the results. It is clear that the experimental results are consistent with the exo bromine being the first to be removed. Thus the reaction is proceeding via the *endo*-5-bromobicyclo[2.1.1]hexenyl cation in analogy to the hexamethyl derivative case.

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Solvation Numbers of Strong Electrolytes in Methanol Determined from Temperature Effects on Proton Shift[1a]

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Abstract: Experimental techniques, involving spinning side bands, are developed and used for determining the chemical shifts, relative to gaseous methane, of the hydroxyl and methyl protons of pure methanol and of methanol in the presence of strong electrolytes. The strong temperature dependence of the chemical shift of the hydroxyl proton is similar to that of water and is consistent with the model developed earlier for aqueous solutions. In this model the single resonance line is interpreted to be a time average of the proton in its solvated and unsolvated environments. From these studies the total "effective" solvation numbers of NaI, $LiNO_3$, $CaCl_2$, $LiClO_4$, LiBr, LiI, LiCl, and KI are determined. The fact that the solvation numbers are quite similar to the hydration numbers provides evidence that the ions bind water and methanol primarily through the oxygen atom. The methyl proton shift varies with the concentration of electrolyte but does not vary with temperature. It is shown that these observations are compatible with the proposed model.

Malinowski and coworkers[2-4] have determined the extent of hydration by studying the temperature dependence of the proton chemical shift of water in strong electrolyte solutions. Other investigators[5-8] have also used this technique for aqueous studies. The present investigation is an exploration of the feasibility of using this method for the study of the extent of solvation of strong electrolytes by nonaqueous solvents. Methanol was chosen as the solvent for this study for several reasons. It exhibits extensive hydrogen bonding and therefore the shift of the hydroxyl proton should be temperature dependent. It is a liquid over a temperature range which is adequate for the shift measurements. A number of strong electrolytes are sufficiently soluble in this solvent. In comparison to aqueous studies, the methanol molecule possesses a methyl group which can be used as an additional test of the theoretical equations.

Experimental Procedure

Reagent grade anhydrous salts and spectro grade methanol were used. The solutions were prepared in a dry atmosphere. Low-temperature proton spectra showed no evidence of water; whereas the addition of water produced an extra peak, visible only at low temperatures, as expected. Salt concentrations were determined by an ion-exchange procedure using Dowex 50W-X8 cation exchange resin. The resin was purified by successive washings with salt solution acid, and distilled water. After the sample solution was exchanged on the column, the effluent was titrated with standard acid to the phenolphthalein end point. For the calcium salt solution no precipitate was observed near the end point, indicating complete ion exchange.

Proton chemical shifts were measured with a Varian A-60A spectrometer equipped with a temperature controller and a wide-range oscillator which was used to accurately measure the shifts. Wilmad coaxial cells were used for referencing the shifts with respect to external standards. Negative values indicate shifts which are downfield from the standard. Each shift was measured at least three times and the average taken. Probe temperatures were determined by measuring the internal shift of pure methanol and referring to a graph (published by Varian Associates[9]) of the internal shift as a function of temperature.

Bulk susceptibility corrections were made by using the spinning side band technique.[10,11] The shifts were referenced with respect to gaseous methane. Methane gas serves as an excellent standard for these studies since it has been shown[12] that its proton shift is independent of temperature.

Temperature Dependence of the Chemical Shift of Methanol. The chemical shift of the hydroxyl proton of pure methanol was experimentally measured relative to gaseous methane. Methane, at approximately 6 atm, was sealed in the central cell of a coaxial-cell system and methanol was placed in the annular region. The observed shifts, $\delta_{\mathrm{obsd,MeO}H}(\mathrm{CH_4})$, were measured at ten different temperatures ranging from −47 to +50°. A least-squares fit of the observed, uncorrected shifts, as a function of the celsius temperature T, gave the following relationship

$$\delta_{\mathrm{obsd,MeO}H}(\mathrm{CH_4}) = 0.01015T - 6.37\ \mathrm{ppm} \qquad (1)$$

In order to obtain the corrected shift, $\delta_{\mathrm{corr,MeO}H}(\mathrm{CH_4})$, an appropriate correction for the difference in bulk magnetic susceptibility between the materials in the two regions must be made

$$\delta_{\mathrm{corr,MeO}H}(\mathrm{CH_4}) = \delta_{\mathrm{obsd,MeO}H}(\mathrm{CH_4}) + \frac{2\pi}{3}(\chi_{\mathrm{CH_4}} - \chi_{\mathrm{MeOH}}) \qquad (2)$$

Here χ is the bulk magnetic susceptibility. The value of $\chi_{\mathrm{CH_4}}$ is less than the experimental error and can be neglected, thus

$$\delta_{\mathrm{corr,MeO}H}(\mathrm{CH_4}) = \delta_{\mathrm{obsd,MeO}H}(\mathrm{CH_4}) - \frac{2\pi}{3}\chi_{\mathrm{MeOH}} \qquad (3)$$

We determined the bulk susceptibility of methanol as a function of temperature by using a coaxial-cell system in conjunction with a spinning side band technique. This experiment enabled us to determine the bulk susceptibility of pure methanol by using the NMR spectrometer itself. Details of the procedure are described below.

