearly perpendicular benzene rings of course cannot be ruled out.

The inferred ion-pair structure with a single hydrogen bond between cation and anion is consistent with x-ray crystallographic and chemical evidence. Thus, Tsoucaris[19] summarizes a substantial body of crystal-structure data for amine and aniline hydrochlorides by means of a model in which the crystal is structured so that each N-H proton interacts with a *separate* chloride ion with nearly linear N-H- - -Cl conformations. For anilinium chloride, Brown[20] finds that the nearest-neighbor N-Cl distances are 3.16-3.18 Å, and that the C-N-Cl angles are 106-115°. Proton exchange rates for ion pairs in acetic acid[21] and *tert*-butyl alcohol[22] indicate that only one N-H bond in the cation becomes less reactive by interacting with the anion.

For *N*-trimethylanilinium *p*-toluenesulfonate, where the cation lacks an N-H bond, Θ is 128°, approximately 20° greater than the tetrahedral angle (Table III). As will be shown, this significant difference cannot be explained on the basis of electrostatic interactions alone. Undoubtedly steric repulsions and directional London dispersion forces are also important.

Böttcher's Model. Electrostatic models have long played a dominant role in the interpretation of ion-pair properties. While familiar and (in many ways) successful theories of ionic association[24] involve explicitly only the charge-charge interaction, such theories are inapplicable to discussions of ion-pair "structure" in which the interaction energy depends not only on the distance but also on the topology and geometry of interionic attachment.

The first electrostatic approximation which allows for ion-pair structure is that of Böttcher's model.[23] In this electrostatic model an ion is represented as a point charge, point dipole, and isotropic point polarizability, all located at a single site called the electrical center. An ion pair is a pair of such centers at a fixed distance *r* and with fixed angles between μ_+ and r, and μ_- and r.

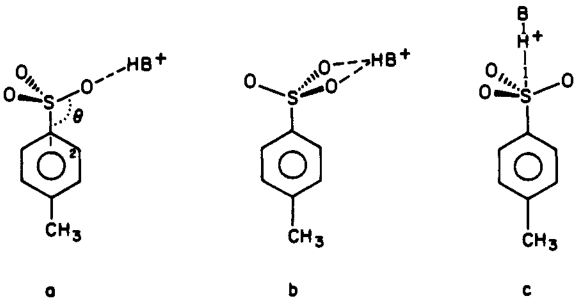

Figure 1. Three kinds of hydrogen-bonded structures of BH^+Ts^-: (a) corner, (b) edge, (c) axial.

For polyatomic cations, the electrical center is in first approximation the centroid of charge for all those atoms in the cation that bear formal positive charges. For anions, similarly, it is close to the centroid of charge for all atoms bearing formal negative charges. Actual electrical centers differ somewhat from these formal centroids owing to charge displacements between and within atoms caused by electronegativity differences and electrostatic fields.[3] Thus for *p*-toluenesulfonate ion, the electrical center is not precisely at the center of the triangle described by the three oxygen atoms, but is displaced toward the sulfur atom.[3] The distance between the electrical centers is a parameter whose value is adjusted so as to fit the electric dipole moment or some other property of the ion pairs.

In the present calculations, all cations and Cl^- will be treated as single, isotropically polarizable, electrical point-centers. In Ts^-, the electrical center is so far removed from the centroid of the atomic polarizabilities that this ion will be represented as an electrical center plus an auxiliary isotropic point polarizability, as described previously.[3] The calculations utilize eq. 9-13 of ref 4. When the structure of the ion pair is known, that is, when the vector r joining the electrical centers and the angles it makes with μ_+ and μ_- are known, the equations enable us to calculate the dipole moment μ of the ion pair as well as electrostatic interaction energy *W*. When μ is known from experiment, the model enables us to calculate one unknown structural parameter if we set no condition concerning *W*, or two parameters if we require that *W* be a minimum. These possibilities will now be explored.

In the present case, μ_+ is small in the free cation, and its effective value in the ion pair is further reduced by rotation about the N-H- - -O hydrogen-bond axis. We shall equate μ_+ in the ion pair to the component of the free-cation moment along the N-H- - -O axis, and assume that this vector is parallel to r.

