NMR in Molten $[N(Bu)_4]_2MBr_4$. 1. Contact and Pseudocontact Shifts[1,2]

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Abstract: The ^{1}H and ^{13}C NMR shifts produced by the paramagnetic ions of $[N(Bu)_4]_2NiBr_4$, $[N(Bu)_4]_2CoBr_4$, and $[N(Bu)_4]_2MnBr_4$ in the molten state, both neat and diluted with $[N(Bu)_4]_2CdBr_4$, have been determined. It is argued that the structure of the molten salts per se implies that any dipole-dipole mechanism must be a great deal less important than that which has been attributed to ion pairs of these salts in indifferent solvents. Dipole-dipole interactions, local density fluctuations, or ion-induced anisotropy do not explain the experimental results. It is concluded that the shifts are largely contact in nature and involve both spin transfer and spin polarization.

Introduction

There is, by now, a considerable body of literature on the NMR shifts produced by nearby paramagnetic ions.[3] At what appears to be a sufficient level of approximation, the shifts may be taken to be produced either by a through-space (dipole-dipole or pseudocontact) mechanism or by an electron-mediated (Fermi or contact) mechanism. In various cases it is interesting and sometimes important to determine the relative significance of these two means by which the magnetic moment of the electron influences an NMR experiment. For example, the widely used "shift reagents" often utilize the geometrical properties of the dipole-dipole interaction to establish the conformation of the "host" molecule so that the contribution, if any, of the contact mechanism must first be subtracted.[4]

One class of systems that has presented some puzzling aspects despite a number of studies is the $N(Bu)_4^+$ species exposed to various di- and trivalent ions of the first transition series.[3,5] A prototypical system is a dilute solution of a $N(Bu)_4^+$ salt to which a salt containing, say, $NiCl_4^{2-}$ has been added. The observation of a substantial shift in the proton resonances of the $N(Bu)_4^+$ has been taken to imply that the interaction of each kind of proton with the paramagnetic anion is not completely random but rather that there is a definite geometrical relation between the cation and anion which furthermore is accompanied by an anisotropic susceptibility on the part of the Ni(II) species. The pseudocontact shift for an axially symmetric ion is then given by

$$\left(\frac{\Delta H}{H}\right)_{\text{dip}} = \frac{1}{3}\left\langle\frac{1 - 3\cos^2\theta}{r^3}\right\rangle(\chi_{\parallel} - \chi_{\perp}) \qquad (1)$$

where θ is the angle between the anion's axis of symmetry and the observed nucleus and $\langle\ \rangle$ denotes averaging over all interionic configurations. For anions expected to be magnetically isotropic in solution, cation-induced anisotropy has been postulated to explain the observed shift.[5d,6,12,13] On the other hand, ^{14}N shifts strongly suggest[7] the presence of a contact contribution.

One of the foci of research in our laboratory has long been the study of a class of melts which includes molten $[N(Bu)_4]_2MBr_4$ (M = Mn, Ni, Co, Cd) by a variety of spectroscopic and classical methods. We undertook NMR measurements on these systems in order to study the mechanism of electron-nuclear spin-spin interactions and to investigate the structure and dynamics of these molten electrolytes at the same time. In this publication we describe the results of ^{1}H and ^{13}C shift measurements and in a second the results of the ^{1}H and ^{13}C R_1 relaxation measurements.[2]

Before describing the NMR measurements, it may be helpful to say a few words about the fused salt system. The $[N(Bu)_4]_2MX_4$ salts melt near 100 °C to mobile, electrically conducting liquids.[8] Analysis of optical absorption spectra (Mn(II), Ni(II), Co(II), and Cu(II) systems),[8a] phosphorescence emission spectra,[8d,e] phosphorescence lifetimes, and ESR spectra (Mn(II) system)[8b,c] shows that the tetrahalometalate anions (which may be expected to substitute for each other approximately isomorphously in the liquid) are more or less tetrahedral. In the $MnCl_4^{2-}$ system,[8b,c] the rotational correlation time of the anion is less than 10^{-6} s just above the melting point and becomes smaller with increasing temperature. Thermal properties of $N(Bu)_4^+$ systems in the solid state[8d,f] indicate that the side chains of the bulky cation may pack in several ways, being largely extended in the liquid.[8b,d,e] Since the NMR spectra reported below show separate lines for each of the four kinds of carbon atoms, the system is isotropic when averaged over times of the order of milliseconds. (A direct experimental examination of the ionic dynamics of this system, by means of spin-lattice relaxation measurements, is the subject of the second paper of this series.[2])

Thus we picture these liquids as consisting of ions which may be taken as roughly spherical for processes with sufficiently long characteristic times. It is assumed that $CdBr_4^{2-}$ can be substituted for each of the MBr_4^{2-} species without producing any significant changes other than in the magnetic properties. When dilution is referred to below, it refers to the replacement of the paramagnetic ion by the corresponding diamagnetic (cadmium) ion. The relative sizes of the ions, as shown by molecular models, indicate that they form an approximately antifluorite structure with the anions octahedrally and the cations tetrahedrally coordinated. The features of the liquid structure which are relevant at this stage are that the various nuclei of the $N(Bu)_4^+$ species are at all times subjected to the fluctuating magnetic influence of an entire set of nearest neighboring paramagnetic anions. A fortiori, each paramagnetic ion is at all times englobed by a set of nearest $N(Bu)_4^+$ neighbors all of which simultaneously are exposed to its instantaneous magnetic field. Consequently, the anions and cations cannot in any sense be treated as belonging to a well-defined, unique ion pair. The average unlike-ion-pair distribution functions are spherically symmetric as expected for liquids. This topic is further pursued in the Discussion.

