Simple estimates, however, are possible if covalent interactions are neglected. In general, the Eigen mechanism[34,35] of stepwise association

$$Zn^{2+} + Cl^- \rightleftharpoons Zn^{2+}(H_2O)_2Cl^- \rightleftharpoons Zn^{2+}(H_2O)Cl^- \rightleftharpoons ZnCl^+ \tag{12}$$

has to be considered. But with 2:1 valent electrolytes the "outer-outer-sphere complex", in which the ions are separated by two layers of water molecules, has not been found so far. We therefore restrict the following discussion to the "outer-sphere complex" with only one solvation shell between cation and anion and the "inner-sphere complex", the contact ion pair. The l values for these species are 4.2 and 2.55 Å, respectively, if the Pauling atomic radii[36] are used and if an obvious structure of the outer-sphere complex is assumed.

Assumption of the inner-sphere complex to be the only dipolar ion structure in the solutions results in $c_1 \approx 0.3c$. A set of equilibrium constants corresponding to such high c_1/c values has indeed been published.[37] This set, however, is based on a reduced reaction scheme in which $ZnCl_4^{2-}$ complexes have been disregarded. If, on the other hand, the dispersion step $\epsilon(0) - \epsilon_1$ is attributed to outer-sphere complexes only, the c_1/c data (Figure 6) nicely agree with those reaction schemes which are also in fair agreement with the c_0/c vs. c relation for the completely dissociated Zn^{2+} ions.

The assumption of the monochloro complex to have $Zn^{2+}(H_2O)Cl^-$ structure is supported by the solute relaxation time τ_2 at low solute concentration. The τ_2 values for zinc chloride agree with those for the outer-sphere complexes of Be, Ni–, Cu–, Cd–, and Mn–sulfates for which relaxation times between 50 and 70 ps had been found.[14]

Also in agreement with the assumption of outer-sphere complexes are estimates based on the Debye theory of dielectric relaxation[16] while this theory predicts considerably smaller τ_2 values ($\approx$7 ps) for the contact ion pair.[21]

Acknowledgment. We thank Professor H. G. Hertz, University of Karlsruhe, for valuable discussions on the aqueous zinc chloride system.

Registry No. $ZnCl_2$, 7646-85-7.

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Electric Dipole Moments and Interionic Structure of Para-Substituted *N*-Alkyl-*N*,*N*-dimethylanilinium Benzenesulfonate Ion Pairs[1]

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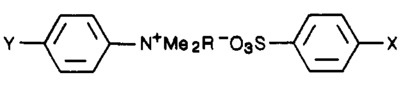
(Received: November 11, 1986)

Twenty-two salts of the type p-$YC_6H_4NMe_2R^+ \, ^-O_3SC_6H_4X(p)$ were synthesized. R = Me, Et; X = CH_3, Cl, Br, NO_2; Y = H, Br. These salts exist as ion pairs in dilute solutions in octanoic acid. Eight salts were soluble enough to permit measurement of ion-pair dipole moments. Analysis indicates that, in the ion pairs, the N^+ center of the cation is adjacent to one of SO_3^- oxygen atoms. Preliminary results for infrared S–O stretching frequencies in the free anions and ion pairs are consistent with this analysis. A novel concentric spherical dielectric cell is described.

A familiar method for clarifying the architecture of polar molecules is based on the analysis of electric dipole moments.[2,3] The substrate molecules must contain two or more polar sites whose bond or group moments are already known. The moment at one site then provides a reference direction. The other sites are directed so that vector addition yields the experimental dipole moment for the molecule.

In principle this method can also clarify interionic architecture in ion pairs (thus giving specific information about electrostatic and other intermolecular interactions),[4] but there are electrical charge-connected problems in predicting dipole moments for molecular ions,[5] even though the ion pair as a whole is uncharged. In this paper we deal with these problems, report dipole moments for a series of para-substituted *N*-alkyl-*N*,*N*-dimethylanilinium benzenesulfonate ion pairs (**1**), and analyze the results. The dipole



1, R=Me,Et; Y=H,Br; X=CH_3,Cl,Br,NO_2

moments are deduced from dielectric constants of dilute solutions of these salts in octanoic acid (ϵ_0 = 2.46 at 25 °C). Previous work[6,7] has shown that perturbation of solvent dipole correlation by polar solutes is negligible in octanoic acid.

To complement these results, we report a brief study of para-substituent effects on ν_{max} for the S–O stretching band in benzenesulfonate anions, comparing free ions (in dimethyl sulfoxide) with ion pairs (in methylene chloride). The substituent effects in the free ions were practically the same as those in the ion pairs.

Theoretical Part

Dipole vectors point from negative pole to positive pole, following physical rather than physical-organic convention. Vector quantities are given in boldface type. The present development is more general and can be applied more objectively than the formally correct development given earlier by I and Grunwald.[6]

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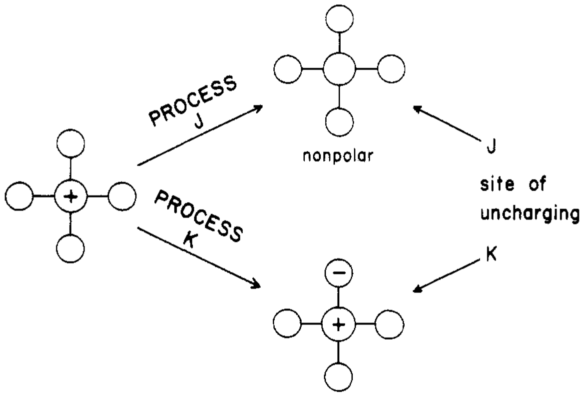

Figure 1. Illustration of alternative uncharging processes. The ionic electrical center is the site from which the ionic charge is removed. In process J it is the central atom. In process K it is the atom that gains the negative charge.

