These results demonstrate that the chlorine leaving group KIE can indeed serve to differentiate between the operation of the classical S_N mechanisms of nucleophilic attack and that of the ion pairs mechanism under appropriate conditions and within the limits of the assumptions made. In this case, the data support the ion pairs mechanism to the exclusion of simultaneous S_N1 and S_N2 processes and indicate that further investigation and theoretical development of the KIE probe based upon this hypothesis are warranted. The question of the generality of the ion pairs mechanism[22] remains open. Perhaps the results of future work based upon these preliminary findings and directed toward the goals mentioned above will help to resolve the controversy evoked by its suggestion.

Solvent Effects on the Proton Magnetic Resonance Spectra of Tetraalkylammonium Tetraalkylborides

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Abstract: Solvent effects on proton chemical shifts of molten tetraalkylammonium tetraalkylborides have been measured in binary molten salt–solvent mixtures containing 0–90 mol % solvent at 50 and 90°. Hydrocarbon analogs of the molten salt ions are shown to be the best reference compounds for solvent-induced shifts. Aromatic solvents cause upfield shifts of the cation resonances as large as 1.5 ppm and downfield shifts of the anion resonances as large as 1.0 ppm. The sizes of the solvent shifts are linearly related to the volume magnetic susceptibility anisotropy of the solvent. Although the aromatic solvent-induced shifts are large, the ion–dipole and ion–induced dipole interactions which cause them are weak. Simple equilibrium models for formation of collision complexes between solvents and tetraalkylammonium tetraalkylborides do not fit the chemical shift data.

The preparation of large quantities of tetraalkylammonium tetraalkylborides which are liquid at or near room temperature makes available a class of solvents different from any previously studied.[1] These viscous liquid salts are miscible with many organic compounds but not with water or paraffins. Since they cannot participate in Lewis acid–base interactions with solutes or with each other, their intermolecular and interionic interactions are limited to coulombic, ion–dipole, ion–induced dipole, and dispersion forces. To determine qualitatively the nature of interactions between these molten salts and organic compounds, we have measured pmr chemical shifts of 0–90 mol % solutions of a wide variety of organic solvents in the homologous series of molten salts $N_{1116}B_{1116}$, $N_{2226}B_{2226}$, $N_{3333}B_{3336}$, and $N_{4446}B_{4446}$.[2]

The screening constant $\sigma_{solvent}$ for the difference in chemical shifts of a molecule in the gas phase and in solution has been expressed as a sum of four terms (eq 1), which are contributions from the bulk sus-

$$\sigma_{solvent} = \sigma_b + \sigma_a + \sigma_w + \sigma_E \qquad (1)$$

ceptibility of the medium σ_b, magnetic susceptibility anisotropy of solvent molecules σ_a, van der Waals forces between solute and solvent σ_w, and a polar (electric field) effect of solvent molecules on the solute σ_E.[3] To these four terms is added sometimes a fifth term, σ_c, for specific complexation between solute and solvent. Bulk susceptibility corrections σ_b are readily made from volume magnetic susceptibilities. Numerous attempts to evaluate the other terms for uncharged solutes both experimentally and theoretically have led to the conclusions that σ_a is usually the major contributor in aromatic solvents, that σ_w is important in most solvents, particularly ones containing heavy atoms, and that σ_E is negligible in nonpolar solvents and difficult to distinguish from σ_w in polar solvents.[4-18] In principle, σ_c can be evaluated from concentration-dependent chemical shifts of the two complexing species

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either diluted in an inert solvent or as a binary mixture.[4,6,19-22]

Compared to neutral solutes much less is known about the effects of organic solvents on chemical shifts of ionic solutes. Ion pair dissociation constants have been calculated from concentration-dependent chemical shifts of tetra-n-butylammonium salts in nitrobenzene.[23] Tetraphenylboride, tetraphenylphosphonium, tetraphenylarsonium, and tetraphenylstibonium ions drastically affect proton chemical shifts of their counterions and of solvents.[24-26] In the most extensive study available of solvent effects on pmr chemical shifts of ions, Taylor and Kuntz[24] examined the chemical shifts of tetraalkylammonium, tetraalkylphosphonium, methyltriarylphosphonium, methyltriphenylarsonium, methyltricyclohexylboride, and methyltriarylboride ions in dilute solutions. They found that ion size and shape, electrolyte concentration, temperature, and the polarity and hydrogen-bonding ability of the solvent all affect chemical shifts of the ions but that magnetic anisotropy of aromatic solvents has the greatest influence. We report here a pmr investigation of binary mixtures of molten tetraalkylammonium tetraalkylborides and organic solvents to determine at least qualitatively the contributions of σ_a, σ_w, σ_E, and σ_c to the molten salt chemical shifts.