Experimental Section

The salts were prepared by conventional means and carefully purified.[1b,c] All samples were degassed by pumping for several freeze-melt cycles under high vacuum (10^{-4} Torr). Aside from pilot experiments, the studies were carried out on a Varian XL-100 spectrometer with a Nicolet TT-100 Fourier transform accessory. The proton spectra were obtained in the CW, the ^{13}C spectra in the FT mode. Samples were run in the inner tube of a coaxial cell with the

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Table I. Densities and Effective Molecular Volumes

salt	temp, °C	density, g/cm^3	effective mol vol, Å^3
$[N(Bu)_4]_2CdBr_4$	122	1.291	1179
$[N(Bu)_4]_2NiBr_4$	121	1.225	1170
$[N(Bu)_4]_2CoBr_4$	124	1.229	1167

Table II. $N(Bu)_4^+$ ^1H Shifts in CH_2Cl_2[a] [c]

counterion	H_α	$H_{\beta,\gamma}$	H_δ
$NiBr_4^{2-}$	−0.55	−0.72	−0.53
$CoBr_4^{2-}$	2.45	0.93	0.20

[a] In parts per million upfield from the corresponding resonance of $N(Bu)_4Br$. [b] Reprinted with permission from ref 6. [c] 0.25 M CH_2Cl_2 at room temperature.

Table III. Susceptibilities and Effective Magnetic Moments

salt	mass susceptibility, cm^3/g × 10^6	temp, °C	μ_{eff} (powder)	μ_{eff} (melt)
$N(Bu)_4Br$	−0.705	119		
$[N(Bu)_4]_2CdBr_4$	−0.600	117		
$[N(Bu)_4]_2NiBr_4$	4.77	119	3.69	3.99
$[N(Bu)_4]_2CoBr_4$	8.00	119	4.85	5.13
$[N(Bu)_4]_2MnBr_4$[a]	0.289	120	5.87[b]	6.08[b]

[a] Mole fraction = 0.07 in $[N(Bu)_4]_2CdBr_4$. [b] Extrapolated from 0.01, 0.03, and 0.07X solutions.

Table IV. Diamagnetic Shifts[a]

salt	temp, °C				
		^1H			
		H_α	$H_{\beta,\gamma}$	H_δ	
$[N(Bu)_4]_2CdBr_4$	120	5.1	3.3	2.6	
		^{13}C			
		C_α	C_β	C_γ	C_δ
$N(Bu)_4Br$	125	60.84	25.94	21.12	14.74
$[N(Bu)_4]_2CdBr_4$	120	60.60	26.02	21.31	15.36

[a] In parts per million downfield from Me_4Si at room temperature.

Table V. Concentration Dependence of Shifts at 148 °C[a]

^1H			
H_α	$H_{\beta,\gamma}$	H_δ	
$[N(Bu)_4]_2NiBr_4$			
$4.66X^b - 0.16$	$4.02X - 0.18$	$3.88X - 0.20$	
$[N(Bu)_4]_2CoBr_4$			
$8.79X + 0.04$	$7.08X + 0.09$	$6.36X + 0.06$	
^{13}C			
C_α	C_β	C_γ	C_δ
$[N(Bu)_4]_2NiBr_4$			
$-0.6X - 0.4$	$-3.9X + 0.0$	$-6.3X + 0.0$	$-8.9X + 0.0$
$[N(Bu)_4]_2CoBr_4$			
$-2.3X + 0.0$	$-4.6X + 0.0$	$-8.4X + 0.0$	$-12.0X + 0.0$

[a] In parts per million upfield from the corresponding resonance of $[N(Bu)_4]_2CdBr_4$. [b] X denotes mole fraction of paramagnetic ion with respect to cadmium ion.

Table VI. Linear Inverse Temperature Dependences of Shifts of Pure Salts[a,b]

^1H		
H_α	$H_{\beta,\gamma}$	H_δ
$[N(Bu)_4]_2NiBr_4$		
$4.93 \times 10^3 T^{b-1} - 7.5$	$4.38 \times 10^3 T^{-1} - 6.8$	$4.34 \times 10^3 T^{-1} - 6.8$
^{13}C		
C_γ		C_δ
$[N(Bu)_4]_2NiBr_4$		
$-2.95 \times 10^3 T^{-1} + 0.2$		$-4.52 \times 10^3 T^{-1} + 0.0$
$[N(Bu)_4]_2CoBr_4$		
$-3.64 \times 10^3 T^{-1} + 0.0$		$-5.21 \times 10^3 T^{-1} + 0.0$

[a] In parts per million upfield from the corresponding resonance of $[N(Bu)_4]_2CdBr_4$. [b] Temperature in kelvin.

