Closed-shell Ion Pair Aggregation in Non-Polar Solvents characterized by NMR Diffusion Measurements

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Closed-shell ion pairs, formed by tetrabutylammonium chloride, aggregate in C^2HCl_3 solution; stimulated-echo NMR experiments incorporating pulsed field gradients yielded diffusion coefficients for the aggregates and comparison of aggregate diffusion with that of an internal standard of similar size and shape (Bu_4Si) was used to determine the extent of aggregation; temperature and concentration effects indicate that aggregation is primarily entropy-driven.

Electrolytes dissolved in low polarity solvents often exist as ion pairs, and the behaviour of these species has been a subject of intense scrutiny for many years.[1,2] It has been concluded that higher order aggregates beyond a simple ion pair are often present, and may even predominate in some cases.[3–5] Recently, we noted that the intensities of interionic $^1H\{^1H\}$ nuclear Overhauser effects (NOE) in a closed shell ion pair formed by tetrabutylammonium tetrahydridoborate **1a** in C^2HCl_3 solution decrease in intensity with decreasing temperature in a manner suggestive of aggregation of simple ion pairs into larger assemblages.[6,7] Freezing-point depression measurements on solutions of **1a** in $CHCl_3$ support this conclusion, but a loss of solubility of **1a** at low temperatures makes it difficult to determine accurate aggregation numbers in this manner.[6]

Diffusion measurements provide another means of characterizing ion aggregates. For a large spherical particle in a solvent of low relative mass, the diffusion coefficient D of the particle can be related to its radius r by the Stokes–Einstein equation (1):

$$D = k_BT/6\pi\eta r \qquad (1)$$

where η is the viscosity, k_B is Boltzmann's constant and T is the absolute temperature. It was proposed by Hahn that diffusion coefficients could be obtained from the magnitude of attenuation of NMR signals in a spin-echo experiment performed in the presence of a linear magnetic field gradient.[8] An inherent disadvantage of the Hahn experiment was that the broadened signals resulting from a static field gradient were difficult to detect. Stejskal and Tanner later demonstrated that pulsed field gradients (PFGs) could be used to overcome this difficulty.[9,10] The advantages of using diffusion to characterize molecular association has not escaped notice.[11–13] We now describe the characterization of aggregation of closed-shell tetrabutylammonium chloride **1b** ion pairs in non-polar solvents *via* PFG diffusion measurements. Rather than attempting to extrapolate to infinite dilution in order to calculate the diffusion coefficient of a single ion pair (an inherently risky extrapolation, since this assumes no variation in solvent properties with changing solute concentration as well as complete dissociation of the aggregate at low concentrations), we have prepared samples containing equal concentrations of ion pair **1b** and a non-polar (and presumably non-aggregating) molecule of similar size, mass and shape, tetrabutylsilane **2**, as an internal diffusion standard. Aggregation numbers are calculated using the ratios of the diffusion coefficients of **1b** and **2**, $D_{1b}:D_2$. If aggregate shape is assumed to be spherical, then the ratio of diffusion coefficients should be the inverse of the ratio of the radii of the two species and the cube root of the ratios of their volumes. Dipole moment measurements suggest that ion aggregates typically have low or zero dipole moments in non-polar solution, so the assumption of a roughly spherical aggregate is not unreasonable, since this minimizes the dipole moment of the aggregate.[3c,4]

The pulse sequence used in the present series of experiments is shown in Fig. 1. The intensities of signals resulting from this sequence are modified by diffusion during Δ, the delay between the two gradient pulses. Signals due to rapidly diffusing species are attenuated relative to those from more slowly diffusing species. If the static magnetic field B_0 is sufficiently homogeneous or the pulsed field gradient strength is weak relative to B_0, the relationship between echo amplitude and field gradient strength is given by eqn. (2):

$$A = A_0f(\tau_i,T_1,T_2)\exp[-K^2D(\Delta - \delta/3)] \qquad (2)$$

where A and A_0 are the echo amplitudes in the presence and absence of PFGs, respectively, and D is the diffusion coefficient of the observed species.[9] The $f(\tau_i,T_1,T_2)$ is determined by the nuclear relaxation times and experimental delays (constants for a given resonance in the present experiments). $K = \gamma G\delta$, where γ is the gyromagnetic ratio of the observed nucleus, G is the gradient amplitude and δ is the duration of the gradient pulse.