The proton spectrum of the material in the annular region of a spinning coaxial system exhibits side bands which conform to the following relationship[10,11]

$$\nu_{\mathrm{m}} = \frac{2\pi}{kr^2}[a^2\chi_{\mathrm{center}} + (b^2 - a^2)\chi_{\mathrm{glass}} - b^2\chi_{\mathrm{annular}}] \qquad (4)$$

Here k is a function of the relative intensities of the main signal and the spinning side bands produced by the coaxial system. If the intensities of the main signal and the first side band are made equal by adjusting the spinning rate of the sample cell, then k has a value of 1.4347. The separation between the two first side bands flanking the main signal is twice the modulation frequency. This quantity, $2\nu_{\mathrm{m}}$, is four times the rotational frequency of the sample cell. The values of the bulk susceptibilities of the material in the annular region, glass, and the material in the central region are χ_{annular}, χ_{glass}, and χ_{center}, respectively. The symbols a and b represent the inner and outer radii of the inner tube, and r is the mean radius of the annular region.

The value of ν_{m} was determined at seven different temperatures (from 4 to 45°) with methanol in the center and water in the annular region, $\nu_{\mathrm{mH_2O}}(\mathrm{MeOH})$. The sign of the modulation frequency was determined in each case by studying the asymmetry of the intermediate side bands caused by magnetic field gradients.[11] Over the same temperature range another set of measurements, labeled $\nu_{\mathrm{m\,MeOH}}(\mathrm{H_2O})$, was carried out with water in the center and methanol in the annular region of the coaxial cell system. Using eq 4 for both experiments and inserting values for the cell dimensions gave us the following expression

$$\chi_{\mathrm{MeOH}} = 0.00128(2\nu_{\mathrm{m,H_2O}}(\mathrm{MeOH}) - 2\nu_{\mathrm{m,MeOH}}(\mathrm{H_2O})) + \chi_{\mathrm{H_2O}} \qquad (5)$$

In this expression the bulk susceptibilities and modulation frequencies are in parts per million units. A linear least-squares fit of the data, along with published data on the bulk susceptibility of water, yielded the following.

$$\chi_{\mathrm{MeOH}} = 0.00075T - 0.542\ \mathrm{ppm} \qquad (6)$$

The published value for χ_{MeOH} at 20° is −0.530 ppm. This is in excellent agreement with the value −0.527 ppm calculated with eq 6.

By substituting eq 1 and 6 into 3 we obtained

$$\delta_{\mathrm{corr,MeO}H}(\mathrm{CH_4}) = 0.00857T - 5.24\ \mathrm{ppm} \qquad (7)$$

Subtraction of the internal shift of the methyl protons from $\delta_{\mathrm{corr,MeO}H}(\mathrm{CH_4})$, at the corresponding temperatures, yielded the corrected shift of the methyl protons relative to external methane. Surprisingly we found that the shift of the methyl protons, when referenced to methane, is independent of the temperature and is a constant within experimental error, ±0.01 ppm, i.e.

$$\delta_{Me\mathrm{OH}}(\mathrm{CH_4}) = -3.47\ \mathrm{ppm} \qquad (8)$$

It should be noted that eq 7 and 8 were obtained from measurements over the temperature range of 4° to 45° as limited by the bulk susceptibility measurements.

Determination of the Corrected Chemical Shift of Solutions. The proton chemical shifts of methanol in the presence of strong electrolytes were measured relative to external hexamethyldisiloxane (HMD). The standard was contained in the annular region of a coaxial cell system. The shifts were then rereferenced to methane gas by using the equation

$$\delta_{\mathrm{corr,soln}}(\mathrm{CH_4}) = \delta_{\mathrm{corr,soln}}(\mathrm{HMD}) - \delta_{\mathrm{corr,MeOH}}(\mathrm{HMD}) + \delta_{\mathrm{corr,MeOH}}(\mathrm{CH_4}) \qquad (9)$$

The subscript soln refers to the solution, i.e., methanol in the presence of an electrolyte. Equation 9 can be applied to either the methyl protons or the hydroxyl proton.