Charge-Dipole Models for Free Ions. Molecular ions, whose electron distributions are at least partly localized, cannot be represented realistically as conducting spheres. While an ion simulating a conducting sphere can be charged reversibly in only one way, the Born charging process, a molecular ion can have its charge removed in a variety of ways. Figure 1 illustrates this schematically for a model cation with formal charge on the central atom. In process J, the charge is removed from the central atom and the resulting uncharged structure is nonpolar. In process K, the central charge remains but the ion is converted to an uncharged zwitterion by adding a negative charge on an outer atom.

Corresponding to the various ways of charge removal, there are various charge-dipole models for representing the given charge distribution of the molecular ion. The relationships among them will now be derived as a prelude to interpreting the dipole moments of ion pairs. We define the following terms: The *electrical center* is the site (or centroid of sites) from which the ionic charge is removed in the given uncharging process. μ_{model} is the dipole moment of the resulting uncharged structure. $\mathbf{r}$ is the radius vector to the electrical center from an arbitrary, constant origin. ze is the ionic charge, where z is the charge number (±1 for univalent ions) and e is the unit of ionic charge. In this terminology, the electric moment $\mathbf{M}$ (about the origin) of the ionic charge distribution relative to the chosen origin is expressed by

$$\mathbf{M} = ze\mathbf{r} + \mu_{\text{model}} \tag{1}$$

where $\mathbf{r}$ and μ_{model} are specific for the given uncharging model. However, because the electric moment of the ion cannot depend on the arbitrary choice of the uncharging model, any pair of electrical centers ($\mathbf{r}_J$, $\mathbf{r}_K$) and model dipole moments is related according to

$$ze\mathbf{r}_J + \mu_J = ze\mathbf{r}_K + \mu_K \tag{2}$$

Let $\delta\mathbf{r}_{J,K} = \mathbf{r}_K - \mathbf{r}_J$. Substitution in (2) then leads to

$$\mu_K = \mu_J - ze\delta\mathbf{r}_{J,K} \tag{3}$$

Because $\delta\mathbf{r}_{J,K}$ is independent of the location of the origin, eq 3 is a key equation. It permits us to remove ionic charge in any desired way, such that μ_{model} in the uncharged structure can be estimated. If the corresponding electrical center is not convenient for the given problem, the center is simply moved to the desired location and the new μ_{model} calculated.

Choice of Uncharging Process. For the free ions of interest in the present work, convenient uncharging processes are shown in Figure 2. *tert*-Butylbenzene serves as uncharged model for the *N,N,N*-trimethylanilinium ion. This places the electrical center at the N nucleus and gives a value for μ_{model} of 0.4 D.[8] Benzenesulfonyl fluoride and chloride serve as uncharged models for the benzenesulfonate ion. Because the electronegativity of O (3.5) is intermediate between that of F (4.0) and Cl (3.0),[9] μ_{model} is taken as the mean, 4.58 D, of the experimental dipole moments.[8] Owing to the threefold symmetry of the SO_3^- group, the electrical center is at the center of the O_3 triangle. μ_{model} points from this center toward the S atom and along the 1,4 axis of the benzene ring. Because of its large magnitude and known direction, this model dipole provides a valuable reference direction in the dipole analysis of the ion pairs.

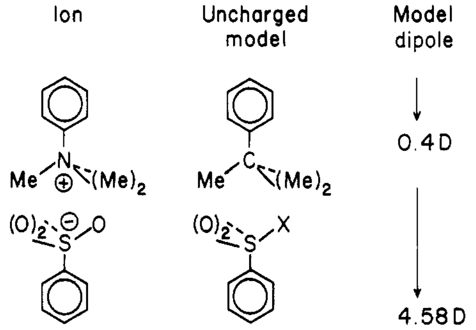

Figure 2. Model structures and dipoles for the ions used in this work.

Ion Pairs. In the following, the subscript + refers to cation and − to anion. IP denotes the ion pair. Due to mutual polarization, the electric moments of the ions in the ion pair differ somewhat from those of the free ions.[4-6] It is convenient to treat this as a displacement of the electrical centers, letting μ_{model} be the same as in the free ions.

Let $\mathbf{r}'_+$ and $\mathbf{r}'_-$ denote the displacement vectors from the common origin to the respective electrical centers in the ion pair. The electric moment of the ion pair then is given by

$$\mu_{IP} = \mathbf{M}'_+ + \mathbf{M}'_- = e(z_+\mathbf{r}'_+ + z_-\mathbf{r}'_-) + \mu_{\text{model},+} + \mu_{\text{model},-} \tag{4}$$

For univalent ion pairs this reduces to

$$\mu_{IP} = e(\mathbf{r}'_+ - \mathbf{r}'_-) + \mu_{\text{model},+} + \mu_{\text{model},-} \tag{5}$$

The vector difference $(\mathbf{r}'_+ - \mathbf{r}'_-)$, and hence μ_{IP}, are independent of the choice of origin, as expected for a species with zero net charge.