Experimental Section

Materials. Preparation of the tetraalkylammonium tetraalkylborides is described elsewhere.[1] Cyclohexylamine, 3-pentanone, and dimethylformamide were distilled before use. All other chemicals were reagent grade and were used without further purification.

Densities of tetraalkylammonium tetraalkylborides were measured to ±0.0005 g/ml at temperatures accurate to ±0.1°. Results of the highest and lowest temperature measurements for each compound are in Table I. From these values and one or two measurements at

Table I. Densities of Tetraalkylammonium Tetraalkylborides

Compd	Temp., °C	d, g/ml
$N_{1116}B_{1116}$	61.3	0.7884
	70.2	0.7795
$N_{2226}B_{2226}$	22.2	0.8360
	65.3	0.8193
$N_{3333}B_{3336}$	24.2	0.8346
	66.7	0.8153
$N_{4446}B_{4446}$	23.5	0.8336
	57.6	0.8197

intermediate temperatures, the densities were found to vary linearly with temperature. Extrapolated values of the densities were used to calculate compositions of the solutions at the temperatures used in pmr measurements.

Bulk magnetic susceptibilities were determined empirically from the pmr peak separation of bromoform enclosed in a sphere and in a cylindrical capillary, both suspended in a cylinder of the material of

unknown susceptibility.[27,28] Measurements were made at 41° on a Varian A-56/60 spectrometer whose frequency range was calibrated by the audio side-band method. The cell was calibrated with acetone, methanol, cyclohexane, and water using Broersma's[29] values of volume magnetic susceptibilities. The least-squares slope of the calibration line was 2.11 (vs. $2\pi/3 = 2.094$ according to theory) with a correlation coefficient of 0.9989. Bulk susceptibility values determined (as $-\chi_v \times 10^6$) were: 2,2-dimethyloctane 0.592, 3,3-diethylpentane 0.617, $N_{1116}B_{1116}$ 0.664, $N_{2226}B_{2226}$ 0.684, $N_{3333}B_{3336}$ 0.702, and $N_{4446}B_{4446}$ 0.667. Bulk susceptibility values from other sources employed in chemical shift corrections were: methanol 0.530,[29] acetonitrile 0.532,[28] 3-pentanone 0.550,[30] benzene 0.615,[29] toluene 0.618,[29] and 1-bromonaphthalene 0.840.[31]

Since literature values of χ_v at 20-25° were used as calibration for our measurements, the χ_v values measured at 41° actually approximate 20-25° values and contain errors due to differences between coefficients of volume expansion of the calibration compounds and of the compounds whose χ_v values we determined. These volume expansion errors are negligible with respect to other experimental errors (±0.005 × 10⁻⁶) inherent in the method.

Pmr chemical shifts were measured at 100 MHz on a Varian HA-100 spectrometer equipped with a Varian V-4315 frequency counter. A thermocouple was used to measure the probe temperature, which varied <0.2° at 50° and <0.5° at 90°. All samples were referenced to external distilled water, which provided the frequency lock signal. The water was sealed in a capillary, which was placed in a standard 5-mm nmr tube of the sample. Many samples also were referenced to ca. 0.5% internal hexamethyldisiloxane (HMDS). Chemical shifts of tetraalkylammonium tetraalkylborides were taken as centers of gravity of multiplets. Each chemical shift was measured at least twice with a mean variation of 0.1 Hz. The accuracy of the capillary external reference method was checked by repeating experiments at 50° with a coaxial cell containing water in the inner capillary and benzene-$N_{2226}B_{2226}$ mixtures in the annular region. Results with the two different cells agreed within 0.5 Hz. Experiments with benzene-$N_{2226}B_{2226}$ mixtures at 50° also were repeated with a second independently prepared sample of $N_{2226}B_{2226}$. Results agreed with the previous ones within 0.5 Hz.