The first two terms on the right of eq 9 were obtained in the following manner. For a coaxial system, with HMD in the annular region, the shift of the solution relative to pure methanol is given by the difference

$$\delta_{\mathrm{corr,soln}}(\mathrm{HMD}) - \delta_{\mathrm{corr,MeOH}}(\mathrm{HMD}) = \delta_{\mathrm{obsd,soln}}(\mathrm{HMD}) - \delta_{\mathrm{obsd,MeOH}}(\mathrm{HMD}) + \frac{2\pi}{3}[\chi_{\mathrm{soln}} - \chi_{\mathrm{MeOH}}] \qquad (10)$$

The difference in bulk susceptibilities required by eq 10 was obtained by a spinning side band technique similar to the procedure described earlier. From eq 4 we can derive the following expression

$$\frac{2\pi}{3}[\chi_{\mathrm{soln}} - \chi_{\mathrm{MeOH}}] = \frac{kr^2}{3a^2}[\nu_{\mathrm{m,HMD}}(\mathrm{soln}) - \nu_{\mathrm{m,HMD}}(\mathrm{MeOH})] \qquad (11)$$

The values of $\nu_{\mathrm{m,HMD}}(\mathrm{MeOH})$, at equal first side band and main signal intensities, were experimentally determined. Recall that under these conditions the value of k is 1.4347. The chemical shift of methanol was also measured as a function of temperature from −64 to +36°. The results of these measurements are summarized by the following equations

$$\nu_{\mathrm{m,HMD}}(\mathrm{MeOH}) = 0.00225T - 0.1075\ \mathrm{ppm} \qquad (12)$$

and

$$\delta_{\mathrm{obsd,MeO}H}(\mathrm{HMD}) = 0.00872T - 4.94\ \mathrm{ppm} \qquad (13)$$

From eq 10, 11, 12, and 13, we found

$$\delta_{\mathrm{corr,soln}}(\mathrm{CH_4}) = \delta_{\mathrm{obsd,soln}}(\mathrm{HMD}) + 0.01498\nu_{\mathrm{m,HMD}}(\mathrm{soln}) + 0.00266T - 1.61\ \mathrm{ppm} \qquad (14)$$

The use of the above expression enabled us to obtain the corrected

Table I. Experimental Results and Results of Calculations Concerning the Shifts of the Hydroxyl Protons and Methyl Protons (Asterisk) of Methanol[a]

Solute	Molality	$d\delta/dT$, ppm/°C × 100	$\delta(0)$, ppm ($T = 0°$)	S	δ_S, ppm	δ^*, ppm	δ_S^*, ppm
None	0.00	0.857 ± 0.001	−5.24			−3.47 ± 0.01	
NaI	1.11	0.725 ± 0.007	−5.07	4.3 ± 0.4	−4.12	−3.64	−4.58
NaI	2.80	0.526 ± 0.005	−4.83	4.3 ± 0.1	−4.17	−3.97	−4.77
$LiNO_3$	2.32	0.753 ± 0.009	−5.39	1.6 ± 0.4	−6.47	−3.62	−4.73
$CaCl_2$	1.02	0.568 ± 0.015	−5.65	10.3 ± 0.6	−6.46	−3.74	−4.27
$LiClO_4$	1.92	0.760 ± 0.013	−5.15	1.9 ± 0.6	−4.47	−3.60	−4.58
$LiClO_4$	5.90	0.402 ± 0.010	−4.50	2.8 ± 0.2	−3.84	−3.82	−4.13
LiBr	3.19	0.561 ± 0.011	−5.52	3.4 ± 0.2	−6.06	−3.89	−4.68
LiI	5.28	0.393 ± 0.020	−5.16	3.2 ± 0.2	−5.10	−4.15	−4.73
LiCl	2.03	0.605 ± 0.006	−5.53	4.5 ± 0.2	−6.23	−3.69	−4.22
KI	0.75	0.802 ± 0.013	−5.10	2.7 ± 1.0	−3.13	−3.57	−5.01

[a] The shifts are referenced to gaseous methane and are corrected for bulk-susceptibility effects. Negative values indicate downfield shifts.

shifts, relative to gaseous methane, by measuring $\delta_{obsd,soln}(HMD)$ and $\nu_{m,HMD}(soln)$ at the particular temperature of interest.