Table VII. i/δ Shift Ratios for Pure Melts at 148 °C

^1H			
H_α	$H_{\beta,\gamma}$	H_δ	
$[N(Bu)_4]_2NiBr_4$			
1.22	1.04	1.00	
$[N(Bu)_4]_2CoBr_4$			
1.36	1.09	1.00	
^{13}C			
C_α	C_β	C_γ	C_δ
$[N(Bu)_4]_2NiBr_4$			
0.11	0.42	0.71	1.00
$[N(Bu)_4]_2CoBr_4$			
0.14	0.41	0.70	1.00

Table VIII. Slope of Shift vs. $S'(S' + 1)$ at 148 °C

^1H			
H_α	$H_{\beta,\gamma}$	H_δ	
$[N(Bu)_4]_2NiBr_4$			
1.17	1.00	0.97	
$[N(Bu)_4]_2CoBr_4$			
1.71	1.38	1.23	
^{13}C			
C_α	C_β	C_γ	C_δ
$[N(Bu)_4]_2NiBr_4$			
−0.15	−0.98	−1.58	−2.23
$[N(Bu)_4]_2CoBr_4$			
−0.58	−0.90	−1.64	−2.34

locking compound (Me_2SO-d_6 or D_2SO_4) in the outer tube. The temperature was regulated by the Varian variable-temperature accessory and was checked before and after each experiment with a thermocouple. The controller was stable to within ±2 °C over periods of a few hours. The shifts were measured on at least two samples on two different occasions. The ^{13}C spectra were proton noise decoupled.

In order to be able to correct the observed shifts for the large bulk susceptibilities, the static susceptibilities were determined in an automatic recording Faraday balance[9] as functions of temperature and composition (dilution with the Cd(II) salt). For all the systems studied, the observed susceptibilities were reasonably linear in $1/T$ over the range measured. In addition, they were also found to be linear in composition, suggesting the absence of cooperative magnetic interactions. The effective dipole moments were extracted from the data, assuming Curie-Weiss behavior. (The differences between the values calculated for μ_{eff} for the powders and the melts are near the limits of reliability and may not necessarily be significant.)

The densities which were required to convert from the weight susceptibilities, as determined by the Faraday method, to the volume susceptibilities needed for the corrections were determined pycnom-

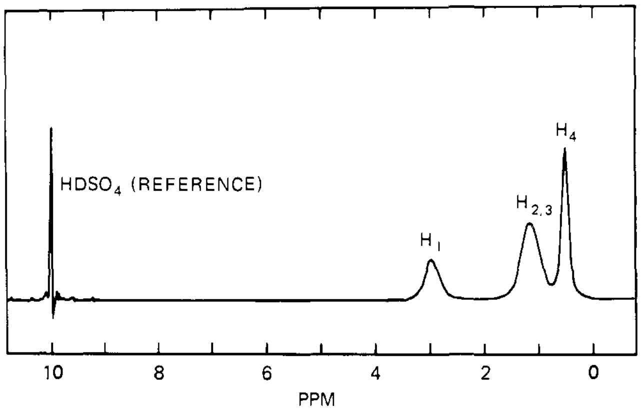

Figure 1. $[N(Bu)_4]_2CdBr_4$ ^1H spectrum at 148 °C.

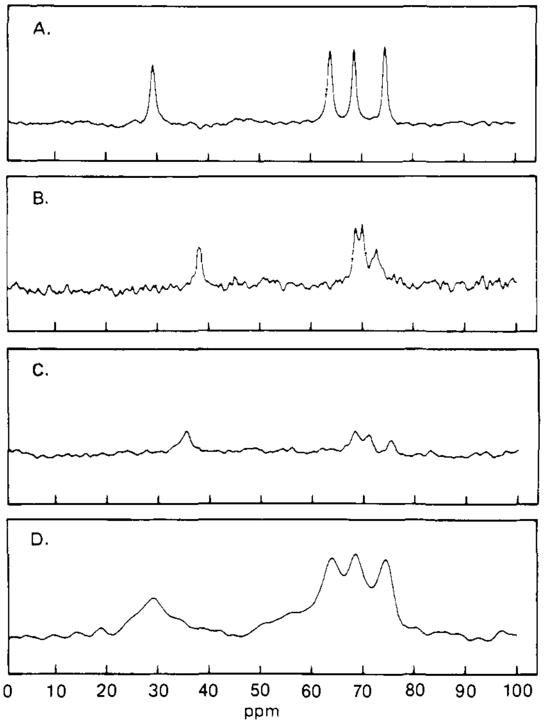

Figure 2. ^{13}C spectra over identical range, sweep width 100 ppm, origin arbitrary: (A) $[N(Bu)_4]_2CdBr_4$ at 140 °C; (B) $[N(Bu)_4]_2NiBr_4$ at 120 °C; (C) $0.5X[N(Bu)_4]_2CoBr_4$ at 140 °C; (D) $0.07X[N(Bu)_4]_2MnBr_4$ at 148 °C. X denotes mole fraction of paramagnetic ion with respect to cadmium ion.

etrically.[1c] The accuracy was better than 0.2% (which is sufficient for the purpose).

Results

A comparison of the densities and effective molecular volumes at 124 °C (Table I) shows the melts to be isomorphic and hence isodynamic to a good approximation. The magnetic susceptibilities near 119 °C and in the powder are given in Table III. The values of μ_{eff} in the powder are comparable with the values obtained for $[N(Et)_4]_2MBr_4$ salts, differences being attributable to cation and packing effects and to experimental scatter. An effective spin S' can be defined by

$$S'(S' + 1) = \mu_{eff}^2/g_e^2\beta_e^2 \tag{2}$$

where g_e is the free electron g value.

In the ^1H spectrum of $[N(Bu)_4]_2CdBr_4$, the β and γ peaks are merged, while in the ^{13}C spectrum all four peaks are distinct (Figures 1 and 2). The proton shifts of $[N(Bu)_4]_2MnBr_4$ were not observed owing to line broadening. The proton shifts of $[N(Bu)_4]_2NiBr_4$ and $[N(Bu)_4]_2CoBr_4$ solutions are all upfield, linear in concentration, and diminish down the chain (Figure 3, Table V). The proton shifts of $[N(Bu)_4]_2NiBr_4$ were studied as functions of temperature. They vary downfield with increasing temperature, being linear in $1/T$ over the temperature range studied and have large downfield values when extrapolated to infinite temperature (Figure 4, Table VI).

