Hydrogen-1 Nuclear Magnetic Resonance Studies of the Ion Association of some Unsymmetrically Substituted Tetra-alkylammonium Tribromo-(triphenylphosphine)cobaltate(II) Complexes in Various Solvents

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The concentration association constant of [NMe(n-C_8H_{17})$_3$][CoBr$_3$(PPh$_3$)] in nitrobenzene at 34 °C has been determined by n.m.r. spectrometry. On comparing this result with those obtained earlier for [NRBu$^n{}_3$][CoBr$_3$-(PPh$_3$)] (R = Me and Bu^n), it is concluded that the symmetry of the cation plays a very important role in determining the extent of ion association for this type of ion-pair complex. There is a linear correlation between the observed difference in isotropic shift of the *N*-methyl and *N*-methylene protons and the dielectric constant (ε) of the solvents for $\varepsilon \leqslant 10$, but not at higher values of ε. This is interpreted in terms of the preferred orientation of the *N*-methyl group towards the anion, the decrease in interionic distance with decreasing ε, the formation of micelles in solvents of low dielectric constant, and the 1 : 1 ion-pair formation in solvents of higher dielectric constant. The problem of analyzing the concentration dependence of observed isotropic shifts in solvents of low dielectric constant is discussed.

THE isotropic n.m.r. shift of cationic protons in the presence of paramagnetic anions can serve as a powerful tool for investigating ion pairing in electrolyte solutions.[1] The shift is generally believed to arise from the following two terms:[1-3] the Fermi contact shift and the dipolar or 'pseudo-contact' shift. Although there is still the problem of estimating the relative contribution of the contact and dipolar shift to the total isotropic shift,[1] certain useful conclusions concerning the ion-pair geometries and concentration association constants can still be obtained from isotropic shift measurements.[4,5]

In our earlier study[5] of [NMeBu$_3$][CoBr$_3$(PPh$_3$)] in non-aqueous solvents by ^{1}H n.m.r. spectroscopy it was found that the observed *N*-methyl shift (with reference to the diamagnetic analogue) was greater than that of the *N*-methylene shift, and that the signal for the *N*-methyl protons was very much broader than that of the *N*-methylene protons in solvents of low dielectric constant. It was also qualitatively observed that the shift difference between these two types of protons increased with decreasing dielectric constant of the solvent and that in propylene carbonate, of relatively high dielectric constant, the shift difference was no longer detectable. This observation has been rationalized in terms of a reduction in interionic distance with decreasing dielectric constant, and a preferred orientation of the asymmetrical quaternary ammonium ion with respect to the magnetic axis of the anion. In order to examine this result more thoroughly, we have carried out further work on this complex and also examined the analogous complex [NMe(C_8H_{17})$_3$][CoBr(PPh$_3$)] where the cation is bulkier. The results from this study further confirm the trend in shift difference and also throw some light on the relative importance of the size and symmetry of the cation on the extent of ion association.

EXPERIMENTAL

Preparation of Complexes.—The salt [NMe(n-C_8H_{17})$_3$]Br was prepared by treating N(n-C_8H_{17})$_3$ (Fluka) with MeBr (Fluka, Purum) using a mixture of cyclohexane and acetone as solvent in the dark. The complex [NMe(n-C_8H_{17})$_3$]-[CoBr$_3$(PPh$_3$)] was prepared by a method based on that of Rettig and Drago[6] with a slight modification in the precipitation step. That is, in order to precipitate the complex, the solvent (acetone) had to be completely removed, followed by the addition of a mixture of diethyl ether and light petroleum and cooling in a bath of solid CO_2. The complex is photosensitive and was dried in the dark *in vacuo* over silica gel, m.p. 71—72.5 °C (uncorrected) (Found: C, 55.45; H, 7.35; Br, 25.9. Calc. for $C_{43}H_{69}Br_3CoNP$: C, 55.55; H, 7.45; Br, 25.8%). The zinc(II) analogue was prepared in the same way, m.p. (uncorrected) 55—57 °C (Found: C, 54.0; H, 7.30; Br, 25.2. Calc. for $C_{43}H_{69}Br_3$-NPZn: C, 55.15; H, 7.40; Br, 25.65%). The complex [NMeBu$^n{}_3$][CoBr$_3$(PPh$_3$)] and its zinc(II) analogue were samples obtained previously.[5]

Analyses were by the Australian Microanalytical Service, Division of Applied Chemistry, CSIRO, and the University of Melbourne. All solvents used in this work were purified according to methods described earlier.[4,5]

N.m.r. Measurements.—The n.m.r. spectra were obtained on a Hitachi–Perkin-Elmer R-20B spectrometer with a probe temperature of 34 °C. Tetramethylsilane was used as the internal reference.