For the salt solutions involving NaI, $LiNO_3$, and $CaCl_2$, the corrected chemical shifts of the hydroxyl protons of methanol varied linearly with temperature. The results of these measurements are summarized in Table I, which lists the salts studied, their respective concentrations, slope $d\delta_{corr,soln}(CH_4)/dT$ (abbreviated $d\delta/dT$), intercept $\delta_{corr,soln}(CH_4)$ at $T = 0°$ (abbreviated $\delta(0)$).

The corrected chemical shifts of the methyl protons of methanol δ^* in the presence of various salts were found to be dependent upon the salt and its concentration but independent of temperature, as in the case of pure methanol. The results of these measurements are shown in column 7 of Table I.

For $LiClO_4$, LiBr, LiI, and KI solutions, the hydroxyl proton shifts of methanol were measured relative to the methyl protons. At one temperature, the shift of the methyl protons relative to external HMD was measured along with the data needed for bulk-susceptibility corrections. From these data, and the fact that the shift of the methyl protons is independent of temperature, we were able to obtain the shifts at the other temperatures. The results of this procedure are shown in the bottom six rows of Table I.

Theory and Discussion

A. Chemical Shift of the Hydroxyl Proton. The chemical shift of the hydroxyl proton of methanol is an average value dependent upon the different environments it can experience. The strong temperature dependence of the chemical shift of the hydroxyl proton of methanol is similar to that of water and is consistent with the belief that hydrogen and nonhydrogen bonded environments exist in liquid methanol. As the temperature is increased, hydrogen bonds are broken and the NMR signal moves to higher field as a result of the larger shielding experienced by the nonhydrogen bonded proton.

The addition of a strong electrolyte to pure methanol provides additional environments. In such solutions a methanol molecule can interact not only with other methanol molecules, as in the pure liquid, but also with any of the ions in the solution. The observed shift δ is a statistical average of the shift δ_i of the solvent molecule in each possible environment. This average depends upon the mole fraction X_i of solvent molecules in each environment. In other words

$$\delta = \Sigma X_i \delta_i = X_S \delta_S + X_0 \delta_0 \qquad (15)$$

In the above expression subscript S refers to methanol solvated to ions and subscript 0 refers to (pure) methanol. The value of δ_0 represents an average over all the possible environments available to the hydroxyl proton of pure methanol. For our purpose here we need not specify exactly what these environments are. Similarly, the value of δ_S represents the average shift of those hydroxyl protons which are affected by the ions in the solution, averaged over primary and possibly secondary layers of both the cations and the anions.

If S is the "effective" solvation number, that is, the number of moles of methanol solvated to 1 mol of solute, and m is the molality of the solute, then $X_S = Sm/31.25$. From eq 15 we conclude that

$$\delta = \frac{Sm}{31.25}[\delta_S - \delta_0] + \delta_0 \qquad (16)$$

If the solvation number and the shift of the solvent bound to the ions are independent of temperature then, from eq 16, we find

$$S = \frac{31.25}{m}\left[1 - \frac{d\delta/dT}{d\delta_0/dT}\right] \qquad (17)$$

This equation was used to determine the solvation numbers listed in column 5 of Table I.

For both NaI and $LiClO_4$ solutions, solvation numbers were determined at two different concentrations. As seen in Table I, the solvation numbers of these two electrolytes are constant, within experimental error, at the two different concentrations.

The total effective solvation numbers of LiCl, LiBr, and $CaCl_2$, as shown in Table I, are 4.5 ± 0.2, 3.4 ± 0.2, and 10.3 ± 0.6, respectively. These values can be compared with the total effective hydration numbers which were obtained by applying this method to aqueous electrolyte solutions,[2a] namely 2.8 ± 0.4, 4.6 ± 0.2, and 9.9 ± 0.6, respectively. It is interesting to note that the hydration and solvation numbers are quite similar in spite of the fact that water has two protons attached to the oxygen atom whereas methanol has only one. This provides evidence that the major binding by the ions is through the oxygen atom of the solvent molecule and not through the hydroxyl proton. On the basis of ion-dipole interaction it is reasonable to assume that the positive ion tends to bind to the oxygen atom whereas the negative ion tends to bind to the hydroxyl proton. Hence, upon considering the results above, we suspect that the positive ion is more highly solvated than the negative ion. Furthermore an increase in the charge of the positive ion (compare Ca^{2+} with Na^+ or Li^+) is accompanied by an increase in solvation, as expected.

Recall that δ and δ_0 are temperature dependent due to hydrogen bonding. If the solvated molecules are completely removed from the bulk solvent and are effectively bound to the ions, then we should expect δ_S to be independent of temperature. With this in mind, we see, from eq 16, that at some temperature δ equals δ_0 and that at this temperature δ and δ_0 also equal the constant δ_S. Values so calculated from the experimental data are listed in the sixth column of Table I.