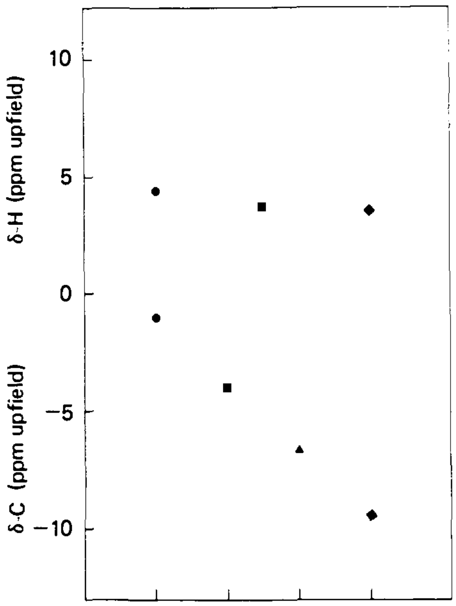

Figure 3. $[N(Bu)_4]_2NiBr_4$ ^1H and ^{13}C shifts in parts per million upfield from the corresponding resonance in $[N(Bu)_4]_2CdBr_4$ at 148 °C: (●) $^1H_\alpha$ or $^{13}C_\alpha$; (■) $^1H_{\beta,\gamma}$ or $^{13}C_\beta$; (▲) $^{13}C_\gamma$; (◆) $^1H_\delta$ or $^{13}C_\delta$.

Carbon shifts were measured for the nickel, cobalt, and manganese salts. Significant shifts for the manganese were observable only in the 0.07 mole fraction solution. For systems in which the electron spin relaxation time is much below the inverse nuclear Larmor frequency, the static and dynamic susceptibilities are the same. This is the case for the nickel and cobalt melts but not for the manganese. In the latter instance the dynamic susceptibility is less than the static one so that the correct susceptibility may be overestimated, leading to a shift that could be somewhat further upfield than the one obtained by use of the static value.[10] The raw observed shifts are downfield, so that the net shifts, while not precisely determined, are real.

The nickel and cobalt ^{13}C shifts are all downfield except for those at the two lowest temperatures studied, these being upfield (Figures 5 and 6). The nickel and cobalt ^{13}C shifts have similar temperature dependences. While the α carbon shift varies downfield (changing sign) with increasing temperature, the β carbon shift varies slightly downfield with increasing temperature, and the γ and δ carbon shifts are linear in $1/T$ over the range studied, having values near to zero when extrapolated to infinite temperature.

Whereas the proton shifts for the nickel and cobalt melts are both upfield, in dichloromethane solutions of the same salts[6] the cobalt shifts are upfield and the nickel shifts downfield, both decreasing in magnitude on moving downchain (away from the nitrogen) (Table II). The shifts of $N(Bu)_4Ph_3NiI_3$ and $N(Bu)_4Ph_3CoI_3$ in $CDCl_3$ have similar signs and downchain dependences to the dichloromethane case.[5b,c]

Like the paramagnetic contribution to the proton shifts, the paramagnetic contribution to the proton and ^{13}C relaxation rates decreases on moving downchain. Typical ι/δ shift ratios are given in Table VII. Typical $S'(S' + 1)$ dependences are shown in Table VIII. The C_α values in both tables cannot be taken as representative since they vary so much with concen-

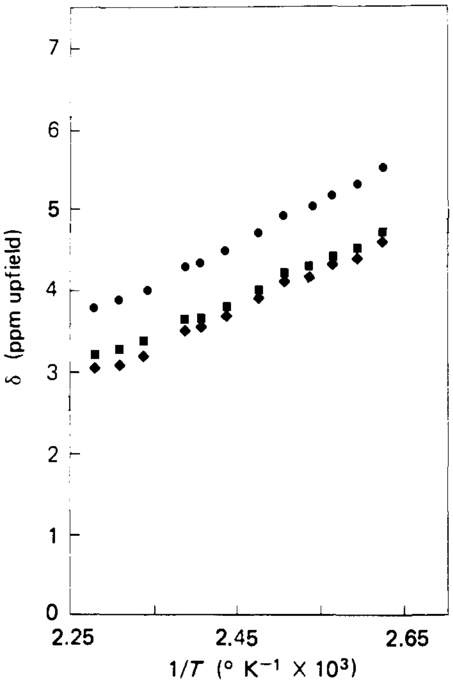

Figure 4. $[N(Bu)_4]_2NiBr_4$ ^1H shifts in parts per million upfield from the corresponding resonance of $[N(Bu)_4]_2CdBr_4$ vs. $1/T$: (●) $^1H_\alpha$; (■) $^1H_{\beta,\gamma}$; (▲) $^{13}C_\gamma$; (◆) $^1H_\delta$.