The data obtained in nitrobenzene were treated according to the 1 : 1 association equilibrium (1) by the Rose–

$$\mathrm{C} + \mathrm{A} \rightleftharpoons \mathrm{CA} \quad (\mathrm{C} = \text{cation};\ \mathrm{A} = \text{anion}) \qquad (1)$$

Drago method as described previously.[4] No attempt was made to fit the data in solvents of low dielectric constant ($\varepsilon \leqslant 10$) as it is now well documented that a simple 1 : 1 association model cannot be used to describe such systems. For [NMe(n-C_8H_{17})$_3$][CoBr$_3$(PPh$_3$)], the *N*-methylene proton shifts were measured directly, but in solvents with $\varepsilon < 6$ the resonance signals of the *N*-methyl protons at 0.06 mol dm^{-3} concentration were located in a region beyond the range of our n.m.r. spectrometer and hence their positions were determined indirectly by a mole-ratio method,[7] *i.e.*

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[1] For a review see G. N. La Mar in 'N.M.R. of Paramagnetic Molecules' eds. G. N. La Mar, W. Dew. Horrocks, jun., and R. H. Holm, Academic Press, New York, 1973, ch. 10.

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[6] M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, 1966, **88**, 2966.

[7] J. C. Fanning and R. S. Drago, *J. Amer. Chem. Soc.*, 1968, **90**,3987.

by extrapolating a plot of the observed isotropic shift against the mole fraction of the paramagnetic complex in solutions containing various amounts of the paramagnetic and diamagnetic species and where the overall cation concentration was kept constant at 0.06 mol dm^{-3}. The reliability of this method was confirmed by the good agreement between the *N*-methylene shift values which were measured directly and those obtained by this method.

TABLE 1

Equilibrium-constant data for $[\text{NMe}(n\text{-C}_8\text{H}_{17})_3][\text{CoBr}_3(\text{PPh}_3)]$ in nitrobenzene at 34 °C

[Complex]/ mol dm^{-3}	$\Delta\nu(\text{N–CH}_3)$ [a]		$\Delta\nu(\text{N–CH}_2)$ [a]	
	Obs. (±2.0 Hz)	Calc.	Obs. (±2.0 Hz)	Calc.
0.010	61.0	61.2	48.0	48.2
0.015	79.0	78.5	63.0	62.1
0.020	91.0	91.8	74.0	73.0
0.025	104.0	102.6	82.0	81.8
0.030	111.0	111.6	87.0	89.2
0.035	119.0	119.3	94.0	95.5
0.040	*b*		100.0	101.0
0.045	*b*		105.0	105.8
0.060	*b*		121.0	117.5

[a] The diamagnetic reference complex was $[\text{NMe}(n\text{-C}_8\text{H}_{17})_3][\text{ZnBr}_3(\text{PPh}_3)]$. [b] The N–CH$_3$ peaks overlapped with the other aliphatic hydrogen peaks at these concentrations.

TABLE 2

Effects of the cations on the association parameters in nitrobenzene [a]

Cation	$\Delta\nu_p$/Hz	K_{as}/dm^3 mol^{-1}
$[\text{NMe}(n\text{-C}_8\text{H}_{17})_3]^+$	290 ± 9 [b]	33.9 ± 2.2
	239 ± 7 [c]	31.6 ± 1.8
$[\text{NMeBu}^n{}_3]^+$ [d]	257 ± 7 [b]	38.1 ± 2.3
	226 ± 4 [c]	36.0 ± 1.6
$[\text{NBu}^n{}_4]^+$ [e]	265 ± 15 [c]	17.9 ± 1.4

[a] The anion is $[\text{CoBr}_3(\text{PPh}_3)]^-$. [b] Isotropic shift for *N*-methyl protons. [c] Isotropic shift for *N*-methylene protons. [d] From ref. 5. [e] From ref. 4.

