thalpy is from adduct formation. Further support for this position comes from this study because the base parameters can be used to predict data obtained both in the gas phase and in poorly solvating solvents. This statement should not be taken as universally true for all systems in the E and C correlation. The problem is complicated by our lack of knowledge of the nature and structure of species in solution as well as a poor understanding of subtle, specific solvent-solute interactions.

The direct determination of the neutral-neutral gas-phase enthalpy of interaction is a difficult experiment. For example, the enthalpy of dimerization of formic acid has been investigated in detail[19] and the pitfalls in these studies revealed by this work. The results obtained are, for example, very much dependent upon the surfaces of the containers. When donors with competitive binding sites are used, the comparison of solution and gas phase data is further complicated. It is generally established that the equilibrium constant for donor-acceptor interactions is very different in the gas phase than in CCl_4 or alkanes. If the ratio of the interacting sites on the bases is different under the different sets of conditions, the enthalpies will differ but the cause will not involve a solvation contribution to the enthalpy.

In summary, we have been able to obtain an excellent fit of thermodynamic data to the e, c, and t equation, to provide a theoretical justification for the addition of the $t_A t_B$ term, to obtain parameters that are meaningful in terms of the electrostatic covalent transfer model imposed, and to provide new insights relative to the comparison of solution and gas-phase data.

It must be remembered that the E and C equation is still the preferred equation when dealing only with neutral-neutral acid-base interactions because of the larger data base. However, as new gas-phase ion-ion, ion-molecule, and molecule-molecule enthalpies become available and as existing enthalpies are corroborated and improved, the e, c, and t equation should eventually be able to satisfactorily replace the E and C equation.

The data analysis reported here suggests several important criteria for gas-phase ion-molecule experiment design. For example, little information about the coordination tendencies of an acid (or base) will be obtained by studying more than one base (or acid) with similar e/c and c/t ratios. When a new acid is investigated, the bases $(CH_3)_2S$, $(CH_3)_3N$, $(CH_3)_2O$, NH_3, H_2O, $(CH_3)_2CO$, and $(CH_3)_3P$ should be routinely used to best characterize the coordination tendencies of that acid. It would be interesting to have data for H_3O^+ interacting with the above bases. More anion-neutral acid data is sorely needed. Bases in the E and C correlation[1] that are not listed in Table I should be studied with H^+, K^+, CH_3^+, Li^+, and either Pb^+ or Bi^+. The tentative values reported in Table I should be investigated with the systems needed to complete their characterization. Accurate gas-phase data on neutral acid-neutral base systems are needed in order to understand what is occurring in solutions of poorly solvating solvents. It should be emphasized that these recommendations are independent of the e, c, t model and can be viewed as requirements for fully characterizing the coordination chemistry of acids or bases.

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Study of Methanesulfonates and Trifluoromethanesulfonates. Evidence for Hydrogen Bonding to the Trifluoro Group

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Abstract: Osmotic and activity coefficients are reported for the lithium, sodium, and potassium salts of methanesulfonic acid and trifluoromethanesulfonic acid and for the latter parent acid. Nuclear magnetic resonance chemical shift data are reported for ^{19}F vs. ^{13}C nuclei for trifluoromethanesulfonic acid and for its sodium and tetramethylguanidinium salts. The activity coefficient data indicate that the hydronium and tetramethylguanidinium ions, which are capable of hydrogen bonding, do not associate appreciably with the sulfonate group. Both colligative property and NMR data indicate ion pairing to the trifluoro group of the trifluoromethanesulfonate ion.