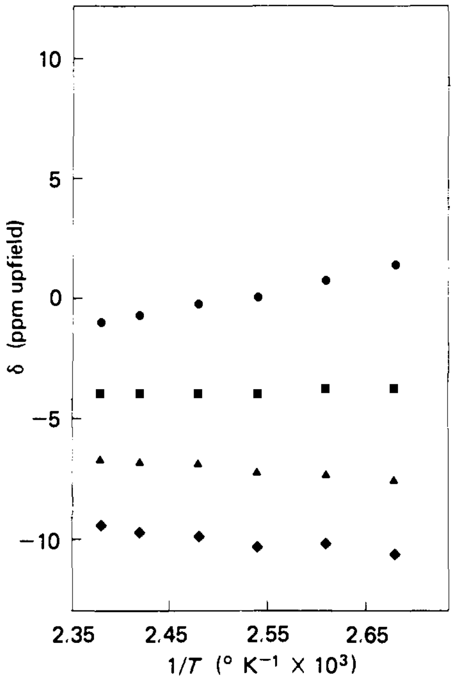

Figure 5. $[N(Bu)_4]_2NiBr_4$ ^{13}C shifts vs. $1/T$: (●) $^{13}C_\alpha$; (■) $^{13}C_\beta$; (▲) $^{13}C_\gamma$; (◆) $^{13}C_\delta$.

tration and temperature. The best agreement for both dependences is between the corresponding β–δ carbons of the nickel and cobalt melts.

Discussion

Almost all of the proton shifts are upfield whereas almost all of the carbon shifts are downfield. There must be some contact contribution to either or both of the nuclides' shifts, because the protons and their respective carbons describe much the same average paths, so that their respective values of the geometric factor $\langle(1 - 3\cos^2\theta)/r^3\rangle$ cannot have opposite signs.

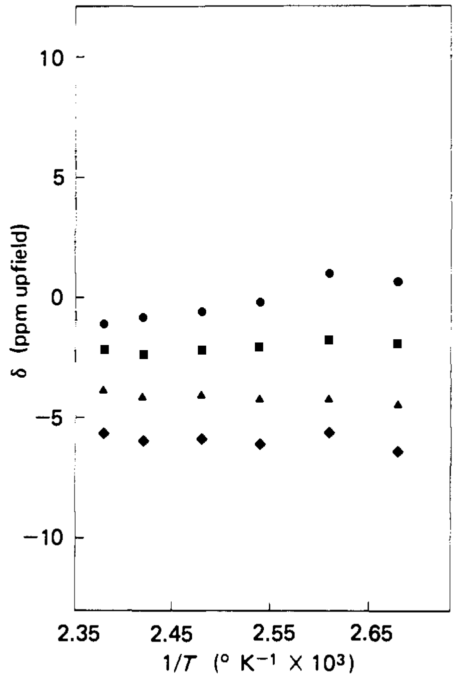

Figure 6. $[N(Bu)_4]_2CoBr_4$ ^{13}C shifts vs. $1/T$ for mole fraction = 0.5: (●) $^{13}C_\alpha$; (■) $^{13}C_\beta$; (▲) $^{13}C_\gamma$; (◆) $^{13}C_\delta$.

In treating the paramagnetic shifts in the fused $[N(Bu)_4]_2$-MBr_4 systems, it is important to note the significant difference between these systems and the ones composed of the same salts in dilute solutions in room temperature nonelectrolytic solvents. The latter have been extensively discussed in terms of dipolar shifts of ion pairs and the presumed accompanying anisotropic $\hat{g}$ tensor or susceptibility tensor of the paramagnetic ion.[5,6] In the fused salt system, however, there is no indifferent solvent. On the average the particles surrounding a given paramagnetic complex ion are all $N(Bu)_4^+$ ions so that any anisotropy in the magnetic susceptibility of the anion makes itself felt not only at the axially located cations but also on the equatorially placed ones. Consequently, for an anisotropic anionic susceptibility, both upfield and downfield shifts will be experienced by the various cations. Assuming rapid rotation and translational diffusion, any observed dipolar shift will reflect space and time averaging of the local magnetic fields.

The complete dynamical behavior of a liquid containing a nucleus of interest embedded in a large, nonspherical molecule and many nearest neighbors, some of which carry unpaired electrons, certainly cannot be modeled in detail. Nevertheless, it is possible to obtain some useful results which will permit discussion of the role of various properties of specific systems.[11]

Vega and Fiat[13] have argued that this sort of system can be treated by use of the orientation-dependent density matrix without consideration of the relaxation processes. Then the intramolecular pseudocontact shift is given by the equation of Kurland and McGarvey:[12]

$$\left(\frac{\Delta H}{H}\right)_{\rm dip} = \frac{1}{2r^3}\left[(1 - 3\cos^2\theta) \times \left(\frac{2}{3}\chi_{zz} - \frac{1}{3}\chi_{xx} - \frac{1}{3}\chi_{yy}\right) + \sin^2\theta\cos 2\Omega(\chi_{yy} - \chi_{xx})\right] \quad (3)$$

where $\hat{\mathbf{r}}$ is the interspin vector, $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ are unit vectors along the principal magnetic axes of the anion, with $\hat{\mathbf{z}}$ along the axis of symmetry, $\{\chi_{ii}\}$ are the components of the susceptibility tensor along these axes, and $(\hat{\mathbf{r}}\cdot\hat{\mathbf{z}})/|\hat{\mathbf{r}}| = \cos\theta$ and $(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}})/|\hat{\mathbf{r}}| = \sin\theta\cos\Omega$. The generalization of (3) to the case where r, θ, and Ω are not constant and there are N equivalent nuclei in rapid exchange which feel the effects of a single anion is given by

$$\left(\frac{\Delta H}{H}\right)_{\text{dip}} = \left(\int \rho(r,\theta,\Omega)\frac{1}{2r^3} \times \left\{(1-3\cos^2\theta)\left(\frac{2}{3}\chi_{zz} - \frac{1}{3}\chi_{xx} - \frac{1}{3}\chi_{yy}\right) + \sin^2\theta\cos 2\Omega(\chi_{yy}-\chi_{zz})\right\}\mathrm{d}V\right)\Big/\int \rho(r,\theta,\Omega)\,\mathrm{d}V \quad (4)$$

where $\rho(r, \theta, \Omega)$ is the distribution function of the observed nucleus in the anionic frame normalized so that $\int\rho(r,\theta,\Omega)\,\mathrm{d}V = N$. Equation 4 is expected to hold independently of the relative magnitudes of $1/\tau_{1s}$, the electron spin-lattice relaxation rate, $|\nu_{\max} - \nu_{\min}|_{\text{nuclear}}$, and $\{\tau_i\}$, where $\{\tau_i\}$ are the times that characterize the motional modulation of $\hat{\mathbf{r}}$.

