The Sign of the Nuclear Overhauser Effect as a Function of Temperature in Contact Ion Pairs

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The signs and magnitudes of nuclear Overhauser effects observed in closed-shell ion pairs in C^2HCl_3 show an unusual temperature dependence; freezing point depression measurements support the proposal that the observed dependence is due at least in part to the formation of ion aggregates.

We recently reported the application of the interionic nuclear Overhauser effect (NOE) to the determination of structure of closed-shell ion pairs in non-polar media.[1] Interionic NOEs in the tetra(n-butyl)ammonium tetrahydroborate ion pair **1** (0.2 mol dm^{-3} in C^2HCl_3, 298 K) indicate a close equilibrium association between the cation and anion.[1] Similar models may be proposed based on observed NOEs for both the tetra(isopentyl)ammonium **2** and tetra(n-octyl) ammonium **3** tetrahydroborate ion pairs. In the course of this work, we noted an unusual temperature dependence of the signs and magnitudes of observed NOEs in these ion pairs.

The temperature dependence of interionic NOEs in the three ion pairs is shown in Fig. 1. For ion pair **1** the NOE observed at the BH_4^- protons upon saturation of the 1-CH_2 protons reaches zero at *ca.* 223 K. The corresponding NOE in ion pair **2** is -4.5% at 223 K. In ion pair **3**, this NOE reaches a value of -13.9% at 223 K. Increased solvent separation of aryllithium ion pairs in tetrahydrofuran (THF) with decreasing temperature has been observed and is ascribed to the enthalpic favourability of lithium ion coordination by solvent lone pairs.[2] However, in the present case, solvent separation does not account for the fact that NOEs become negative for
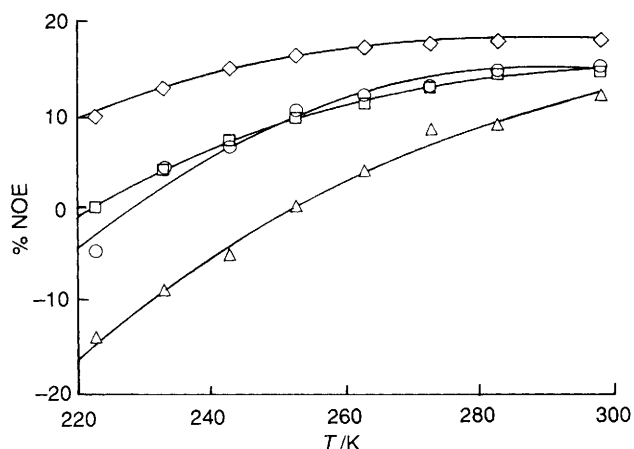
Fig. 1 Steady state interionic $^1H\{^1H\}$ NOE observed upon saturation of the 1-CH_2 resonance of the tetraalkylammonium ion at the BH_4^- resonance in ion pairs **1** (□), **2** (○) and **3** (△) as a function of temperature. Concentration of all ion pairs was 0.2 mol dm^{-3} in deacidified $CDCl_3$. All spectra were obtained on a Varian XL-300 NMR spectrometer operating at 300 MHz. NOE-enhanced spectra were obtained by saturation on-resonance for 10 s. Also shown is the expected NOE based on temperature and experimentally determined solvent viscosity (Table 1), and scaled to a maximum positive NOE of 18%, assuming no change in the effective radius of the species (◇).

Table 1 Solvent viscosities (η) in poise (10^{-1} Pa s) as a function of temperature for a 0.2 mol dm^{-3} solution of **1** in $CHCl_3$ interpolated from experimental data. (See ref. 7). Viscosities at 298 and 223 K are extrapolated from the same data. Values for τ_c are calculated from eqn. (2) using a value of 4.6 Å for the radius of the ion pair, as estimated from CPK models. Maximum fractional enhancements (f_{max}) are calculated from eqn. (1) using the values for τ_c shown and a transition frequency of 1.884×10^9 rad s^{-1}.