On applying eq 5, $\mu_{\text{model},+}$ and/or $\mu_{\text{model},-}$ are reference dipoles and establish a coordinate system in which $(\mathbf{r}'_+ - \mathbf{r}'_-)$ is evaluated. When the displacements of electrical centers ($\mathbf{r}_+ \to \mathbf{r}'_+$; $\mathbf{r}_- \to \mathbf{r}'_-$) due to mutual polarization can be known, the vector $(\mathbf{r}'_+ - \mathbf{r}'_-)$ expresses the interionic geometry. When these displacements are not known, one may assume that the components of $(\mathbf{r}'_+ - \mathbf{r}'_-)$ are smaller than those of $(\mathbf{r}_+ - \mathbf{r}_-)$ in an hypothetical unpolarized ion pair of equal interionic geometry. In typical cases, excluding uncommonly high polarizabilities due to resonance,[9] the reductions due to mutual polarization are of the order of 10–30%.[4,10]

Experimental Part

Solvents and Salts. The solvents used in the physical measurements, octanoic acid, methylene chloride, and dimethyl sulfoxide, were analytical or "gold label" reagents and were free from significant impurities.

Because the solubility of salts of the general type of **1** is hard to predict, we prepared a total of 22 salts, with the assistance of undergraduates Steven Farrell and Leo B. Slater. Initially these salts were purified by recrystallization only to synthetic purity. If the solubility proved adequate, the substrate was then recrystallized further to analytic purity, established by constancy and quality of melting points on repeated recrystallization and, less sensitively, by the NMR spectrum. Proton NMR spectra, taken at 90 MHz in $CDCl_3$ or $CDCl_3$/dimethyl-d_6 sulfoxide, showed no unassigned lines. Eight of the highly purified salts were used for dipole moment measurements, and these and nine others of purified less carefully were used for IR measurements. Relevant

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TABLE I: Data for *N*-Alkyl-*N*,*N*-dimethylanilinium Benzenesulfonate Salts

					ν_{max}, cm^{-1} for 0.03 M solutions			
					S–O stretch		Ph–S stretch	
no.	R	Y	X	mp, °C	Me_2SO	CH_2Cl_2	Me_2SO	CH_2Cl_2
1	Me	H	CH_3	162	1203[a]	1193	1122	1122
2	Me	H	Cl	223–226	1208	1198	1121	1122
3	Me	H	Br	226–228	1210	1198	1117	1119
4	Me	H	NO_2	246–250	1217		1121	
5	Me	Cl	CH_3	293 (dec)	1202		1121	
6	Me	Cl	Cl	260	1210		1121	
7	Me	Cl	Br	237–239	1210		1119	
8	Me	Cl	NO_2	222–225	1217		1121	
9	Me	Br	CH_3	284 (dec)	1203		1122	
10	Me	Br	Cl	268.5	1210		1122	
11	Me	Br	Br	261–263	1210		1118	
12	Me	Br	NO_2	226–228	1216		1120	1120
13	Me	CN	CH_3	239–242	1202		1121	
14	Me	CN	Cl	234–235				
15	Me	CN	Br	220				
16	Me	CN	NO_2	226–228	1216		1120	
17	Et	H	CH_3	80–81	1203	1194	1121	1122
18	Et	H	Cl	117–118	1210	1201	1120	1123
19	Et	H	Br	125–126	1210	1203	1118	1119
20	Et	H	NO_2	146–148	1217	1210	1121	1121
21	Et	Cl	CH_3	192–195	1202	1193	1120	1120
22	Et	Br	CH_3	211–212	(1202)	1192	(1121)	1122
sodium tosylate					1203		1120	

[a] 1206 (in DMF; $\epsilon = 36.7$).

properties are listed in Table I. Most of the salts have not been reported previously.

The *N*,*N*,*N*-trimethylanilinium benzenesulfonate salts were prepared from the corresponding *N*,*N*-dimethylaniline and methyl benzenesulfonate reagents by heating in methanol under nitrogen at reflux for about 30 min. (In some cases the reagents were heated neat for 10–15 min prior to addition of methanol.) In most cases, crystalline reaction products could be observed after 5 min by letting the flask cool to room temperature. The solid crystals were recrystallized from ethanol or (when X = Cl or Br) 2-propanol. Methyl *p*-chloro- and *p*-bromobenzenesulfonate were not available commercially and were synthesized under rigorously anhydrous conditions from the benzenesulfonyl chloride and sodium methoxide (from sodium metal and anhydrous methanol) in toluene.[11]

The *N*-ethyl-*N*,*N*-dimethylanilinium benzenesulfonate salts were prepared by two different methods. Salts with Y = H (no. 17–20, Table I) were prepared from *N*-methyl-*N*-ethylaniline and the appropriate methyl benzenesulfonate in methanol under nitrogen at reflux for 10–15 min. Salts with Y = Cl, Br (no. 21 and 22) were prepared from the *p*-halo-*N*,*N*-dimethylaniline and ethyl tosylate under nitrogen in dimethylformamide by heating overnight at about 80 °C. Salts 17, 18 and 20 were recrystallized from acetone/cyclohexane; salt 19 from *i*-PrOH/THF; salt 21 from *i*-PrOH/ether; and salt 22 from EtOH.