For an ion pair in room temperature solution, in which there is no preferred mutual configuration, the distribution of the diamagnetic counterions and hence the observed nuclei will be spherically symmetric such that $\rho(r, \theta, \Omega) = \rho(r)4\pi$ and (4) will equal zero even if $\tilde{\chi}$ is anisotropic.[5]

Lamar and others explained the observed shifts in terms of a pseudocontact mechanism by postulating that the ion is locked into a preferred configuration so that $\rho(r, \theta, \Omega) \neq 4\pi\rho(r)$. If, in addition to this, $\tilde{\chi}$ is anisotropic, $(\Delta H/H)_{\text{dip}} \neq 0$.[5]

In the fused salt, however, there can be no preferential bonding or ion pairing between anion and cation. Each cation is surrounded at all times by approximately four nearest-neighboring anions, while each anion is surrounded at all times by approximately six nearest-neighboring cations. The distribution function of the cations around the anion will be continuous and roughly spherical.[8] If $\rho(\theta, \Omega, r)$ is of tetrahedral or higher symmetry, by (4) $(\Delta H/H)_{\text{dip}} = 0$, even if $\tilde{\chi}$ is anisotropic. However, the contact shift, which results from a scalar rather than a vectorial interaction, will not be quenched by the symmetry of the melt, but rather will be enhanced by the greater number of anions coordinating a cation.

Some characteristics of the real melt may require us to modify conclusions drawn from this model. $\rho(\theta, \Omega, r)$ may contain terms of lower than tetrahedral symmetry due to slightly asymmetric packing and the rattling of the anion in the cation cage. Also, the cations may induce anionic anisotropy so that the interspin vector $\hat{\mathbf{r}}$ will be correlated with the electron magnetic moment $\hat{\mu}$. Still, for realistic anionic displacements, the shifts felt by the various coordinating cations can be shown to largely cancel each other out (Appendix A). Also the fairly symmetric Coulombic potential felt by the anion in the melt will be less likely to distort it than the asymmetric potential felt in the ion pair, again leading to a reduced shift (Appendix A).

We conclude then that the dipolar shift in the melt must be smaller than in the corresponding ion pair. However, the observed ^{1}H shifts in the ion pair are generally much smaller than in the melt (Tables II and V). This means that the dipole-dipole interaction cannot be the dominant factor producing the paramagnetic shifts in the fused salt systems, even if it is the main source of the shifts in the dilute, room temperature systems.

Estimates of the maximum possible dipolar shifts in the melts, based upon $[N(Et)_4]_2MBr_4$ crystal anisotropies, are much smaller than the observed shifts (Appendix B). Since the electron-nuclear interaction is predominantly dipolar (part 2) the shift due to higher order terms in the multipolar expansion is even smaller. Such shifts have only been established intramolecularly, and then over one or two bonds at most, and are mentioned only for completeness.[14]

Table IX. $\rho_N \times 10^4$ at 148 °C

^{1}H			
H_α	$H_{\beta,\gamma}$	H_δ	
$[N(Bu)_4]_2NiBr_4$			
−0.288	−0.246	−0.236	
$[N(Bu)_4]_2CoBr_4$			
−0.456	−0.362	−0.329	
^{13}C			
C_α	C_β	C_γ	C_δ
$[N(Bu)_4]_2NiBr_4$			
0.0114	0.0431	0.0729	0.1030
$[N(Bu)_4]_2CoBr_4$			
0.0160	0.0423	0.0723	0.1025
$[N(Bu)_4]_2MnBr_4$			
0.0593	0.0489	0.0454	0.0454

It also follows from the above considerations that the melt pseudocontact shift per mole fraction of paramagnetic will decrease with increasing paramagnetic concentration. The linear concentration dependence of most of the shifts provides added evidence against a significant pseudocontact contribution.

Having ruled out a predominantly dipolar origin of the observed shifts, we consider a predominantly contact mechanism. A quantitative theoretical treatment is beyond the scope of this study, but a contact mechanism is consistent with the order of magnitude of the proton and carbon shifts, their different signs, and downchain and temperature dependences. Pople and coworkers[15] have found that observed shifts can be related to molecular structure fairly accurately and reasonably by

$$\rho_N S'(S'+1) = \frac{A_N}{K_N} = -\left(\frac{\Delta H}{H}\right)_{\text{con}} \frac{3\hbar\gamma_N kT}{g_e\beta K_N}$$

where ρ_N is the effective one-electron spin density in the s orbital and K_N is a constant related to the charge density at the nucleus. They found $K_H = 540$ and $K_C = 820$.

Typical values of ρ_C and ρ_H computed from our data assuming a completely contact shift are given in Table IX. For the Curie law shifts ρ is empirically independent of temperature. For nickel and cobalt, $\rho S'(S' + 1)$ at the β carbons increases with temperature, and at the α carbons it increases with temperature dramatically, going from negative to positive values. For both the nickel and cobalt salts, the corresponding $\rho_H S'(S' + 1)$ and $\rho_C S'(S' + 1)$ values differ only by a constant offset. (For the α carbons, however, this is an artifact due to the temperature chosen.) The values for the β–δ carbons of the nickel and cobalt salts are very similar.