It was reported by Covington et al.[1] that the measurement of carboxyl ion concentration by Raman spectroscopy enabled the calculation of the ionization constant of aqueous trifluoroacetic acid in the range of 2 to 5 depending on the activity coefficients that were used. Previous measurements, largely based on measurement of hydrogen ion activities, yielded a constant that is a power of 10 lower. After repeating the Raman measurements,[2] we postulated[3] that the anomalous behavior was caused by ion pairing of the hydronium ion to the trichloro group of the trichloroacetate ion. This postulate has received further confirming evidence[4] in that activity coefficient data involving the tetramethylguanidinium ion indicate significant ion pairing of this ion with the trichloroacetate anion but not with the acetate ion. This cation cannot, of course, form covalent bonds with the anions in the manner of the acids. We reported[4] at the same time that the tetramethylguanidinium cation also ion paired with the trifluoromethanesulfonate anion but not with the methanesulfonate ion. The investigation reported in this paper was undertaken for the purpose of (1) determining whether the activity coefficients of the sulfonic acids would indicate the same difference in ion pairing as was found for the tetramethylguanidinium salts and (2) confirming by a different type of evidence (nuclear magnetic resonance) that the association really involved the trihalo group of the molecule.

Experimental Section

The best grades of methanesulfonic acid and trifluoromethanesulfonic acid available from Aldrich Chemical Co. were vacuum distilled and the center fractions retained. Aqueous solutions of these acids were almost

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Table I. Osmotic Coefficients at 298.15 K[a]

m	LiMS	NaMS	KMS	HTFMS	LiTFMS	NaTFMS	KTFMS
00.1	0.939	0.932	0.927	0.950	0.953	0.939	0.923
0.2	0.939	0.925	0.916	0.956	0.966	0.938	0.908
0.3	0.942	0.922	0.909	0.964	0.979	0.940	0.898
0.4	0.947	0.921	0.903	0.974	0.994	0.943	0.889
0.5	0.955	0.923	0.901	0.986	1.011	0.949	0.883
0.6	0.964	0.925	0.899	0.998	1.027	0.954	0.878
0.7	0.973	0.928	0.897	1.012	1.043	0.961	0.874
0.8	0.982	0.931	0.896	1.024	1.059	0.969	0.870
0.9	0.992	0.935	0.897	1.037	1.076	0.976	0.867
1.0	1.001	0.939	0.897	1.051	1.093	0.983	0.863
1.2	1.019	0.944	0.897	1.078	1.123	0.995	0.857
1.4	1.036	0.950	0.898	1.108	1.156	1.008	0.851
1.6	1.052	0.961	0.901	1.138	1.191	1.021	0.844
1.8	1.070	0.970	0.904	1.171	1.223	1.032	0.838
2.0	1.086	0.980	0.908	1.205	1.255	1.043	0.832
2.5	1.130	1.006	0.916	1.288	1.333	1.067	0.817
3.0	1.172	1.023	0.923	1.376	1.407	1.086	0.803
3.5	1.211	1.043	0.928	1.470	1.477	1.106	0.787
4.0	1.244	1.062	0.933	1.570	1.545	1.118	0.771
4.5	1.277	1.076	0.935	1.679	1.615	1.128	0.756
5.0	1.308	1.089	0.937			1.136	0.741
5.5	1.335	1.099	0.938			1.141	0.727
6.0			0.938				0.711
6.5			0.939				0.699
7.0							0.685
7.5							0.673
8.0							0.662
8.5							0.651
9.0							0.639
9.5							0.627
10.0							0.615
10.5							0.607
11.0							0.602

[a] MS, methanesulfonate; TFMS, trifluoromethanesulfonate.

neutralized with reagent grade lithium, sodium, or potassium carbonate. The solutions were evaporated to dryness in a vacuum dessicator over concentrated sulfuric acid. Pellets of solid NaOH were also placed in the desiccator. This removed both the water and the slight amount of remaining acid from the salts. They were then recrystallized at least three times from methanol–ether solutions and dried under vacuum over H_2SO_4 and then P_2O_5. Weighed samples of the salt were dissolved in water and passed through a cation-exchange column in the hydrogen form, the eluent being titrated with standard NaOH solution. The observed molecular weights of the salts agreed with those calculated for the anhydrous salts within the experimental error of the titration (0.1–0.2%). The samples of trifluoromethanesulfonic acid used in the isopiestic experiments were regenerated from the recrystallized sodium salt by ion exchange.