For the chloride ion pairs $\mu_- = 0$. Thus, with μ_+ defined as above, *r* is the only structural unknown. Results obtained for *r* and *W* for the chloride salts are listed in Table III. Compared to crystallographic distances of 3.16-3.18 Å, the values calculated for *r* for *N*-Me and *N*-Me_2 seem rather large, the discrepancies being greater than in previous applications of Böttcher's model[3,13] in which hydrogen bonding was not involved. If this be granted, then the calculation shows that forces and electron displacements other than electrostatic ones are significant.

For the Ts^- ion pairs where $\mu_- = 5.2$ D, we can calculate both *r* and the angle it makes with μ_- by insisting that *W* be a minimum. For at least approximate consistency with the preceding section, we let Θ denote the complement of the angle between *q*r and μ_-. After choosing a specific

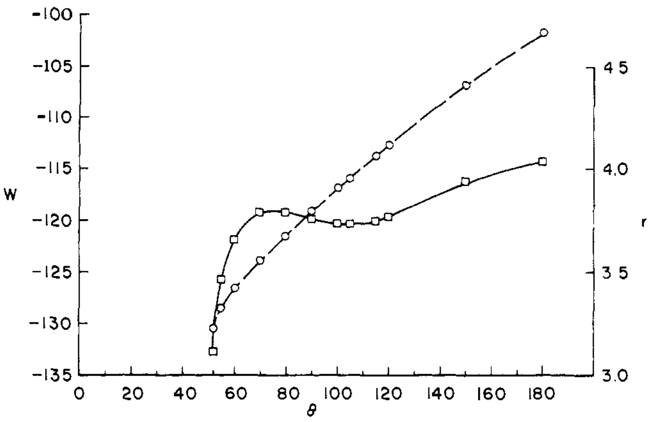

Figure 2. Application of Böttcher's model to N-dimethylanilinium p-toluenesulfonate. Dashed line, r vs. Θ. Solid line, W vs. Θ. The angle Θ is defined in Figure 1.

value for Θ, we then calculate r and W so as to reproduce the experimental dipole moment. By repeating this calculation for various values of Θ, we can then construct consistent graphs of r vs. Θ and W vs. Θ, as shown for N-Me$_2^+$, Ts$^-$ in Figure 2. The plot of W vs. Θ shows a minimum at 104° and decreases steeply below 70°. However, if we allow that r must be at least as great as for the N-Me$_2^+$, Cl$^-$ ion pair, then values of $\Theta < 75°$ must be ruled out on steric grounds. Thus W is at a minimum when $\Theta = 104°$. This result and results of similar calculations for the other ion pairs are listed in Table III. The calculation is instructive because it shows that electrostatic forces favor near-tetrahedral values of Θ. For the hydrogen-bonded ion pairs, electrostatic and quantum-mechanical forces apparently cooperate to produce nearly tetrahedral values of Θ, which makes us have considerable confidence in the preferred model shown in Figure 1a. On the other hand, for the N-Me$_3^+$, Ts$^-$ ion pairs, the present result deviates significantly from that of the method of model compounds.

Experimental Section

Materials. p-Toluenesulfonic acid monohydrate was recrystallized twice from chloroform and dried and stored under vacuum. Substituted anilines were purchased in the highest available purity and subjected to further purification. N-Methyl- and N,N-dimethylaniline were vacuum distilled and the middle fractions were collected. 4-Fluoro- and 4-bromo-N,N-dimethylaniline were recrystallized twice from methanol.

The p-toluenesulfonate salts of the anilines were prepared by mixing equivalent quantities of purified p-toluenesulfonic acid and purified aniline in methylene chloride or methanol, precipitated by addition of anhydrous ether, and recrystallized three times from a CH_2Cl_2-ether or CH_3OH-ether mixture. The purity of the salts was confirmed by NMR spectroscopy, by comparing the area of the N-methyl proton peak in the cation with that of the 4-methyl proton peak in the anion.

The substituted anilinium chloride salts were prepared by passing dry HCl gas through a solution of the corresponding aniline in anhydrous ether. The solid crystals were washed thoroughly with anhydrous ether, dried, and stored under anhydrous conditions.