RESULTS AND DISCUSSION

The isotropic shifts for $[\text{NMe}(n\text{-C}_8\text{H}_{17})_3][\text{CoBr}_3(\text{PPh}_3)]$ at various concentrations were obtained in carbon tetrachloride, chloroform, and nitrobenzene. The general shift pattern with concentration was the same as before [4,5] and there is no need for further discussion here. The treatment of the data in nitrobenzene is summarized in Table 1, where there is a good fit between the observed and calculated isotropic shifts. The concentration association constant, K_{as}, is 32.8 ± 2.0, the average of the values obtained from the observed isotropic shifts of the *N*-methyl and *N*-methylene protons. It is interesting to compare the K_{as} value with those for the cations $[\text{NMeBu}^n{}_3]^+$ and $[\text{NBu}^n{}_4]^+$ obtained earlier,[4,5] and the results summarized in Table 2 show that the trend in K_{as} values is as follows: $[\text{NMeBu}^n{}_3]^+ > [\text{NMe}(n\text{-C}_8\text{H}_{17})_3]^+ > [\text{NBu}^n{}_4]^+$.

Based on conductance measurements, Evans *et al.*[8] reported that, for the symmetrical tetra-alkylammonium halides and picrates in acetonitrile and methanol, the association constant increases with decreasing size of the cation. However, our finding that K_{as} for $[\text{NMe}(n\text{-C}_8\text{H}_{17})_3]^+$, a larger cation, is greater than that for $[\text{NBu}^n{}_4]^+$ indicates that, besides the size factor, the symmetry of the cation also has to be taken into consideration. For cations having the same symmetry, the trend reported by Evans *et al.*[8] still holds. The role played by symmetry can be understood if we recall our earlier finding [5] that on the average the *N*-methyl group is nearer to the anion than the *N*-methylene group in the ion pair. Thus as far as the steric requirement for approach of the cation to the anion is concerned, both $[\text{NMe}(n\text{-C}_8\text{H}_{17})_3]^+$ and $[\text{NMeBu}^n{}_3]^+$ would have similar size effects and hence the concentration association constants are quite comparable. On the other hand, $[\text{NMe}(n\text{-C}_8\text{H}_{17})_3]^+$ would appear to be smaller in size than $[\text{NBu}^n{}_4]^+$ from the anionic point of view and hence would give a larger K_{as} value.

The n.m.r. data for solutions of 0.059 mol dm^{-3} $[\text{NMeBu}^n{}_3][\text{CoBr}_3(\text{PPh}_3)]$ and 0.06 mol dm^{-3} $[\text{NMe}(n\text{-C}_8\text{H}_{17})_3][\text{CoBr}_3(\text{PPh}_3)]$ at 34 °C in various nonaqueous solvents are listed in Tables 3 and 4. As can be seen, in the region of low dielectric constant there is no relation between $\Delta\nu(\text{N–CH}_3)^0$ and ε or between $\Delta\nu(\text{N–CH}_2)^0$ and ε for either complex. This result is at variance with that obtained from the $[\text{NMe}(n\text{-C}_8\text{H}_{17})_3]_3[\text{Fe(CN)}_6]$ system by Fanning and Drago [7] where a linear relation between $\Delta\nu(\text{N–CH}_3)^0$ and ε was found. In order to account for the observation that hydrogen-bonding solvents also fall on the linear plot for the 3 : 1 electrolyte, they proposed that the bulky cation can

TABLE 3

N.m.r. data [a] for 0.059 mol dm^{-3} solutions of $[\text{NMeBu}^n{}_3][\text{CoBr}_3(\text{PPh}_3)]$

Solvent	ε [b]	$\Delta\nu(\text{N–CH}_2)^0$ [c]	$\Delta\nu(\text{N–CH}_3)^0$ [c]	$\delta(\Delta\nu_H{}^0)$ [d]	$\Delta\nu(\text{N–CH}_3)^0 : \Delta\nu(\text{N–CH}_2)^0$
			Hz		
Chloroform	4.56	450	745	295	1.66
Bromobenzene	5.27	507	798	291	1.57
Chlorobenzene	5.47	505	787	282	1.56
Methylene chloride	8.57	372	553	181	1.49
1,2-Dichloroethane	9.86	243	364	121	1.50
o-Nitrotoluene	25.3	160	198	38	1.24
Nitrobenzene	33.2	115	132	17	1.15
Propylene carbonate	63.0	8	9	1	1.13

[a] At 60 MHz and 34 °C. [b] Dielectric constant data from ' Handbook of Chemistry and Physics,' 53rd edn., The Chemical Rubber Co., and corrected for the temperature effect. [c] Observed isotropic shift for *N*-methylene and *N*-methyl protons. The error is estimated to be ±2 Hz for the *N*-methylene protons, ±4 Hz for the *N*-methyl protons, except in nitrobenzene and propylene carbonate where it is ±2 Hz. The diamagnetic reference complex was $[\text{NMeBu}^n{}_3][\text{ZnBr}_3(\text{PPh}_3)]$. [d] $\Delta\nu(\text{N–CH}_3)^0 - \Delta\nu(\text{N–CH}_2)^0$.