Activity coefficients were reported[5] some time ago for methanesulfonic acid and certain of its salts. These were determined by the isopiestic technique but the osmotic coefficients were not reported. Covington et al. subsequently repeated[6] the measurements on the acid and reported somewhat lower values for the activity coefficients. They also reported the osmotic coefficients for the acid. We have repeated Gregor's[5] work on the lithium, sodium, and potassium salts, both to check the activity coefficients and to determine experimentally the osmotic coefficients. The coefficients of trifluoromethanesulfonic acid and its salts were also measured. In order to conserve space, the extensive data for isopiestic solutions of the seven systems are not included but may be obtained from the author. This osmotic coefficients in Table I were calculated from the relation

$$\phi = (\nu_{ref} m_{ref}/\nu m)\phi_{ref}$$

The sodium chloride data (reference electrolyte) are those of Robinson and Stokes.[7] The activity coefficients of Table II were calculated from the equation[8]

$$\ln \gamma = \ln \gamma_{ref} + \ln (m_{ref}/m) + 2\int_0^{m_{ref}} (m_{ref}/m - 1)\, d \ln (m\gamma)_{ref}^{1/2}$$

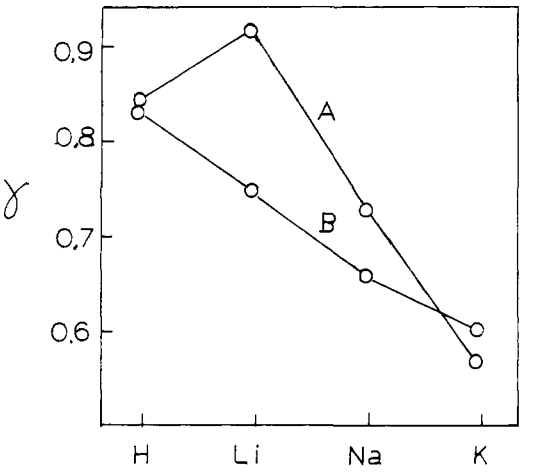

Figure 1. Activity coefficients at 1.0 m: (A) trifluoromethanesulfonates, (B) methanesulfonates.

Nuclear magnetic resonance data were obtained on a modified Varian XL100-15 (^{19}F) and on a Varian CFT-20 (^{13}C). All spectra were obtained using internal ^2H lock for field stabilization. Sweep widths and acquisition times were selected to ensure accuracy in chemical shift measurement of at least ±0.05 ppm. Spectra were obtained at 20 °C, and chemical shifts were determined relative to the appropriate carrier radio frequency. The same ^{19}F and ^{13}C carrier radio frequencies were used for all samples. The same 0.1 and 1.0 m solutions, containing 20% v/v D_2O for internal lock, were used for obtaining both the ^{19}F and ^{13}C data. Since the magnetic field was stabilized by locking the D_2O signal into resonance with a fixed frequency of source, one can calculate the shift of ^{19}F relative to ^{13}C by comparing the ^{19}F chemical shift (in ppm) relative to the ^{19}F carrier with the ^{13}C chemical shift (in ppm) relative

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Table II. Activity Coefficients at 298.15 K