Although the absolute chemical shift of liquid water is temperature dependent, the use of water as an external reference does not affect the molten salt results because all molten salt chemical shifts are reported relative to internal HMDS, a hydrocarbon peak in neat hydrocarbon, or a molten salt peak in neat molten salt. HMDS was chosen as the internal reference because its signal is separated from aliphatic hydrocarbon signals and it is less volatile than TMS. Its chemical shifts in ppm downfield from TMS in representative solvents are: acetonitrile 0.065, methanol 0.067, chloroform 0.070, benzene 0.110, and 1-bromonaphthalene 0.123.

Results and Discussion

Chemical Shift References. All of the solvent-induced shifts in this paper are referenced either to internal hexamethyldisiloxane (HMDS) or to hydrocarbon analogs of tetraalkylammonium tetraalkylborides. The chemical shift of HMDS (corrected for bulk susceptibility and relative to external water) in mixtures of $N_{2226}B_{2226}$ and aromatic solvents is not linearly related to the volume per cent composition of the mixture.[32] On the other hand, the chemical shifts of the CH_2 quartet of 3,3-diethylpentane and of the CH_3 singlet of 2,2-dimethyloctane in mixtures with the same aromatic solvents are linearly related to the volume per cent composition of the mixture. These

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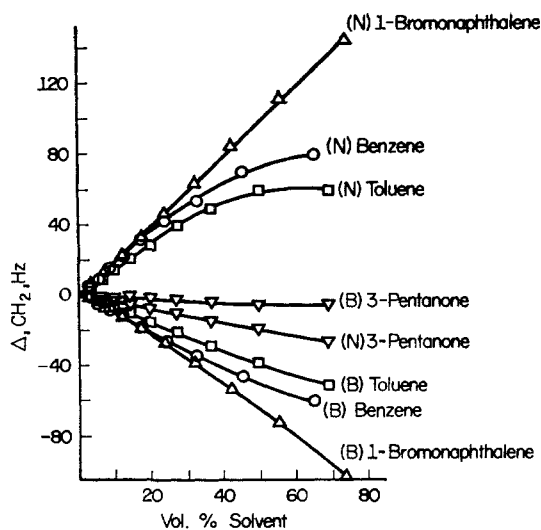
Figure 1. Chemical shifts of NCH₂ and BCH₂ protons of N₂₂₂₆-B₂₂₂₆ referenced to CH₂ protons of 3,3-diethylpentane at 50°. (N) and (B) denote protons of N₂₂₂₆ and B₂₂₂₆, respectively. (See text for explanation of referencing method.)

results indicate that alkanes are more inert references than HMDS in aromatic solvents. The alkanes could not be used directly as references for tetraalkylammonium tetraalkylboride chemical shifts because of overlapping alkane and ion resonances. However, some solvent-induced shifts of $N_{2226}B_{2226}$ were measured relative to the CH_2 of 3,3-diethylpentane by a more laborious indirect method.[32] 3,3-Diethylpentane is a particularly good reference compound for $N_{2226}B_{2226}$ because the accessibility of its CH_2 group to solvent, its "site factor,"[9–17,33–35] should be nearly identical with those of the NCH_2 and BCH_2 groups of the ions. Others[14,15] also have concluded that hydrocarbon analogs of the substrate are the best references for solvent-induced shifts.

Solvent-Induced Shifts of Tetraalkylammonium Tetraalkylborides. To survey the effects of a wide variety of organic materials on tetraalkylammonium tetraalkylboride chemical shifts, mixtures of $N_{2226}B_{2226}$ and 14 solvents were studied. Chemical shifts of the NCH_2 and BCH_2 protons relative to internal HMDS for 10 mol % $N_{2226}B_{2226}$ solutions at 50° are in Table II. The chemical shifts of the NCH_2 signals of the ethyl and n-hexyl groups were the same within experimental error, as were the chemical shifts of the two BCH_2 signals.