The proton NMR spectra of the salts all exhibit similar features. Typical chemical shifts (ppm vs. Me_4Si) in the *N*-ethyl-*N*,*N*-dimethylanilinium ion are 3.7 for *N*,*N*-dimethyl, 1.0 and 4.1 for *N*-ethyl, and a multiplet at 7–8 ppm due to the aromatic protons. The *p*-methyl protons in tosylate ion are at 2.3 ppm.

Electrical Measurements. Capacitance and conductance of the substrate liquids were measured with a General Radio type 1615A audiofrequency bridge with Type 1238 phase-sensitive detector, operating at 5–20 kHz.[6,12] The bridge had been modified previously[13] to extend the conductance range to 10 μmho and was calibrated at the beginning of this work by (1) checking the standard bridge capacitors for internal consistency and (2) determining the reactance of the standard bridge resistors by intercomparison and calibration against our 10 μmho/(0.14 ± 0.05) pF laboratory standard certified by Dr. John Hersh of General Radio Co. A new function, eq 6, gave better fit than that reported

$$C_R = 0.0709R/(1 + 4.823R) + 0.0110\mathrm{DEC}(R/100) - 3.455 \times 10^{-7}R^2 \quad (6)$$

$$\text{std error of fit} = 0.002 \text{ pF}$$

previously by Pan and Grunwald.[13] In (6), R is the bridge-resistor setting at bridge balance, DEC(R/100) is the decimal part of R/100, and C_R is the resulting addition to the bridge capacitance. At high R, C_R becomes negative.

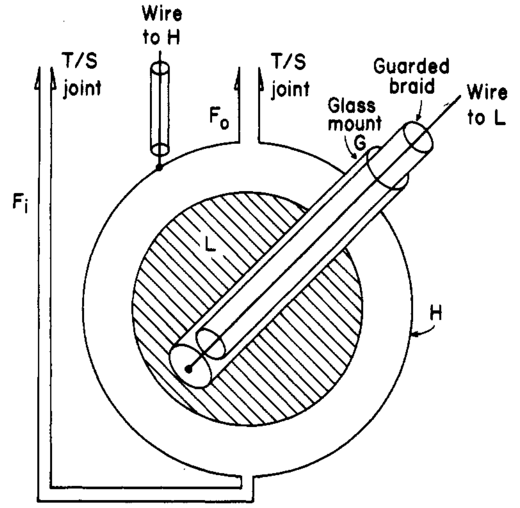

Figure 3. Schematic diagram of spherical dielectric cell. The H and L electrodes and the filling tubes F_i and F_o are made of stainless steel. The glass mount is made of precision ground Pyrex tubing. Details are available as supplementary material.

Solution conductances were small, <0.01 μmho. Capacitances were of the order of 8 or 18 pF, depending on cell size. Salt concentrations ranged typically from 0 to 4.5 mM. Dielectric increments $\Delta\epsilon = \epsilon_{solution} - \epsilon_{solvent}$ accordingly were small, ranging from 0 to 0.05. A precision of 0.0015 was achieved by differential measurement design, comparing solution and pure solvent side by side in the same dry-nitrogen atmosphere. The nitrogen temperature was controlled by heat exchange with a thermostatted water flow in a 4-ft heat exchanger.

Dielectric Cells. The only major change from previous practice was the use of a new cell design. In previous reports we had used the Balsbaugh cell or its smaller sister, the Eaton cell.[6,12,13] Disadvantages of these cells are as follows: (1) They require fairly large amounts of liquid (>20 mL). (2) Electrical insulation and guarding inside the cell involve fairly large amounts of Teflon. When the cell temperature is cycled, the Teflon volumes change inelastically and tend to lose their fit. (Ability to change the temperature is important for detecting the existence of isomeric ion pairs at equilibrium.[14]) (3) The cells must be taken apart to be cleaned between experiments, which is inconvenient and reduces the precision of the measurements. (4) In case of conducting solutions, there are complicated capacitance corrections for conductance from the high-voltage electrode to guard.[12]

Trying to overcome these problems we experimented with a concentric spherical design, shown schematically in Figure 3. The spherical shape, in which the high-voltage electrode H surrounds the low-voltage electrode L, eliminates the need for separate guard electrodes. The stainless-steel tubes F_i and F_o permit filling, rinsing, and cleaning without disassembly. Perhaps more important, they make it convenient for the cell to be dryed by pumping and for liquid to be introduced into the cell after evacuation, thus minimizing the entrapment of air bubbles. Furthermore, by connecting the standard taper joint to a small

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buret, liquid can be metered into the cell without exposure to the atmosphere. It turned out that this precaution was unnecessary, and in our later experiments the cell was filled in a nitrogen atmosphere from a syringe. For cleaning, the cell was rinsed six times with pure methanol, placed in a vacuum desiccator, and pumped dry.