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[8] D. F. Evans, C. Zawoyski, and R. L. Kay, *J. Phys. Chem.*, 1965, **69**, 3878.

form micelles and hence shield the anion from the specific influence of the solvent. In the light of that proposition, our finding would seem to suggest that for the 1 : 1 electrolyte the clusters of bulky cations are not able to protect the anion from specific interactions of the solvents. Further work to examine the effects of the charge on the anion or any other factors is now in progress.

TABLE 4

N.m.r. data [a] for 0.06 mol dm^{-3} solutions of $[NMe(n\text{-}C_8H_{17})_3][CoBr_3(PPh_3)]$

Solvent	ε [b]	$\Delta\nu(N{-}CH_2)^0$ [c]	$\Delta\nu(N{-}CH_3)^0$ [c]	$\delta(\Delta\nu_H{}^0)$ [d]	$\Delta\nu(N{-}CH_3)^0 : \Delta\nu(N{-}CH_2)^0$
			Hz		
Carbon tetrachloride	2.21	504	1 026 [e]	522	2.04
Benzene	2.26	611	1 106 [e]	495	1.81
Chloroform	4.56	529	946 [e]	417	1.79
Chlorobenzene	5.47	602	991 [e]	389	1.65
Methylene chloride	8.57	393	646	253	1.64
1,2-Dichloroethane	9.86	259	416	157	1.61
o-Nitrotoluene	25.3	176	220	44	1.25
Nitrobenzene	33.2	121	146 [f]	25	1.21
Propylene carbonate	63.0	11	11	0	1.00

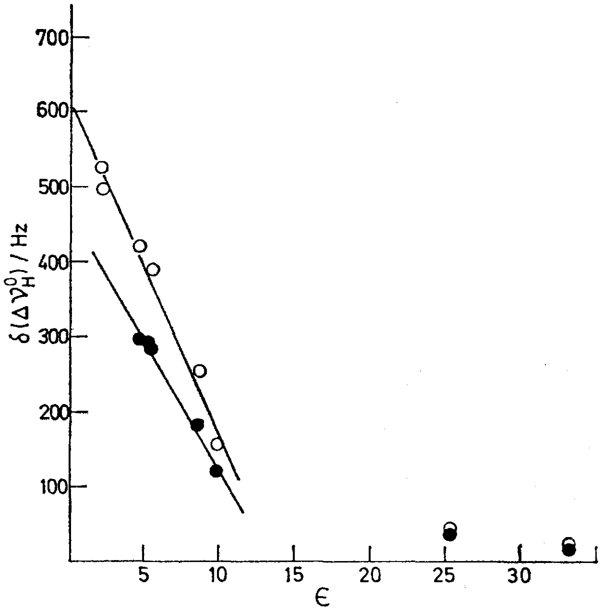
[a] At 60 MHz and 34 °C. [b] Dielectric constant data from ' Handbook of Chemistry and Physics,' 53rd edn., The Chemical Rubber Co., and corrected for temperature effect. [c] Observed isotropic shift for *N*-methylene and *N*-methyl protons. The error is estimated to be ±2 Hz for the *N*-methylene protons and ±4 Hz for the *N*-methyl protons, except in nitrobenzene and propylene carbonate where it is ±2 Hz. [d] $\Delta\nu(N{-}CH_3)^0 - \Delta\nu(N{-}CH_2)^0$. [e] Determined by the mole-ratio method (see text); error, ±6 Hz. [f] Calculated by substituting K_{as} and $\Delta\nu_p$ values in equation (2) of ref. 5.