The major effects apparent in Table II are that the aromatic solvents toluene, benzyl alcohol, benzene, and 1-bromonaphthalene shift the cation resonances markedly upfield, and the same aromatic solvents as well as pyridine and nitrobenzene shift the anion resonances markedly downfield. The effects of all other solvents on the chemical shifts are much smaller than those of aromatic solvents.

The chemical shifts of $N_{2226}B_{2226}$ also were examined as a function of the composition of binary mixtures of $N_{2226}B_{2226}$ and most of the same solvents. Results for a

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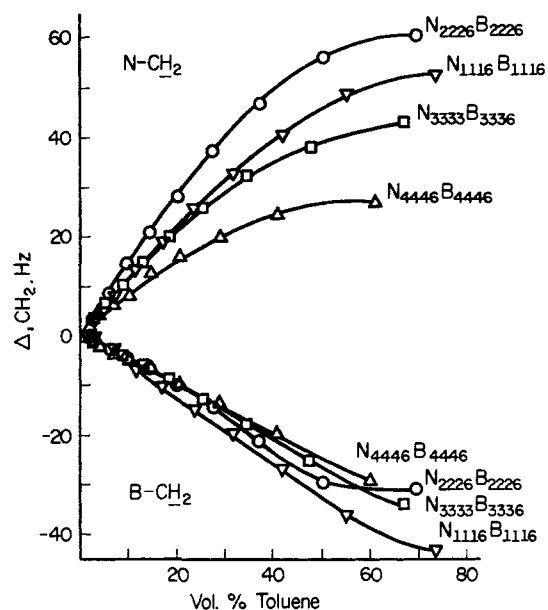(35) J. K. Becconsall, T. Winkler, and W. von Philipsborn, Chem. Commun., 430 (1969).

Figure 2. Chemical shifts of NCH₂ and BCH₂ protons of tetra-alkylammonium tetraalkylborides referenced to internal HMDS in toluene at 90°.

Table II. Pmr Spectra of 10 Mol % N₂₂₂₆B₂₂₂₆ in Various Solvents at 50°

Solvent	v, Hz downfield from HMDS[a] NCH₂	BCH₂
3-Pentanone	346.7	−17.2
Nitrobenzene	336.3	35.4
Dimethylformamide	331.6	−13.4
Cyclohexylamine	328.9	−20.4
1,1,2,2-Tetrachloroethane	326.4	−22.6
Methanol	321.8	−21.6
N₂₂₂₆B₂₂₂₆[b]	321.4	−20.3
Chloroform	321.3	−22.9
Pyridine	317.7	46.6
1,2-Dichloroethane	315.5	−25.6
Acetonitrile	312.1	−23.7
Toluene	249.4	17.8
Benzyl alcohol	237.7	31.6
Benzene	232.8	31.4
1-Bromonaphthalene	153.5	60.4

[a] At 100 MHz. [b] 100% N₂₂₂₆B₂₂₂₆.

few of the more dramatic effects appear in Figure 1, in which chemical shifts are referenced to the methylene quartet of 3,3-diethylpentane. Similar graphs (not shown)[32] referenced to internal HMDS for mixtures of $N_{2226}B_{2226}$ and all of the solvents in Table II resemble Figure 1 with Δ $vs.$ vol % curves that terminate at the chemical shift values for 90 mol % solutions listed in Table II.

The Δ values in Figure 1 were obtained as follows. Chemical shifts of (a) $N_{2226}B_{2226}$ containing 0–90 mol % solvent and (b) 3,3-diethylpentane containing 0–90 mol % of the same solvent were obtained relative to external water, corrected for bulk susceptibility, and plotted against volume per cent solvent. Differences in chemical shift between $N_{2226}B_{2226}$ and 3,3-diethyl-pentane found for each $N_{2226}B_{2226}$ data point are plotted in Figure 1 relative to their values in 100% $N_{2226}B_{2226}$.