Spin "on" one entity can induce spin "on" another by either spin transfer in which the induced spin is pointing up (ρ positive) or spin polarization in which it is pointing down (ρ negative). The first mechanism will lead to a downfield shift, the second to an upfield shift.[16] Since the d orbitals of the metal ion alone are quite attenuated in the regions of the hydrogen and carbon atoms, the interaction probably is via the bromides. (Chestnut[17] found a ^{35}Cl contact shift in $CoCl_2/HCl$ solutions.)

It has been suggested that the spin density enters via bonding to the nitrogen and propagates down the chain[7a,b] or that it may enter via the α hydrogen.[7c] The experimental work on alkyl radicals[18] indicates that at the carbon γ to the unpaired spin the propagated spin is reduced by over an order of magnitude. Therefore, the primary mechanism cannot involve entry at an upchain point and propagation down the chain.

Rather we suggest that most of the effect is due to the spin

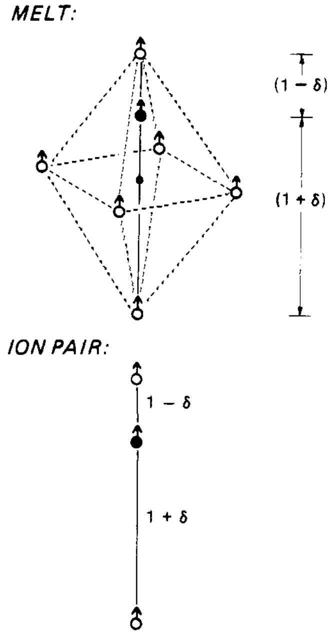

Figure 7. Simple model illustrating quenching of pseudocontact shift: (●) anion; (○) cation.

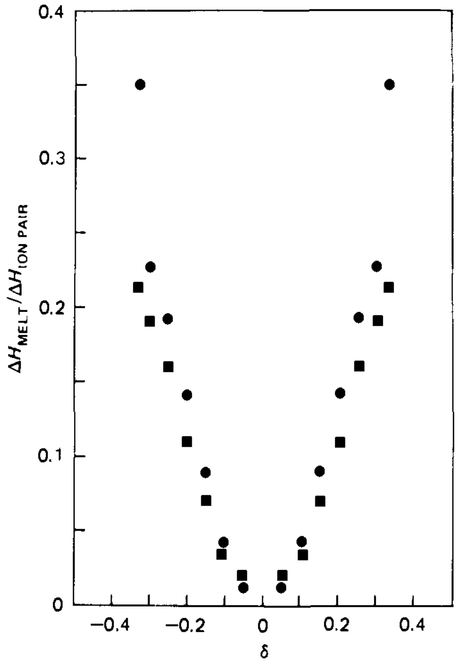

Figure 8. Ratio of shifts in melt and ion pair as a function of fractional displacement: (■) permanent anisotropy; (●) ion-induced anisotropy.

being transferred or induced onto the atoms containing the observed nuclei directly from the bromide or at most through one extra bond. The carbon shifts are mostly due to spin transfer, the proton shifts to spin polarization. Very small spin densities are involved here, so that only very small admixtures into the pristine unimolecular wave function, which in a condensed phase only approximates a very messy reality, are necessary. The difference between the hydrogen and carbon shifts, and their downchain dependences, results both from differences in molecular structure and configurational averaging with respect to the anion. Spin transfer via the nitrogen might influence the shifts over one or two bonds.

Free radical induced ^1H and ^{13}C contact shifts have been observed[19] and INDO calculations based upon plausible configurations performed, obtaining results similar to those observed; for some systems the proton shifts were upfield and the carbon shifts downfield just as in ours.

The similarity of the corresponding ρs of the β-δ carbons of the nickel and cobalt salts indicates similar spin transfer mechanisms for these sites. The differences at the other nuclei are attributable to differences in anionic structure and slight differences in packing.

Some indication of the coexistence of spin transfer and spin polarization mechanisms can be found from the temperature dependence. For dominant spin polarization the shifts will tend downfield with increasing temperature as $1/T$, as is the case for the nickel protons. For dominant spin transfer, the shifts will go upfield with increasing temperature with $1/T$, as is the case for the nickel and cobalt γ and δ carbons. Since the net shift goes downfield with increasing temperature, for the nickel and cobalt α carbons, the spin polarization mechanism seems to have a stronger temperature dependence (the nickel proton shifts for which spin polarization predominates vary more steeply with temperature than any of the carbon shifts for which spin transfer predominates). For the β carbons, the slight net downfield shift means that the two temperature dependences nearly cancel out.

Conclusion

We have found that the pseudocontact contribution to the shifts observed in the tetrabutylammonium tetrabromometalate system is largely quenched because of the nature of the melt and that the shifts are principally attributable to the contact contribution. Such quenching does not occur for the ion pair found in dilute solutions in indifferent low dielectric constant solvents where both contributions to the shift are present. A framework for the interpretation of interspecies electron-nuclear spin interactions in magnetically concentrated liquids has been established.