Although our cell design represents an improvement, three problems remain. First, the glass tube G which serves as a handle for mounting L inside H needs to be adhered to L. After some experimentation we found that Sauereisen No. 1 cement is an acceptable trade-off between chemical inertness toward water, alcohols, carboxylic acids, and hydrocarbons and durability of the glass-to-metal bond. Second, the electrical connection of L to the inner wire of the connecting cable is fragile. We found that "tinning" the wire with low-melting solder (60% tin/40% lead) and heating with a glass-blowing torch for 30 s is somewhat superior to introducing a drop of mercury into the well. Third, guarding by the braided outer wire of the connecting cable as the cable passes through H is not perfect. A residual H-to-L capacitance of 0.09–0.16 pF remains, which can be determined for each cell by calibration with pure liquids and which, being constant, has no effect on $\Delta\epsilon$. In time, these problems will be solved. For instance, the guarding might be improved by continuous inner silvering of the glass tube.

Detailed descriptions of the cell, including engineering drawings and a photograph, are available as supplementary material. (See paragraph at end of text regarding supplementary material.)

To calibrate the cells we used eq 7, where the vacuum capacitance C_0 and the residual H-to-L capacitance k are characteristic parameters for each cell.

$$C = C_0\epsilon + k \tag{7}$$

To evaluate these parameters we used the following fluids at 25 °C: nitrogen (ϵ = 1.0006),[15] benzene (ϵ = 2.275),[16] and chlorobenzene (ϵ = 5.6025).[17] C_0 was either 3.3 or 7.5 pF. Estimated statistical errors were 0.002 pF in $C - k$, and 0.001 in $\epsilon = (C - k)/C_0$. To test the cells we measured the dipole moment of *p*-nitrotoluene in benzene, and the results were in practically exact agreement with the accepted literature value.[8]

Infrared and Conductivity Measurements. IR absorption was measured in Me_2SO and methylene chloride with a Perkin-Elmer Model 683 spectrometer and 0.03 M electrolytic solutions. Conductivity was measured for 0.003–0.03 M electrolytic solutions in methylene chloride with a General Radio Type 1680A automatic impedance bridge.

Results

Dielectric Increments. Typical results for ϵ vs. salt concentration c_2 are shown in Figure 4. Within experimental error the data define straight lines whose intercepts ϵ_{int} consistently are about 0.003 greater than ϵ_0 for the pure solvent. (The linearity of the plots suggests the absence of quadrupoles. Published studies at higher concentrations[4] tend to show curvature.) Linear plots of ϵ vs. c_2, in which ϵ_{int} differs from ϵ_0, have been noted for ion pairs before.[6,18] We suggest, by way of explanation, that ion pairs dissociate near the electrode surface to form a typical electrolytic double layer so that the equivalent capacitance C_Γ of the interface increases substantially. Let C_ϵ denote the capacitance of the liquid dielectric in series with C_Γ. The measured capacitance C_{expt} then is

$$C_{expt} = C_\epsilon C_\Gamma/(C_\epsilon + C_\Gamma) \tag{8}$$

and, since $C_\Gamma \gg C_\epsilon$, it can be linearized to

$$C_{expt} \simeq C_\epsilon(1 - C_\epsilon/C_\Gamma) \tag{9}$$

Given that ϵ_0 = 2.46 and $\epsilon_{int} - \epsilon_0$ = 0.003, we infer from (9) that for the pure solvent $C_\epsilon/C_\Gamma \simeq 0.001$, but this ratio drops to 10^{-4} or less for electrolytic solutions.

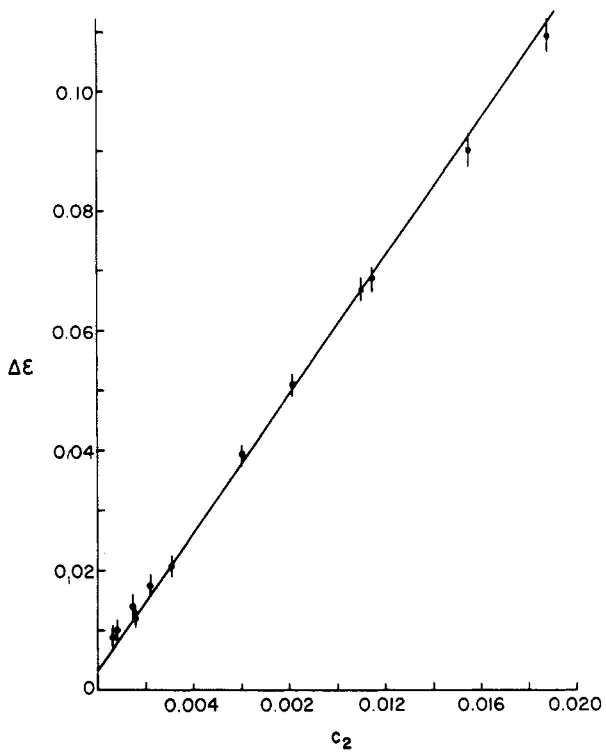

Figure 4. Experimental plot of $\Delta\epsilon$ vs. electrolyte concentration c_2 for *N*,*N*,*N*-trimethylanilinium *p*-toluenesulfonate in octanoic acid at 25 °C. The intercept is an average for all substrates listed in Table II.