Aromatic solvent effects on chemical shifts at chemically different proton sites in tetraalkylammonium and tetraalkylboride ions were determined two ways. Figure 2 shows the effect of toluene on the NCH_2 and
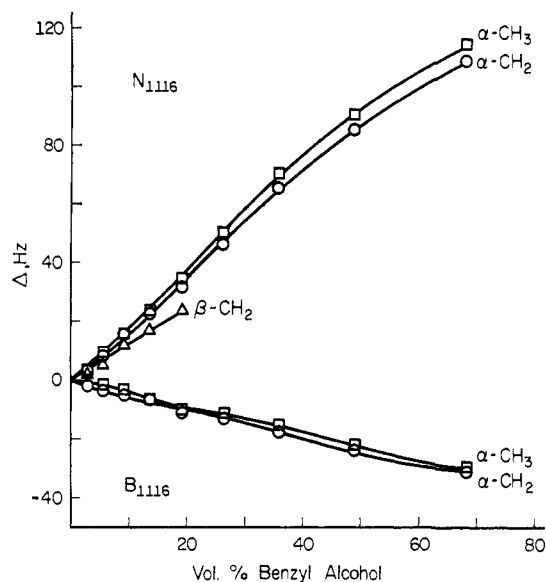
Figure 3. Chemical shifts of $^\alpha CH_3$-N-$^\alpha CH_2$-$^\beta CH_2$ and $^\alpha CH_3$-B-$^\alpha CH_2$ protons of $N_{1116}B_{1116}$ referenced to internal HMDS in benzyl alcohol at 90°.

BCH_2 chemical shifts of $N_{1116}B_{1116}$, $N_{2226}B_{2226}$, $N_{3333}B_{3336}$, and $N_{4446}B_{4446}$. With the exception of N_{1116}, the larger the ion the smaller the observed aromatic solvent-induced shift. If the ions all existed in fully extended conformations, the NCH_2 groups of all four cations would have nearly equal solvent shifts, as would the BCH_2 groups of all four anions. The inequality of solvent-induced shifts of $N_{1116}B_{1116}$, $N_{2226}B_{2226}$, N_{3333}-B_{3336}, and $N_{4446}B_{4446}$ can be explained conformationally. The longer alkyl groups are more likely to exist in folded conformations in which approach of the solvent molecules to the charge site is partially blocked. The smaller solvent-induced shift of N_{1116} than of N_{2226} in Figure 2 cannot be explained this way, but it may be due to an artifact of referencing. If the α-methylene of N_{2226} has a larger site factor (is more sensitive to random solvent shifts) than the α-methylene of N_{1116}, as is suggested by tests of 2,2-dimethyloctane as a reference for $N_{1116}B_{1116}$,[32] use of inert references with the proper site factors in Figure 2 would increase the solvent-induced shift of N_{1116} relative to that of N_{2226}.

Figure 3 shows that the α-CH_3 and α-CH_2 chemical shifts of $N_{1116}B_{1116}$ are about equally affected by the aromatic solvent benzyl alcohol, and that the β-CH_2 of the cation is shifted about 75% as far upfield as the α-CH_2. A space-filling model of these ions indicates that the α-CH_3 and α-CH_2 groups are about equally exposed to solvents as long as the n-hexyl group is in an extended conformation. The lesser solvent-induced shift of the methylene group β to nitrogen must be due to its greater distance from the solvent-orienting charge site.

Ion–Solvent Interactions. The large upfield shifts of tetraalkylammonium ion protons and large downfield shifts of tetraalkylboride ion protons caused by the aromatic solvents 1-bromonaphthalene, benzene, toluene, and benzyl alcohol must be due to preferred orientations between aromatic molecules and the ions that place the cation in the shielding region and the anion in the deshielding region of the aromatic ring

current. Taylor and Kuntz[24] reported similar observations of dilute tetraalkylammonium ion and tetraalkylboride ion solutions and hypothesized that the π-electron system of an aromatic molecule is preferentially directed toward a cation and the edge of the aromatic ring is preferentially directed toward an anion. Figure 1 shows that the absolute magnitudes of the solvent-induced shifts are greater for N_{2226} than for B_{2226}. We shall consider the question of whether there are discrete ion–molecule complexes later.