Although at a fixed concentration of electrolyte, the observed isotropic shifts are dependent on the specific interactions of the solvents, we would expect the observed shift difference between the *N*-methyl and the *N*-methylene protons to be rather independent of them and it would be of interest to see how this difference correlates with the bulk dielectric constant of the solvent. As can be seen from the Figure, the plot of the observed shift difference, $\delta(\Delta\nu_H{}^0)$, against ε has three distinct regions: namely, a region ($\varepsilon \approx 2$—10) where a linear correlation exists; a second region ($\varepsilon \approx 20$—35) where the shift difference is not collinear with the points in the first region; and a third region where the shift difference is not detectable ($\varepsilon \geqslant 60$; this region is not shown in the Figure). In order to rule out the possibility of coincidence at a certain concentration, we made a similar investigation for 0.101 mol dm^{-3} $[NMeBu^n{}_3][CoBr_3(PPh_3)]$ in various solvents and found that the same kind of relation holds. The general decrease in shift difference with dielectric constant is consistent with previous findings[5] that there is a preferred orientation of the *N*-methyl group and that the interionic distance increases with increasing dielectric constant. In solvents of low dielectric constant the interionic distance is so short that it hinders free movement of the cation with respect to the anion in the ion-pair structure and as a result the shift of the *N*-methyl protons is very large. As the dielectric constant increases, the interionic distance increases and the movement of the cation is less restricted. At high dielectric constant ($\varepsilon \geqslant 60$) the interionic distance is so large that there is nearly complete freedom of movement of the cation. The three regions correspond to three dominant forms of the electrolyte in the solution, *i.e.* micelles at $\varepsilon \leqslant 10$, normal 1 : 1 ion pairs at $\varepsilon \approx 20$—35, and free ions at high ε.

Also listed in Tables 3 and 4 are the values of the ratio $\Delta\nu(N{-}CH_3)^0 : \Delta\nu(N{-}CH_2)^0$ in various solvents. The ratio decreases monotonically from low to high ε values in marked contrast to that found with $[NMe(n\text{-}C_8H_{17})_3]_3\text{-}[Fe(CN)_6]$ where the ratio was constant. Although the observed isotropic shifts have contributions from both the dipolar and contact interactions, the bulk of the n.m.r. data are consistent with a predominant dipolar mechanism.[1] When the latter is the case, the ratio of the shifts can be equated to the ratio of the geometry factors as in equation (2). Here θ is the angle between

$$\Delta\nu(N{-}CH_3)^0 : \Delta\nu(N{-}CH_2)^0 = \frac{(3\cos^2\theta_{CH_3} - 1)}{r_{CH_3}{}^3} : \frac{(3\cos^2\theta_{CH_2} - 1)}{r_{CH_2}{}^3} \quad (2)$$

the C_3 axis and the radius vector from the metal to the



Plot of $\delta(\Delta\nu_H{}^0)$ against ε for $[NMe(n\text{-}C_8H_{17})_3][CoBr_3(PPh_3)]$ (○) and $[NMeBu^n{}_3][CoBr_3(PPh_3)]$ (●)

resonating proton and r is the length of this radius vector. The variation of the ratio with solvent implies that the geometry of the ion pairs is changing, in accord with the conclusion drawn in the earlier paragraph. However, in the absence of a proper model of the micelle structure in the solvents of low dielectric constant, the lack of information about the configuration of the alkyl chain, and the uncertain contact contribution to the observed shift, it is not possible to estimate accurately the interionic distance.

Finally, it might be asked whether the concentration dependence of the n.m.r. data in solvents of low dielectric constant is amenable to quantitative analysis so as to yield some information concerning the nature of the micellar species in these solvents. Recently, it was shown that [9,10] the concentration dependence of the n.m.r. data for alkylammonium carboxylates in carbon tetrachloride and benzene can be reproduced equally well using either a single-equilibrium model where the micelle is restricted in size or a multiple-equilibrium model where it is assumed that dimers and all higher species with even aggregation numbers coexist in each solution. Although the latter model may seem to be more realistic, the assumptions of equal chemical shifts for all micellar species and equal equilibrium constants for all equilibria (except the dimerization equilibrium) are certainly open to question, especially in the former model where the observed isotropic shift values are expected to be very dependent on the size (and geometry) of the micelle. In both models, the problem of ionic dissociation of the types (3) and (4) is not considered. Hence we believe that, at this stage, it is not

$$[\mathrm{CA}]_n \rightleftharpoons [(\mathrm{CA})_{n-1}\mathrm{C}]^+ + \mathrm{A}^- \qquad (3)$$

$$[\mathrm{CA}]_n \rightleftharpoons [(\mathrm{CA})_{n-1}\mathrm{A}]^- + \mathrm{C}^+ \qquad (4)$$

possible to obtain meaningful parameters from the analysis of the concentration dependence of n.m.r. data in solvents of low dielectric constant.

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