TABLE II: Molar Dielectric Increments in Octanoic Acid at 25 °C, and Electric Dipole Moments, for the Salts Defined in Eq 1[a]

R	Y	X	$d\epsilon/dc_2$[b]	V_2	R_2	μ_{IP}	μ_X
Me	H	CH_3	5.8	254	86.9	7.0_3	−0.56
Me	H	Cl	9.5	244	87.2	9.0_0[c]	1.69
Me	H	Br	8.2	250	90.0	8.3_9[c]	1.70
Me	H	NO_2	11.6	253	88.1	9.9_7	3.99
Et	H	CH_3	7.1	270	91.5	7.8_3	−0.56
Et	H	Cl	9.4	261	91.8	8.9_6	1.69
Et	H	NO_2	15.1	269	92.5	11.3_6	3.99
Et	Br	CH_3	5.4	294	99.3	6.8_1	−0.56[d]

[a] Units: c_2, mol/L; V_2, R_2, mL/mol; μ, D. [b] $\epsilon_{int} = \epsilon_0 + 0.003$. [c] Results at 40 °C: X = Br, μ_{IP} = 8.4 D. X = Cl, $\mu_{IP} \simeq 9$ D (semiquantitative only). [d] $|\mu_Y|$ = 1.70 D.

If an explanation of this sort can be accepted, then the slopes of our linear plots (such as Figure 4) represent molar dielectric increments $d\epsilon/dc_2$. Slopes obtained for the present salts are given in Table II.

Dipole Moments. For consistency with previous work we calculate dipole moments μ_2 from Kirkwood's equation, using g_2 = 1 and dg_1/dc_2 = 0.[19] Required molar volumes V_2 and molar refractions R_2 were taken from the experimental literature[6,20] or estimated from literature values and additivity relationships.[3,21] Results are given in Table II. Dipole moments for two of the salts were obtained at both 25 and 40 °C. The dipole moments are in good agreement, arguing against the existence of temperature-dependent mixtures of ion-pair isomers, although (as indicated) one of the 40 °C values unaccountably is rather imprecise.

Ion-Pair Structures

Direction of μ_{IP}. It is convenient to define the x axis of the Cartesian coordinate system as the 1,4 ring axis of the benzenesulfonate ion. The y axis is defined such that μ_{IP} lies in the x,y

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TABLE III: Analysis of Dipole Vectors Based on Eq 10

	R = Me	R = Et
$\mu_0{}^a$	7.41 ± 0.22	8.06 ± 0.24
cos θ	0.696 ± 0.19	0.676 ± 0.13
θ^b	46 ± 15	47 ± 10
$(\mu_0)_x$, D	5.16	5.45
$(\mu_0)_y$, D	5.32	5.94
$(r'_+ - r'_-)_x$,^{c} Å	2.1	2.2
$(r'_+ - r'_-)_y$,^{c} Å	1.1	1.2
$\sigma_{\text{fit}}/\sigma_{\text{data}}$	1.37	1.34

^{a}X = Y = H. $^b\theta$ = angle between μ_0 and positive *x* axis. ^{c}Equation 6. μ_{model} as in Figure 2.

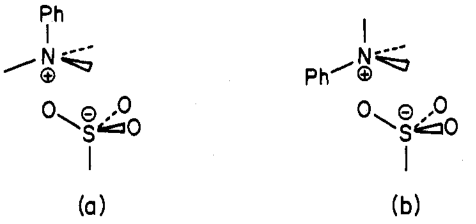

Figure 5. Probable interionic geometries in ion pairs. (a) The phenyl group is transverse. (b) An alkyl group is transverse.

plane. The vector μ_0 denotes the dipole of the para,para′-unsubstituted ion pair (X = Y = H). Positive directions of the *x*,*y* axes are defined so that the components of μ_0 are positive. θ denotes the angle between μ_0 and the positive *x* axis. We shall identify μ_X, the phenyl–X group moment in the anion, with $\mu_{\text{Ph-X}}$ for C_6H_5X, and similarly identify μ_Y in the cation with $\mu_{\text{Ph-Y}}$ for C_6H_5Y. The vector μ_X is directed along the *x* axis. Thus μ_{IP} is related to μ_X, μ_0, and θ according to

$$\mu_{\text{IP}}^2 = (\mu_X + \mu_0)^2 - 2\mu_X\mu_0(1 - \cos\theta) \tag{10}$$

The parameters μ_0 and (1 − cos θ) in (10) were evaluated by least-squares adjustment,[22] using the data in Table II. The fit is summarized in Table III.

The significant result, for ion-pair structure, is that θ is of the order of 46°. Accordingly, the component $\mu_{0,y}$ of μ_0 directed along the *y* axis is relatively large—5.3 D for methyl and 5.9 D for ethyl. According to eq 5, the components of $(\mathbf{r}'_+ - \mathbf{r}'_-)$ are 2.1 and 2.2 Å along *x* and 1.1 and 1.2 Å along *y*, respectively. (The 0.4-D vector $\mu_{\text{model},+}$ is here assigned to the *x* direction.) As indicated in Figure 2, in the free ions the electrical center is on N^+ in the cation, and at the center of the O_3 triangle of the SO_3^- group in the anion.