Also apparent in Figure 1 are downfield shifts of both N_{2226} and B_{2226} in 3-pentanone, although the shift of the anion is so small that cumulative errors in our referencing procedure might account for it. This downfield shift of N_{2226} may be due to ion–dipole interaction with the carbonyl group in which the charged nitrogen lies nearest the carbonyl oxygen and the NCH_2 protons consequently lie nearest the electron deficient carbonyl carbon atom in the favored N_{2226}–3-pentanone orientation.

The data in Table II are referenced to HMDS, whose deficiencies as a reference we have pointed out. All of the other nonaromatic solvent shifts of $N_{2226}B_{2226}$ in Table II are small enough that speculation here about the nature of ion–solvent interactions causing them is not warranted. It is noteworthy that the polar aromatic solvents pyridine and nitrobenzene do not shift the N_{2226} resonance upfield. Apparently a strong permanent dipole in an aromatic molecule is sufficient to overcome the otherwise favored interaction between the π-election system and charged nitrogen. Hyne and Fabris[36] have explained nitrobenzene chemical shifts in the presence of tetra-n-butylammonium ion by specific interaction of the nitro group with the cation, and Taylor and Kuntz[24] proposed a similar explanation for nitrobenzene-induced shifts of pmr signals of cations. On the other hand, since benzyl alcohol gives aromatic solvent-induced shifts almost the same as those of toluene, its polar hydroxyl group apparently exerts little or no influence on its interactions with $N_{2226}B_{2226}$. Since both the nitro group of nitrobenzene and the nitrogen of pyridine are sufficient to prevent the upfield aromatic solvent-induced shift of N_{2226}, ion–dipole and ion–induced dipole interactions between cations and the π-electron systems of the other aromatic solvents can be no stronger than the interactions of the ions with pyridine and nitrobenzene dipoles. This implies that other solvents in Table II which have sizable dipole moments, such as dimethylformamide and acetonitrile, also interact with N_{2226} but that their ion–dipole interactions lead to only small changes in cation chemical shift. Thus even though interactions between the molten salt ions and aromatic solvents are relatively weak, they lead to large solvent-induced shifts because of solvent anisotropy.

Aromatic solvent-induced shifts of $N_{2226}B_{2226}$ are slightly smaller at 90° than at 50°,[32] indicating that the enthalpies of interaction between the ions and aromatic solvents are small and negative.

Solvent anisotropy coupled with weakly orienting ion–dipole and ion–induced dipole interactions is responsible for large solvent-induced shifts of both HMDS and tetraalkylammonium tetraalkylborides. This conclusion is substantiated by Figure 4 in which

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the chemical shift of HMDS is shown to be approximately linearly related to the volume susceptibility anisotropy for eight solvents.[37] Graphs (not shown)[32] similar to Figure 4 with solvent-induced shifts of $N_{2226}B_{2226}$ plotted against $\Delta\chi_v$ for the same solvents also are roughly linear, except that pyridine and nitrobenzene are far off the line in the N_{2226} graph, and pyridine is significantly off the line in the B_{2226} graph. A possible explanation for these deviations based on ion-dipole interactions was discussed earlier.

Are There 1:1 Ion–Solvent Complexes? There is substantial disagreement about whether aromatic solvents form specific molecular complexes with polar solutes. Often 1:1 complexes (eq 2) have been proposed

$$A + B \underset{}{\overset{K_f}{\rightleftarrows}} A \cdot B \qquad (2)$$

to explain pmr chemical shift data, but their formation constants ($K_f < 4.0$ M^{-1}) and heats of formation (<2.0 kcal mol^{-1}), calculated from concentration and temperature dependence of chemical shifts, are small.[4,19-22] Such a "complex" is often called a "collision complex," because its lifetime is thought to be that of one collision. Hence a "collision complex" is just a preferred orientation (due to dipole–dipole and dipole–induced dipole forces) of the average collision between the "complexing" molecules. When one component of the "complex" is aromatic, this nonrandom collision orientation causes a large chemical shift change in the second component.