N-Trimethylanilinium p-toluenesulfonate was prepared by the reaction of N-dimethylaniline with methyl p-toluenesulfonate. An equimolar mixture of the reactants in dioxane was kept under reflux for 8 h and then cooled. The precipitated solid was recrystallized three times from anhydrous methanol-ether and dried under vacuum at 60 °C. The presence of three N-methyl groups per Ts$^-$ ion was confirmed by proton NMR, as before.

Highest purity octanoic acid was partially frozen twice and then triply distilled under reduced pressure. The middle fraction was collected at a reduced pressure at which the head temperature was 100 °C.

Physical Measurements. The dielectric permittivity ϵ of dilute solutions was measured with a high-precision General Radio type 1615 A transformer ratio-arm bridge, as described previously.[3,12] The dielectric cells were suspended in an atmosphere of dry nitrogen, thermostated at 25 °C. Solutions were prepared with quantitative accuracy, using a microbalance, and were transferred and diluted in a dry-tent in a nitrogen atmosphere. Further details have been given in previous papers.[3,4,12]

Densities were measured for 8×10^{-3} to 2×10^{-2} m N-dimethylanilinium p-toluenesulfonate solutions in octanoic acid at 25.0° with a precision of better than 0.01%, using calibrated twin-necked pycnometers with graduated necks. Temperature was controlled to better than ±0.01 °C. Temperature equilibration required 2-3 h. Within the experimental error, density was a linear function of molal concentration. The apparent molal volume was 238 ± 3 ml/mol at 25 °C.

Equilibrium constants for reaction 1 were measured for N-dimethylanilinium chloride and p-toluenesulfonate in octanoic acid at 25.0 °C by a spectrophotometric method described in previous publications.[7,21]

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References and Notes

(1) Support of this work by the National Science Foundation is gratefully acknowledged.
(2) M. M. Davis, *Natl. Bur. Stand. (U.S.), Monogr.*, **No. 105** (1968).
(3) Part I: T. P. I and E. Grunwald, *J. Am. Chem. Soc.*, **96**, 2387 (1974).
(4) Part II: T. P. I and E. Grunwald, *J. Am. Chem. Soc.*, **96**, 2879 (1974).
(5) L. Onsager and S. W. Provencher, *J. Am. Chem. Soc.*, **90**, 3134 (1968).
(6) S. Highsmith and E. Grunwald, *J. Phys. Chem.*, **78**, 1431 (1974).
(7) D. Eustace and E. Grunwald, *J. Am. Chem. Soc.*, **96**, 7171 (1974).
(8) S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2974 (1956).
(9) C. S. Leung and E. Grunwald, *J. Phys. Chem.*, **73**, 1822 (1969).
(10) E. Grunwald, M. R. Crampton, A. Effio, and Ting-Po I, *J. Am. Chem. Soc.*, accepted for publication.
(11) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).
(12) E. Grunwald and A. Effio, *J. Solution Chem.*, **2**, 373 (1973); method A was used in the present work as well as in our previous papers, ref 3 and 4, although it had there been mistakenly identified as method B.
(13) E. Grunwald, S. Highsmith, and T. P. I, "Ions and Ion Pairs in Organic Reactions", Vol. 2, M. Szwarc, Ed., Wiley-Interscience, New York, N.Y., 1974, Chapter 5.
(14) A. A. Maryott, *J. Res. Natl. Bur. Stand.*, **41**, 1 (1948).
(15) J. G. Kirkwood, *J. Chem. Phys.*, 7, 911 (1939).
(16) F. J. Millero, *Chem. Rev.*, **71**, 147 (1971).
(17) D. Eustace, Ph.D. Thesis, Brandeis University, 1974.
(18) Dipole vectors are expressed according to the physical convention, pointing from the negative to the positive pole.
(19) G. Tsoucaris, *Acta Crystallogr.*, **14**, 917 (1961).
(20) C. J. Brown, *Acta Crystallogr.*, **2**, 228 (1949).
(21) M. R. Crampton and E. Grunwald, *J. Am. Chem. Soc.*, **93**, 2987 (1971).
(22) M. Cocivera and E. Grunwald, *J. Am. Chem. Soc.*, **87**, 2070 (1965).
(23) C. F. J. Böttcher, "Theory of Electric Polarization", Elsevier, Amsterdam, 1952, Chapter 5.
(24) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions", 3d ed, Reinhold, New York, N.Y., 1958, pp 291-297.