A series of samples containing 0.092–0.0001 mol dm^{-3} **1b** and a similar concentration of **2** in C^2HCl_3 were sealed in standard 5 mm NMR tubes. The ^1H spectra of both species are well-resolved and do not overlap each other (Fig. 2). A small amount of tetramethylsilane **3** was also added to all samples,

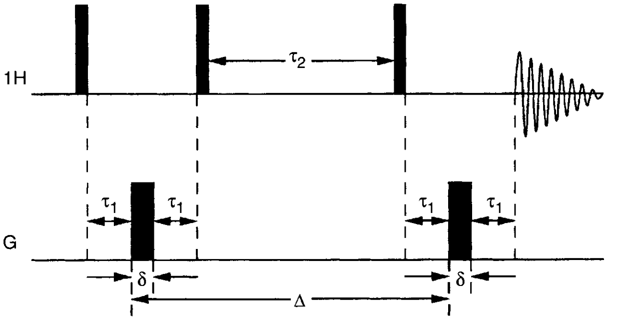

Fig. 1 Stimulated echo pulse sequence used for diffusion measurements. Experimental parameters: τ_1 = 1 ms, τ_2 = 50 ms, δ = 5 ms, Δ = 57 ms. Phase cycling: $\phi = x, -x$; $\psi = x, x, -x, -x$; receiver phase = $x, -x, -x, x$. A 10 s recycle delay was used between experiments.

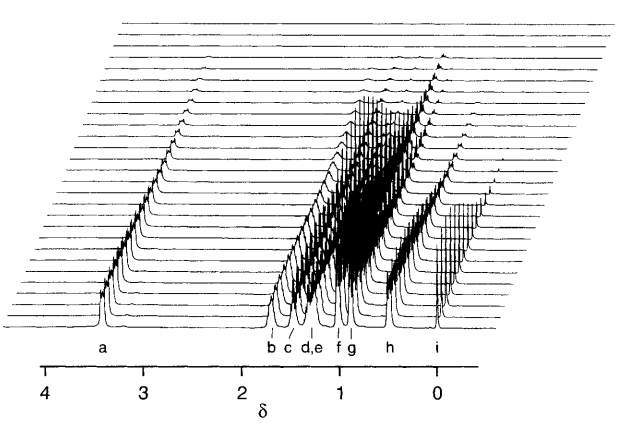

Fig. 2 A series of ^1H spectra obtained using the pulse sequence shown in Fig. 1 for a sample containing 0.092 mol dm^{-3} **1b**, 0.09 mol dm^{-3} **2**, and 0.001 mol dm^{-3} **3** in C^2HCl_3, 298 K. Gradient strength is increasing in 1 G cm^{-1} steps from 0.5 G cm^{-1} to 19.5 G cm^{-1} from front to back relative to $SiMe_4$ **3**. Resonance assignments are as follows: **1b** 1-CH_2 (a), **1b** 2-CH_2 (b); **1b** 3-CH_2 (c); **2** 2-CH_2 (d); **2** 3-CH_2 (e); **1b** 4-CH_3 (f); **2** 4-CH_3 (g); **2** 1-CH_2 (h); **3** (i).

providing a second internal diffusion standard. Two sets of measurements were performed. In the first, diffusion coefficients were measured as a function of concentration at 298 K (Table 1). In the second, measurements were made as a function of both temperature and concentration (Table 2). Data sets consisted of a series of experiments in which gradient strengths were incremented in 1 gauss cm^{-1} steps from 0.5 G cm^{-1} to 19.5 G cm^{-1}. Experiments were performed on a Bruker AMX-500 500 MHz NMR equipped with an Acustar three-channel PFG amplifier and Spectrospin 5 mm three-axis shielded gradient probe. All one-dimensional spectra were processed and phased identically. In some cases, spectra obtained at higher gradient strengths required small additional phase corrections prior to integration.

The negative log of normalized integrated signal intensity is linear with respect to $K^2(\Delta - \delta/3)$, and diffusion coefficients are obtained directly from the slope. Diffusion coefficients for **1b** listed in the Tables were obtained by averaging the coefficients obtained from the individual 1-CH_2, 2-CH_2, 3-CH_2 and 4-CH_3 resonances, and errors were calculated from the maximum deviation of the diffusion coefficients calculated from the individual resonances from the mean value for all four resonances. In all cases, the coefficients calculated from the individual resonances differed from the mean value by less than 10%. Diffusion coefficients for **2** were calculated in the same manner, except that the 2-CH_2 and 3-CH_2 resonances of **2** overlap and so could not be integrated separately.