Recently some authors have rejected the idea of discrete 1:1 complexes between polar and aromatic molecules and described aromatic solvent-induced shifts in terms of a "solvent cluster" around a polar functional group.[14,15,40] According to this viewpoint the interactions between aromatic solvents and solutes are too weak to form complexes of well-defined stoichiometry, and solvent-induced shifts are due only to nonrandom time-average orientations of several solvent molecules around ions and polar functional groups.

Calculation of formation constants of collision complexes from chemical shift data requires fitting the data to at least two adjustable parameters, the formation constant, and the chemical shift of the collision complex.[19-22] However, when the data cover as wide a concentration range as ours do, generally postulation of more aggregates than just a 1:1 complex and correspondingly more adjustable parameters are necessary to fit the data.[19] Both mole fraction and molar concentration scales have been used to treat collision complex data, and there is some disagreement as to which is proper. Regardless of the units employed, in order to calculate a formation constant of a collision complex,

(37) The volume susceptibility anisotropy, $\Delta\chi_v$ in Figure 4, is the molar magnetic susceptibility anisotropy, $\Delta\chi$, of a solvent divided by its molar volume. The $\Delta\chi$ values were obtained either from rotational Zeeman effect measurements or from additive atom or bond contributions to the total susceptibility.[38,39] Values of $\Delta\chi$ (in 10^{-6} erg/(G^2 mol)) used were: 1-bromonaphthalene -119.8 ± 5.0, nitrobenzene -70 ± 10, benzene -59.7, benzyl alcohol -58.3 ± 0.5, toluene -56.6 ± 0.5, pyridine -57.4, dimethylformamide $+3.2 \pm 1.0$, acetonitrile $+5.2$. (Values with error limits were calculated; the others have been determined experimentally.)

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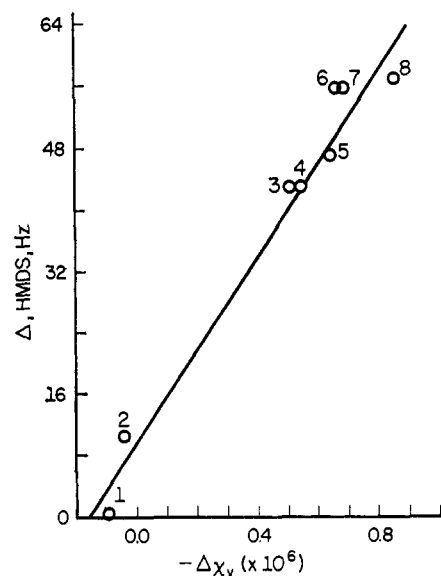
Figure 4. Solvent-induced shifts at 50° of HMDS in 50:50 (v/v) mixtures of $N_{2226}B_{2226}$ and solvents relative to 100% $N_{2226}B_{2226}$ as a function of the volume susceptibility anistoropy $\Delta\chi_v$ of the solvent: (1) acetonitrile, (2) dimethylformamide, (3) toluene, (4) benzyl alcohol, (5) benzene, (6) nitrobenzene, (7) pyridine, (8) 1-bromonaphthalene.

the chemical shift *vs.* concentration graph of the data cannot be a straight line; it must curve to approach a limiting value for the chemical shift of the fully complexed species.

Figures 5 and 6 show solvent-induced shifts of $N_{2226}B_{2226}$ plotted against molar and mole per cent concentrations of solvent relative to 3,3-diethylpentane reference. We regard 3,3-diethylpentane as the only acceptable reference for collision complex determination because chemical shift data referenced to HMDS contain contributions due to specific interactions of HMDS with other solution components. On a molar scale only the data in benzene and toluene for N_{2226} show the curvature necessary for calculation of formation constants of collision complexes. On a mole per cent scale most of the data in aromatic solvents curve in the wrong direction! Application of models which postulate (a) a 1:1 molten salt–solvent collision complex and (b) two 1:1 collision complexes, consisting of N_{2226}–solvent and B_{2226}–solvent, to the data in Figure 5 leads to formation constants of benzene and toluene collision complexes in the range 0.001 to 0.4 M^{-1}. The data for 1-bromonaphthalene will not fit either model with chemically reasonable equilibrium constants.[32] Probably we could find a model with more adjustable parameters which could fit all the data, but we doubt that it would have chemical significance.