On the basis of these results it is probable that, in the ion pairs, the NR_3Ph^+ ion sits adjacent to one of the SO_3^- oxygens, as in Figure 5, rather than axially over the center of the O_3 triangle. This is shown particularly by the 1.1–1.2-Å magnitude of the *y* component of $(\mathbf{r}'_+ - \mathbf{r}'_-)$. By comparison, in crystalline sodium methanesulfonate the distance from the center of the O_3 triangle to an O atom is 1.37 Å. Similarly, in view of the expected mutual polarization, the 2.1–2.2-Å magnitude of the *x* component bears a plausible relation to the 3.1-Å sum of the van der Waals radii of N^+ and O^-.

Interionic Geometry. Granting that the N^+ center of the cation is adjacent to one of the SO_3^- oxygen atoms, one would like to define the disposition of the trialkylphenyl groups. Probably, as shown in Figure 5, three groups are proximate to the oxygen atom, while the fourth is transverse. In principle, the present approach using substituent effects of dipole moments can establish whether the transverse group is alkyl or phenyl. In fact, the single dipole now available (X = CH_3, Y = Br; Table II) is not decisive. According to space-filling molecular models, the 1,4-phenyl axis of the cation can be parallel either to *x* or to *y* without prohibitive steric strains. In the former case one predicts μ_{IP} = 6.7 D; in the latter one predicts 6.5 D. In either case, relative ionic rotation through modest angles can produce exact agreement with the experimental value of 6.8 D.

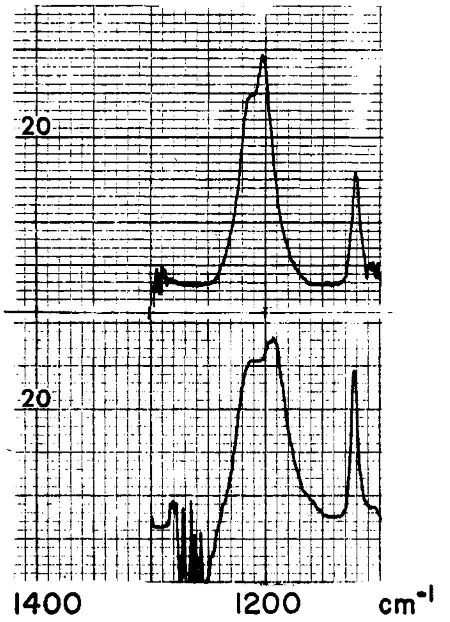

Figure 6. Optical density vs. wavennumber for 0.03 M *N*,*N*,*N*-trimethylanilinium *p*-toluenesulfonate in the 1200-cm^{-1} region: top, Me_2SO solvent; bottom, CH_2Cl_2 solvent.

The reason for the indefiniteness is that the angle between μ_{IP} and the *x* axis is too close to 45° in this case. To overcome this problem we are planning dipole measurements for ion pairs with variable Y and a highly polar X-substituent, such as *p*-nitrobenzenesulfonate instead of *p*-toluenesulfonate.

Infrared Frequencies

In the preceding analysis it was assumed that μ_{IP} is simply the vector sum of μ_0 for the unsubstituted ion pair and μ_X, the phenyl–X moment in the anion. Interaction between these para-situated polar centers was neglected, and accordingly μ_X was identified with $\mu_{\text{Ph-X}}$ for C_6H_5X. Looking for independent evidence to support these assumptions, we examined the S–O stretching frequency in the anion. Although this work was stopped before all of our questions were answered, it went far enough to demonstrate that frequency shifts due to para-substituted polar centers are additive within the framework of sufficient, but not necessary, conditions.

Two IR bands of the benzenesulfonate ions were examined: The S–O stretch near 1200 cm^{-1}, and the Ph–S stretch near 1120 cm^{-1}. The former is sensitive to para substitution and also to ion association and solvent effects which our work did not go far enough to separate. The latter is nearly independent of these perturbations and serves as a control. Electrolyte concentrations were 0.03 M. Solvents were dimethyl sulfoxide (ϵ = 46.7) and methylene chloride (ϵ = 8.93). The electrolytes exist mostly in the form of free ions in Me_2SO and are 99% associated—mostly to ion pairs—in CH_2Cl_2 (see below).

Typical IR spectra are shown in Figure 6. The Ph–S stretching band is a fairly sharp singlet in both solvents. The S–O stretching band due to free benzenesulfonate ions in Me_2SO is a doublet, as expected for weakly coupled symmetric and degenerate antisymmetric S–O_3 stretching motions. In the ion pair, this band becomes broader, and the band shape seems more convoluted. This is consistent with an ion-pair structure in which the threefold symmetry is lost, as implied by the dipole moments.

If perturbations of the S–O stretch due to solvation, para substitution, and ion pairing are additive, one may write eq 11 for free benzenesulfonate ions in Me_2SO and (12) for their ion pairs in CH_2Cl_2 (MC); ν_0 denotes the S–O stretch of unsubstituted free benzenesulfonate ions in the given solvent. For substrates

$$\nu_{\text{max}}(\text{Me}_2\text{SO}) = \nu_0(\text{Me}_2\text{SO}) + \delta\nu(\text{p-substit}) \tag{11}$$

$$\nu_{\text{max}}(\text{MC}) = \nu_0(\text{MC}) + \delta\nu(\text{ion pairing}) + \delta\nu(\text{p-substit}) \tag{12}$$

with the same para substituent, the frequency difference in the

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two solvents is then independent of the nature of the para substituent, as shown in

$$\nu_{\max}(\mathrm{MC}) - \nu_{\max}(\mathrm{Me_2SO}) = \nu_0(\mathrm{MC}) - \nu_0(\mathrm{Me_2SO}) + \delta\nu(\text{ion pairing}) \quad (13)$$