Table 1 Diffusion coefficients for **1b** and **2** in C^2HCl_3 solution as a function of [**1b**], all at 298 K. Concentrations of **1b** and **2** are similar in a given sample. *R* factors are better than 0.99 using a minimum of 12 data points in all cases (experimental errors calculated as described in the text)

[**1b**]/ mol dm^{-3}	10^{10} $D/\mathrm{m}^2\ \mathrm{s}^{-1}$ **1b**	10^{10} $D/\mathrm{m}^2\ \mathrm{s}^{-1}$ **2**	D_2/D_{1b}	Aggregation number for **1b**
0.092	6.20 ± 0.11	9.23 ± 0.50	1.49	3.5
0.076	6.31 ± 0.22	9.55 ± 0.65	1.51	3.7
0.061	6.57 ± 0.18	9.93 ± 0.64	1.51	3.7
0.046	6.83 ± 0.27	10.02 ± 0.56	1.47	3.4
0.031	7.25 ± 0.27	10.29 ± 0.65	1.42	3.0
0.015	7.57 ± 0.42	10.57 ± 0.77	1.40	2.9
0.0076	8.10 ± 0.14	10.54 ± 0.57	1.30	2.3
0.0026	8.40 ± 0.24	10.53 ± 0.35	1.25	2.1
0.0015	8.71 ± 0.35	10.64 ± 0.04	1.22	1.9
0.0001	12.05 ± 0.58[a]	11.78 ± 1.08	0.98	1

[a] Average of the diffusion coefficients calculated using data from the 1-CH_2, 2-CH_2 and 4-CH_3 resonances.

Table 2 Diffusion coefficients for **1b**, **2** and **3** as a function of temperature and concentration in $CDCl_3$. Concentrations of **1b** and **2** are similar in a given sample. Concentrations of **3** are constant at ≈ 1% *v*/*v*. Errors were calculated as described in the text. Errors for *D* of **3** are estimated to be less than 5%. In all cases, *R* factors for linear fits are better than 0.99 using a minimum of 12 data points for the calculation.

[**1b**]/ mol dm^{-3}	*T*/K	10^{10} $D/\mathrm{m}^2\ \mathrm{s}^{-1}$ **1b**	10^{10} $D/\mathrm{m}^2\ \mathrm{s}^{-1}$ **2**	10^{10} $D/\mathrm{m}^2\ \mathrm{s}^{-1}$ **3**	D_2/D_{1b}
0.092	298	6.20 ± 0.11	9.23 ± 0.50	15.3	1.49
	283	4.84 ± 0.08	7.39 ± 0.35	13.0	1.53
	268	3.58 ± 0.05	5.53 ± 0.22	10.5	1.54
	258	2.56 ± 0.04	3.92 ± 0.12	7.5	1.53
0.031	298	7.25 ± 0.27	10.29 ± 0.65	18.6	1.42
	283	5.81 ± 0.13	8.03 ± 0.37	15.0	1.38
	268	4.30 ± 0.11	6.15 ± 0.33	11.5	1.43
	253	3.05 ± 0.08	4.32 ± 0.12	8.2	1.42
0.0076	298	8.10 ± 0.14	10.54 ± 0.57	19.2	1.30
	283	6.33 ± 0.17	8.33 ± 0.46	15.5	1.32
	268	4.64 ± 0.17	6.29 ± 0.34	12.2	1.36
	253	3.27 ± 0.14	4.43 ± 0.23	8.53	1.35
0.015	298	8.71 ± 0.35	10.64 ± 0.04	19.6	1.22
	283	6.92 ± 0.27	8.46 ± 0.22	16.0	1.22
	268	5.18 ± 0.13	6.24 ± 0.16	12.3	1.20
	253	3.77 ± 0.28	4.73 ± 0.27	8.84	1.25

The radii of the tetrabutylammonium cation and **2** are largely determined by the butyl chains, although the silane might be expected to have a slightly larger radius due to the difference in the C–N (1.47 Å) and C–Si (1.94 Å) bond lengths. Comparison of the diffusion coefficients of **1b** and **2** in the least concentrated sample examined (0.0001 mol dm^{-3}) gives the ratio of the radii of **2**:**1b** as 1:0.98. Assuming that this represents the ratio of radius of a single ion pair to that of the silane, and using this value to scale the ratios calculated as a function of temperature and concentration, aggregation numbers were calculated as the cube of the scaled diffusion coefficients ratio.

As expected, the diffusion coefficients of **1b**, **2** and **3** all increase with increasing temperature or decreasing concentration. As concentration is increased at a given temperature, the ratio $D_{1b}:D_2$ also increases, indicating increased aggregation (Table 1). However, for a given sample the ratio $D_{1b}:D_2$ shows little temperature dependence (Table 2). Clearly, the ΔH of aggregation of **1b** is very small. It appears that aggregation of **1b** is a response to crowding in solution rather than a favourable enthalpy change. One interpretation of this observation is that in order for two ion pairs to aggregate, the interionic distance within a single pair must increase, balancing the coulombic attraction between the ion pairs with a decrease in attraction between the ions within a given pair. An alternative hypothesis is that desolvation of the ion pair is necessary prior to aggregation, and that the enthalpic requirements of this process cancel any lowering of enthalpy due to coulombic interactions between the ion pairs.

This work was supported by the US National Science Foundation (CHE-9510131) with additional support from NSF Young Investigator Program and the Camille and Henry Dreyfus Teacher–Scholar Program.

Received, 5th September 1995; Com. 5/05848A

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