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Appendix A

Let $\rho_{sy}(\theta, \Omega, r)$ contain all terms of $\rho(\theta, \Omega, r)$ of tetrahedral or higher symmetry and let $\rho_{asy}(\theta, \Omega, r)$ contain the rest. As the various kinds of spectra of these melts are of liquid rather than of solid character, the distribution function of the cations around the anion is approximately spherical.[2,8] Given the symmetry of the cation and the rotational freedom of its chains, the distribution functions of its sets of equivalent observed nuclei are also highly symmetrical.[2,8] Then without knowing $\rho(\theta, \Omega, r)$ exactly we may state that

$$\int \rho_{sy}(\theta, \Omega, r)\,dV \gg \int \rho_{asy}(\theta, \Omega, r)\,dV \qquad (A1)$$

so that the effect of the lower symmetry terms may be regarded as a perturbation and that the pseudocontact shift is largely quenched.

$\hat{\chi}$ anisotropy can be either intrinsic[20] or cation induced.[5d,6] The effect of each of these on the pseudocontact shift in the melt relative to the corresponding ion pair may be seen in terms of a simple model (Figure 7).

Let the anion in the melt be octahedrally coordinated by cations at unit distance with $\hat{\chi}$ axially symmetric with $\hat{\mathbf{z}}$ oriented along a diagonal of the octahedron. Let the observed nucleus be at the center of the cations and let the anion be displaced a distance δ along the $\hat{\mathbf{z}}$ axis. For the ion pair let everything be the same as in the melt except that there are only two cations at unit distance along the $\hat{\mathbf{z}}$ axis. $\Delta H_{\text{melt}}/\Delta H_{\text{ion pair}}$ as a function of δ is given in Figure 8.

It is seen that the presence of the other ions experiencing the nonaxial shifts greatly reduces the average shifts below those of the free ion pair (indeed to zero for the equilibrium position). A maximum plausible value for δ is about 0.2. The actual melt is much more complicated but the same general considerations hold. That each cation is surrounded by approximately four anions also tends to reduce the net pseudocontact shift.

Strictly (4) cannot be applied to ion-induced anisotropy because ρ and $\hat{\chi}$ do not vary independently. However, we can gain insight into the relative effects of ion-induced anisotropy by considering the shift due to a distortion resulting from a single anion–cations configuration preaveraged with respect to the applied field. Using the same geometric model (Figure 7) and assuming that ($\Delta\chi = \chi_{\parallel} - \chi_{\perp}$) is linear in E_z (the electric field along $\hat{\mathbf{z}}$) both $\Delta\chi$ and ($\Delta H/H$) can be calculated. $\Delta H_{\text{melt}}/\Delta H_{\text{ion pair}}$ as a function of δ is given in Figure 8. The symmetry of the melt reduces both the ion-induced anisotropy and shift due to it relative to the ion pair. This follows from the symmetry of their respective ρs, whatever their detailed form might actually be.

Appendix B

We can estimate an upper limit to the pseudocontact contribution to the shift as follows. The two extreme cases of the observed shift are the ion pair, with the cations antipodal, for which the shift is a maximum, and the structure in which the anions form a perfect tetrahedron around the cation, itself tetrahedral, for which the shift vanishes. The melt falls between these two extremes but it is closest to the perfectly tetrahedral case. For want of the ability to model the melt from first principles, we can think of it as an admixture of these two states, with the observed shifts a linear combination of the shifts in these states. We estimate the ion pair character of the melt to be <10%. An absolute upper limit would be about 25%. This last value would correspond to a much less ordered structure than is the case.

The ion-pair contribution to the melt shift can be estimated by

$$\left(\frac{\Delta H}{H}\right) = \frac{1}{3}\left\langle\frac{1 - 3\cos^2\theta}{r^3}\right\rangle \Delta\chi n \qquad \text{(B1)}$$

where $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ and n is the number of coordinating anions. Estimating $n = 4$, $r = 4.1$ Å, and $\langle 1 - 3\cos^2\theta\rangle = -1$, then, $(\Delta H/H) = -1.94 \times 10^{22}\Delta\chi$.

The molar anisotropy of $[N(Et)_4]_2CoBr_4$ at 298.4 K is 1.57×10^{-4} cgsu ($\Delta\chi/\chi = 1.6 \times 10^{-2}$).[21a] We assume that the crystal is isomorphic with $[N(Et)_4]_2NiCl_4$, whose crystalline axes coincide with its anionic symmetry axes. Extrapolating $\Delta\chi$ from room temperature values by assuming linearity in $1/T$ we get $(\Delta H/H) = -0.28$ ppm for 10% ion-pair character and -0.70 ppm for 25% ion-pair character. For 10% ion-pair character the pseudocontact contribution is ≤10% to all of the shifts save that of the α carbon. For 25% character, the pseudocontact contribution is ≤10% to all of the shifts but those of the α and β carbons. The rest of the shifts may be assigned to the contact mechanism.

$\Delta\chi$ for the nickel salt may be estimated from $[N(Et)_4]_2NiBr_4$ yielding $\Delta\chi = -5.60$ ppm for full, -0.56 for 10%, and -1.40 for 25% ion-pair character. For the 10% case, the pseudocontact shift is ≤15% for all of the nuclei but the α carbon, for the 25% case ≤35% for all of the nuclei but the α and β carbons. This calculation is approximate, but shows that the pseudocontact contribution to the nickel melt shift is greater than to the cobalt melt and that it might be significant. However, the net cobalt melt shift is greater than that of the nickel indicating a predominant contact mechanism.

No value of $\Delta\chi$ for any salt of $MnBr_4^{2-}$ is in the literature, to the best of our knowledge, possibly because it is so small. Because of this, and its phosphorescence, we take it to be magnetically isotropic and attribute its shift entirely to the contact mechanism.

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