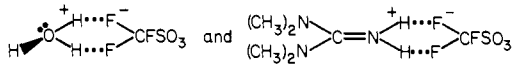
m	LiMS	NaMS	KMS	HTFMS	LiTFMS	NaTFMS	KTFMS
0.1	0.790	0.778	0.770	0.807	0.812	0.789	0.763
0.2	0.756	0.735	0.721	0.784	0.797	0.755	0.710
0.3	0.739	0.710	0.690	0.777	0.798	0.736	0.674
0.4	0.731	0.694	0.668	0.778	0.807	0.727	0.649
0.5	0.729	0.683	0.653	0.785	0.822	0.723	0.629
0.6	0.730	0.675	0.640	0.795	0.838	0.721	0.612
0.7	0.733	0.669	0.629	0.805	0.857	0.720	0.599
0.8	0.738	0.664	0.619	0.818	0.876	0.722	0.586
0.9	0.743	0.662	0.612	0.831	0.897	0.725	0.575
1.0	0.749	0.660	0.605	0.845	0.728	0.728	0.565
1.2	0.765	0.656	0.594	0.879	0.969	0.735	0.547
1.4	0.782	0.656	0.585	0.920	1.023	0.746	0.532
1.6	0.799	0.658	0.580	0.965	1.083	0.757	0.518
1.8	0.820	0.662	0.575	1.014	1.145	0.769	0.505
2.0	0.841	0.665	0.572	1.070	1.214	0.780	0.494
2.5	0.899	0.683	0.566	1.230	1.399	0.809	0.468
3.0	0.963	0.697	0.561	1.425	1.614	0.836	0.445
3.5	1.032	0.714	0.557	1.667	1.852	0.864	0.425
4.0	1.098	0.732	0.554	1.977	2.120	0.889	0.406
4.5	1.170	0.749	0.551	2.376	2.435	0.910	0.389
5.0	1.245	0.766	0.549			0.929	0.373
5.5	1.318	0.780	0.547			0.947	0.359
6.0			0.544				0.344
6.5			0.541				0.332
7.0							0.321
7.5							0.310
8.0							0.300
8.5							0.291
9.0							0.281
9.5							0.272
10.0							0.264
10.5							0.257
11.0							0.251

to the ^{13}C carrier. The carrier frequencies can be factored out, and, in fact, it is convenient to define a quantity that we will call $\delta_{^{13}C-^{19}F}$, which is the ^{13}C chemical shift relative to the ^{13}C carrier minus the ^{19}F chemical shifts relative to the ^{19}F carrier for the same sample.

Results and Discussion

Isopiestic Experiments. The activity coefficients of the methanesulfonate salts that are found in this work agree about as closely with those of Gregor[5] as do the coefficients for the parent acid reported by Covington[6] and Gregor.[5] In all concentrations that were studied the activity coefficients at any given concentration are in the order $H^+ > Li^+ > Na^+ > K^+$. This is the expected order for a strong monoprotic acid and its salts. Trifluoromethanesulfonic acid (triflic acid) has been referred to[9] as the strongest of all acids. Nevertheless, the activity coefficients for the trifluoromethanesulfonates are in the order $Li^+ > H^+ > Na^+ > K^+$ (Figure 1). This order is the same[10] as for the methyl-substituted benzenesulfonate families and suggests some form of association between the hydronium ion and the anion. The apparent association of triflic acid in water is not necessarily in conflict with the statement of Howells[9] since he was referring to the strength of acids in organic solvents, and the methods of association of the hydronium ion and the bare proton are believed[4] to be different. As was mentioned in the introductory paragraph, the activity coefficient data for the tetramethylguanidinium salts of the two sulfonic acids also point to association in the case of the trifluoromethanesulfonate salt.

The **osmotic** coefficients of 5.0 m solutions[4] of the methanesulfonate and trifluoromethanesulfonate salts are 1.244 and 0.348, respectively. The mode of association of the acid and salt may be represented as depicted. The bifurcated hydrogen bonds



probably favor these structures over those containing only a single linear bond. This would also explain the absence of association of the acid in aprotic solvents.[9]

Table III. Nuclear Magnetic Resonance Chemical Shifts for ^{19}F and ^{13}C (ppm)

	^{19}F vs. carrier	^{13}C vs. carrier[a]	$-\delta(^{19}F-^{13}C)$
		0.1 m	
Na^+	3.77	128.17, 144.05	124.40, 140.28
H^+	3.73	128.12, 143.99	124.39, 140.26
Me_4Gu^+	3.77	128.11, 143.98	124.34, 140.22
		1.0 m	
Na^+	3.88	128.26, 144.12	124.38, 140.24
H^+	3.49	127.99, 143.84	124.50, 140.35
Me_4Gu^+	3.70	128.26, 144.13	124.56, 140.43

[a] The bands reported for ^{13}C are the stronger center bands of the quartet.