We note here that δ_S represents a stoichiometric average shift of the solvent molecule bound to both the cations and anions. In other words

$$\delta_S = \frac{n_+S_+\delta_+ + n_-S_-\delta_-}{n_+S_+ + n_-S_-} \qquad (18)$$

where n_+ and n_- are the number of positive and negative ions per salt molecule; S_+ and S_- are the effective number of solvent molecules bound to a positive ion and a negative ion, respectively; and δ_+ and δ_- are the respective proton shifts of a solvent molecule bound to a cation or to an anion.

When the values of δ_S for the salts in methanol are compared with those in water,[2a] we notice that the values for a given salt differ by a constant increment of 2.2 ppm, with the methanol shift lying further downfield. This observation in conjunction with eq 18 gives further evidence that, for the salts studied here, the ion-solvent bonding in methanol is essentially the same as those present in aqueous solution.

For NaI we see, from Table I, that δ_S is independent of concentration, on going from 1.11 to 2.80 *m*. For $LiClO_4$, however, at 1.912 *m* δ_S equals −4.47 ppm and at 5.90 *m* δ_S equals −3.84 ppm. At the higher concentration we should expect the proposed model to fail since ion pairing and ion sharing of solvent molecules are likely to occur, thus introducing additional complications which have not been taken into account in the present model.

B. Chemical Shift of the Methyl Protons. When the model is applied to the proton shift of the methyl group, an equation analogous to eq 16 is obtained, namely

$$\delta^* = \frac{Sm}{31.25}[\delta_S^* - \delta_0^*] + \delta_0^* \qquad (19)$$

Here the asterisk is used to indicate that the shift concerns the methyl protons. This equation is consistent with the experimental observations.

As described in the experimental section, we also discovered that the methyl shift of pure methanol δ_0^* is independent of temperature. Now according to equation (19) if the solvation number and δ_S^* are also independent of temperature, then the observed shift δ^* must be independent of temperature. Indeed this is the case. For all of the salt solutions investigated the shift of the methyl protons was found to be independent of temperature. See column seven in Table I. This fact lends credence to the proposed model.

Furthermore, if the solvation number is independent of concentration, then the shift of the methyl protons, according to eq 19, should be a linear function of the salt concentration. For both $LiClO_4$ and NaI a plot of the chemical shift of the methyl protons as a function of molality yields a straight line with an intercept of approximately −3.49 ppm, the shift of the methyl protons in pure methanol.

From a knowledge of the solvation number, *S*, obtained from temperature studies of the hydroxy proton shift, and from a knowledge of δ_0^* we can determine δ_S^*. Values obtained in this manner are presented in Table I. Although the concentration dependence of the methyl proton shift is not as great as that of the hydroxyl proton, it is clearly measureable.

We see here that eq 19 is in agreement with the observation that, for the electrolyte solutions studied, the methyl proton shift is independent of temperature but dependent upon salt concentration.

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Charge-Transfer Spectra of Some Para-Substituted Phenylpentamethyldisilanes. Substituent Effects on the Relative Intensities of Two Charge-Transfer Bands[1]

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Abstract: Relative intensities of two charge-transfer bands of *p*-R-$C_6H_4SiMe_2SiMe_3$ (R = H, Me, Me_3SiCH_2, and MeO)-TCNE complexes in dichloromethane have been determined by computer-aided analyses of the spectra. Experimentally, the relative intensities were correlated to σ^+ constants of the substituents. The results were then interpreted in terms of the Hückel MO models. The longer wavelength band was assigned to the transition from the highest occupied molecular orbital, constructed by the linear combination of the symmetric highest occupied π MO of a benzene with a silicon-silicon bonding σ MO to the lowest unoccupied MO of TCNE. The relative intensities were closely correlated to the fraction of the σ(SiSi) orbital in the highest occupied molecular orbital.

Charge-transfer (CT) spectra of arylpolysilanes are important as a diagnosis demonstrating the σ(SiSi)-π conjugation in these compounds.[2] The CT spectrum of phenylpentamethyldisilane with tetracyanoethylene (TCNE) was first reported by Bock and Alt.[3] They analyzed the CT spectrum as composed of two bands in which one had an absorption maximum at 25,000 cm^{-1}, and the other had an absorption maximum at 20,400 cm^{-1}. Noteworthy is the fact that the latter band had extremely low intensity compared with the former, while benzyltrimethylsilanes, ani-