One possible complication in the complexation models is ion pair dissociation of the tetraalkylammonium tetraalkylborides. If we assume that the tetraalkylammonium tetraalkylborides have the same ion pair dissociation constants as tetra-*n*-butylammonium iodide in nitrobenzene[23] and methyl tri-*n*-butylammonium picrate in 1-bromonaphthalene,[24] they would have been 1.3% dissociated in nitrobenzene and 0.01% dissociated in 1-bromonaphthalene at the lowest salt concentrations used in our experiments (10 mol %). Therefore, the chemical shifts of tetraalkylam-
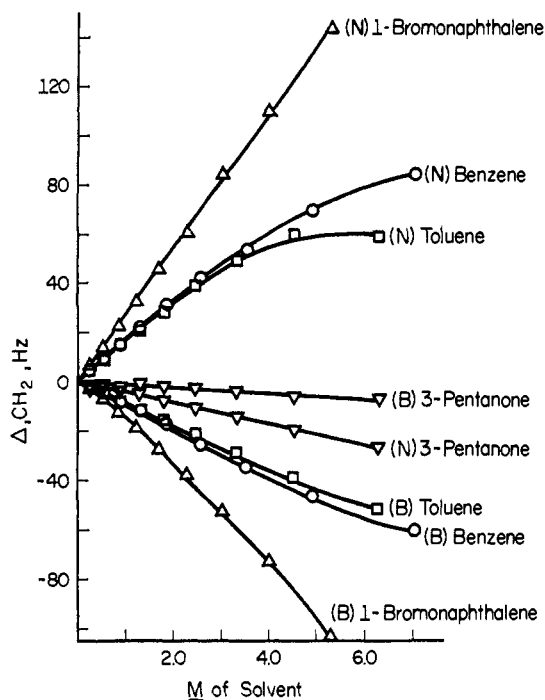
Figure 5. Chemical shifts of $N_{2226}B_{2226}$ referenced to 3,3-diethylpentane plotted as a function of molarity of added solvent. (N) and (B) denote NCH_2 and BCH_2 chemical shifts, respectively.
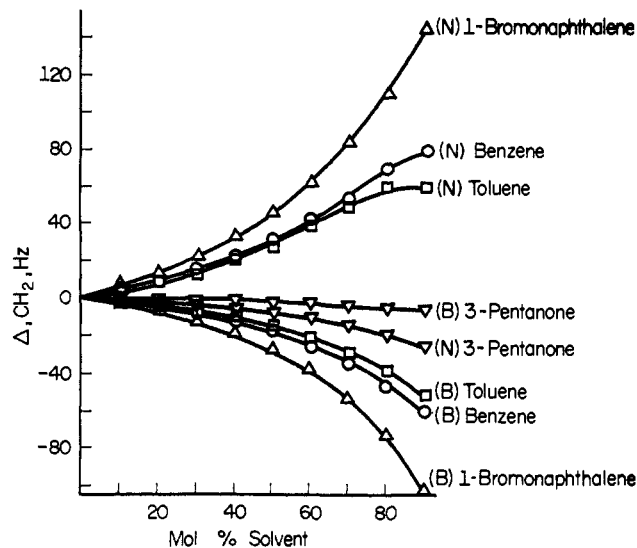

Figure 6. Chemical shifts of $N_{2226}B_{2226}$ referenced to 3,3-diethylpentane plotted as a function of mole per cent of added solvent. (N) and (B) denote NCH_2 and BCH_2 chemical shifts, respectively.

monium and tetraalkylboride ions reported here contain negligible contributions from dissociated ions.

In summary, aromatic solvents drastically influence the proton chemical shifts of tetraalkylammonium tetraalkylborides because of specific ion–dipole and ion–induced dipole interactions. No simple collision complex model fits the chemical shift data. The ion–solvent interactions are so weak that they should be called preferred orientations of ion–molecule collisions in solution rather than complexes. The much larger induced shifts in aromatic solvents than in other solvents are due solely to the much larger influence of solvent anisotropy (σ_a) than of van der Waals or polar effects on the chemical shifts of tetraalkylammonium and tetraalkylboride ions.