Nuclear Magnetic Resonance Experiments. In all of our isopiestic work to date on the trihaloacetic acids, trifluoromethanesulfonic acid, and the tetramethylguanidinium salts of these acids, we have been forced to conclude that association occurred at the trihalo end of the molecule yielding structures like those depicted above; this was based only on the evidence that association does not occur in the corresponding nonhalogenated compounds. The NMR experiments are an attempt to yield positive evidence that such association, indeed, does occur in the case of the trifluoromethanesulfonate compounds. The fluorine chemical shift should give evidence in the same manner that proton chemical shifts give evidence for hydrogen bonding. The carbon nucleus in the interior of the molecule should be essentially unaffected by the fluorine association and was chosen as the reference nucleus. In the two sets of experiments the instruments were "locked" on the deuterium position of the D_2O solvent and ^{19}F and ^{13}C bands were measured relative to its position. The shift of ^{19}F relative to ^{13}C for 0.1 and 1.0 m solutions are reported in Table III. In the 0.1 m solutions the maximum variation of the fluorine chemical shift is 0.06 ppm (the approximate experimental

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uncertainty) while for the 1.0 m solutions the shift varies with the cation, and the Me_4Gu^+ and Na^+ salt shifts differ by 0.18 to 0.19 ppm with the acid having an intermediate value as would be expected from the activity coefficient data. The shift for the sodium salt with concentration is less than the experimental uncertainty. Thus, although the fluorine chemical shifts are small, as was anticipated, they are, nevertheless, greater than the experimental error and are in the expected order.

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Intramolecular Electron Delocalization: A Four-Site Model

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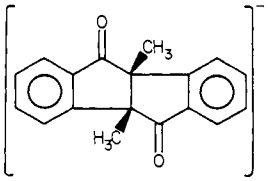
Abstract: The question of electron localization in isolated molecules and mixed-valence vs. averaged-valence structure is examined both from purely electronic and from vibronic viewpoints. Generally, a four-site model, in which two sites encompass a localization region in the molecule, is useful; the variation of the distance between the two sites in each region provides the vibronic coupling to localize the electrons. In a simple Hückel picture, we derive a closed-form perturbation-theoretic criterion for the stability of the localized (distorted) geometry; it is favored except for excessively polar structures. Adding the elastic energy of the framework increases the stability of the delocalized (averaged-valence or undistorted) geometry relative to the localized one. We present a diabatic coordinate curve-crossing analysis of the intramolecular electron-transfer problem, which permits straightforward classification of mixed-valent states and transfer processes. The vibronic picture leading to localization is quite similar to that employed in the pseudo-Jahn-Teller effect.

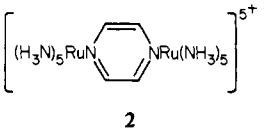
I. Introduction

The area of mixed-valence chemistry has burgeoned following the early reviews by Robin and Day[1] and Hush.[2] The experimental work of Harriman and Maki,[3] Schroeder and Mazur,[4] and in particular Taube and his students[5-10] has established clearly the existence for isolated molecules of the Robin-Day classifications I (localized valence), III (averaged, delocalized valence), and II (partially delocalized). Although experimental criteria for localization can be defined on any given time scale by the appropriate measurement (electronic spectroscopy for times $\sim 10^{-15}$ s, NMR for $\sim 10^{-5}$ s, etc.),[11] the theoretical situation has been considerably cloudier. A number of conditions for delocalization have been proposed,[12-15] most of which are based on the two-site limit of ordinary narrow-band polaron theory, and involve the competition between kinetic-energy lowering via delocalization and potential-energy lowering via localized bond distortion. While this is certainly entirely satisfactory for the two-site molecular crystal for which it was first developed,[16] its application to molecules seems to rest on dicier foundations.

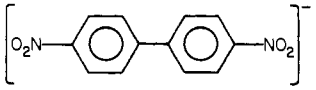
In intramolecular electron-transfer systems such as the diketone **1** studied by Schroeder and Mazur[4] or the Creutz-Taube[5] ion **2**,



1



2



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there is substantial difficulty in establishing precisely the orbital composition of the electron localization site (the Ru-N bonding region in **2** and the C=O chromophore in **1** seem reasonable choices, but they are not, in any real sense, localized electronic states). While considerable formal work on localized electronic states exists,[17] the problem is certainly not uniquely solved, and

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