T/K	η/poise	τ_c/s	f_{max}
298	0.68×10^{-2}	6.79×10^{-11}	0.4834
283	0.81×10^{-2}	8.40×10^{-11}	0.4751
273	0.90×10^{-2}	9.68×10^{-11}	0.4674
263	1.01×10^{-2}	1.13×10^{-10}	0.4563
253	1.22×10^{-2}	1.42×10^{-10}	0.4342
243	1.48×10^{-2}	1.80×10^{-10}	0.4022
233	1.87×10^{-2}	2.35×10^{-10}	0.3495
223	2.45×10^{-2}	3.25×10^{-10}	0.2665

ion pairs **2** and **3**. Furthermore, a ROESY (rotating frame NOE) experiment[3,4] on ion pair **1** performed at 223 K indicates that a tight ion pair still exists at this temperature; cross peaks between the 1-CH_2 and BH_4^- protons are observed.

The observed maximum fractional enhancement, f_{max}, of resonance intensity due to the NOE depends on the molecular correlation time, τ_c, according to eqn. (1) where ω_c is the proton transition frequency and τ_c is related to experimental conditions by eqn. (2) with η being the solvent viscosity, a the

$$f_{max} = (5 + \omega_c^2\tau_c^2 - 4\omega_c^4\tau_c^4)(10 + 23\omega_c^2\tau_c^2 + 4\omega_c^4\tau_c^4)^{-1} \quad (1)$$

$$\tau_c = 4\pi\eta a^3/3kT \quad (2)$$

effective radius of the species, k being Boltzmann's constant and T the absolute temperature.[5] The value of τ_c determines the spectral density of fluctuations in the local magnetic field responsible for dipolar relaxation processes, which in turn give rise to NOE and increases with increasing solvent viscosity or increasing radius. In nonviscous solvents, small molecules have short τ_c values, and relaxation pathways that give rise to positive NOEs predominate. For large molecules or small

molecules in viscous solvents,[6] magnetization transfer is the predominant result of dipolar interactions between nuclei, giving rise to negative NOEs. At intermediate values of τ_c, where $\omega_c\tau_c$ is equal to 1.12, the net effects cancel and an NOE is not observed.

The expected maximum fractional NOE enhancements as a function of solvent viscosity and temperature were calculated from eqns. (1) and (2) using the measured viscosities of solutions of **1** at the appropriate concentrations in $CHCl_3$, assuming a constant molecular radius for the ion pair. The appropriate values are shown in Table 1. Comparable viscosity changes were measured for solutions of **2** and **3**.[7] It is clear from these results that the observed effects are not explained solely by changes in viscosity and temperature. As far as we have been able to ascertain, this study represents the first observation of a change in sign of an NOE that is not wholly attributable to a change in solvent viscosity.[6]

One possible explanation for the discrepancy between expected and observed temperature dependence of the NOE is the assembly of the ion pairs into multi-ion aggregates as temperature decreases. Kraus noted extensive aggregation of ion pairs formed by tetraalkylammonium ions with small anions in benzene using freezing point depression methods.[8] We observed a very slight depression of the freezing point of a 0.2 molal solution of **1** in chloroform ($\Delta T_f = -0.03$ °C) as compared to that of pure chloroform (0.2 molal benzene in chloroform gave a $\Delta T_f = -0.66$ °C under the same conditions). Some loss of solubility of **1** with decreasing temperature is observed, making an accurate aggregation number difficult to calculate by freezing point depression methods. However, the very small ΔT_f we observed is consistent with significant aggregation.

Another possible contribution to the observed temperature dependence of τ_c for these ion pairs may include an increase in solvent ordering from polarization due to charge effects. It has been observed that charged species may show evidence of longer τ_c than their uncharged counterparts.[9] The establishment of relative contributions of aggregation, viscosity and solvent ordering to τ_c will require tandem viscosity, vapour-phase osmometry and NOE measurements.

References

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