Values of $\nu_{\max}$ are included in Table I. The precision is 2 $\mathrm{cm^{-1}}$. For the Ph–S stretch, $\nu_{\max}$ is practically independent of solvent and substituents. For the $\mathrm{S{-}O_3}$ stretch (where $\nu_{\max}$ is measured at the low-frequency maximum), there is significant variation. In $\mathrm{Me_2SO}$, $\nu_{\max}$ varies with the p-X substituent but is independent of the cation, as expected for dissociated ions. The variation with p-X is nearly linear with the Hammett substituent constant σ. In $\mathrm{CH_2Cl_2}$, $\nu_{\max}$ is reduced. Within the experimental error the reduction is independent of the para substituent but depends on the nature of the cation. This is in agreement with (13) in which $\delta\nu$(ion pairing) appears as a variable but ν(p-substit) does not. For R = Me the reduction is 11 ± 1 $\mathrm{cm^{-1}}$ for three different X. For R = Et the reduction is 8 ± 1 $\mathrm{cm^{-1}}$ for four different X and 9 $\mathrm{cm^{-1}}$ for three different Y.

One expects from the dielectric constant (ϵ = 8.93 at 25 °C) that free-ion concentrations in $\mathrm{CH_2Cl_2}$ are relatively small. Actual free-ion fractions were estimated from conductivity measurements on solutions of *N*-ethyl-*N*,*N*-dimethylanilinium *p*-X-benzenesulfonate, X = $\mathrm{CH_3}$, Br. Equivalent conductivities were taken from the work of Denison and Ramsey,[25] by applying modest corrections for differences in viscosity and ionic strength. At 0.03 M electrolyte, the free-ion fraction was 0.010 for X = $\mathrm{CH_3}$ and 0.013 for X = Br. Extrapolation to infinite dilution gave the following association constants for ion-pair formation: For X = $\mathrm{CH_3}$, $K_a = 2.0 \times 10^6\ \mathrm{M^{-1}}$. For X = Br, $K_a = 0.9 \times 10^6\ \mathrm{M^{-1}}$. These constants should be regarded as tentative estimates but are of a plausible magnitude; by comparison, K_a for *N*,*N*,*N*-trimethyl-*p*-toluidinium perchlorate is 4×10^5 in ethylene chloride (ϵ = 10.23) and 5×10^4 in ethylidene chloride (ϵ = 9.90).[25] On the other hand, constants deduced recently by a photochemical kinetic method for certain ion pairs in $\mathrm{CH_2Cl_2}$ are considerably smaller.[26]

Registry No. **1**, 51931-01-2; **2**, 106798-80-5; **3**, 106798-81-6; **4**, 106798-82-7; **5**, 106798-83-8; **6**, 106798-84-9; **7**, 106798-85-0; **8**, 106798-86-1; **9**, 106798-87-2; **10**, 106798-88-3; **11**, 106798-89-4; **12**, 106798-90-7; **13**, 106798-91-8; **14**, 106798-92-9; **15**, 106798-93-0; **16**, 106798-94-1; **17**, 28001-59-4; **18**, 106798-95-2; **19**, 106798-96-3; **20**, 106798-97-4; **21**, 106798-99-6; **22**, 106799-01-3.

Supplementary Material Available: Details of the concentric spherical dielectric cells used in this work (Figures 7–10) (7 pages). Ordering information is given on any current masthead page.

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On the Thermodynamics of Fuel Synthesis

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(Received: December 9, 1986)

An expression for the thermodynamic efficiency of fuel synthesis is derived and applied to elementary examples from thermochemistry, photochemistry, biochemistry, and electrochemistry.

I. Introduction

During the past decade many processes and devices for fuel synthesis and solar energy conversion have been proposed. A computer program which generates new thermochemical cycles for hydrogen synthesis has been reported.[1] Hundreds of thermochemical cycles have been proposed so far,[2-4] and new cycles continue to appear in the literature. Moreover, thermochemical methods represent only a small area of fuel synthesis research; there remain photochemical, biochemical, electrochemical, and several other approaches to fuel production. In the long run at most only a handful of processes are expected to survive to the point of industrial application. From the point of view of technology assessment, detailed prototype evaluation is too time consuming and expensive to be applied to each new process. A preliminary selection procedure is needed that is based on criteria that can be established quickly and cheaply.

One criterion in the technological assessment is the energy efficiency of the process. Although this is strictly a thermodynamic problem, often thermodynamic analysis provides only an upper bound on the efficiency based upon reversible processes. The reversible limit may be so far from actual operating conditions that its bounds on efficiency are irrelevant to the best performance that can be obtained. Of course a considerable literature addresses the extension of thermodynamics to irreversible processes.[5-9] Again it may be questioned whether this is adequate. Standard irreversible thermodynamics is linear,[7,8,10] although few chemical reactions are operated in the linear region.[11,12] Outside the linear region elementary thermodynamic quantities such as temperature and entropy may not be well-defined, or may be subject to somewhat arbitrary definition.[13-17] Tykodi[18] has discussed an

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