Novel Spin-Spin Splitting and Relaxation Effects in the Proton NMR Spectra of Sodium Salicylate in Viscoelastic Micelles

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Dilute aqueous solutions (e.g., 10 mM) of cetyltrimethylammonium bromide (CTAB) have low viscosities and contain spherical micelles.[1] With other anions, or with additives such as sodium salicylate (Nasal), dramatic viscoelastic properties can appear,[2,3] because of the formation of very long, more or less flexible, rodlike micelles.[1,2,4] Recently, however, the viscoelasticity in the CTAB–Nasal system has been ascribed to the presence of strings of spherical micelles linked by salicylate ions, mainly because of the similarity of the salicylate ^1H chemical shifts at 500 MHz in the mobile and viscoelastic CTAB–Nasal solutions.[3]

It is shown in this paper that the salicylate ^1H NMR spectra in the viscoelastic CTAB–Nasal solutions exhibit novel features arising from three factors: (a) the salicylate ion undergoes fast molecular tumbling only along one axis; (b) the vectors joining pairs of ortho protons make very different angles with respect to the fast rotation axis; and (c) the relaxation of H_5 and H_6 takes place via a mutual intramolecular dipole–dipole (DD) mechanism, which is complicated by interference from chemical shift anisotropy (CSA) effects at very high magnetic fields.

NMR spectra and data obtained in the present work on the salicylate ion are given in Figure 1 and Table I, respectively. The salicylate ion in the mobile 4 mM Nasal–CTAB solution shows narrow lines and the expected splittings from ortho and meta couplings.[5] In the viscoelastic 10 mM Nasal–CTAB solution,[5] the H_5 and H_6 resonances are very broad and structureless, whereas H_4 gives a puzzling ca. 1:2:2:2:1 multiplet; only the H_3 signal is a normal sharp doublet. The H_4 signal can be looked upon as a 1:1 doublet superposed on a 1:2:1 triplet, both with ca. 8-Hz splittings. The doublet changes with increasing temperature in a characteristic dynamic NMR fashion, becoming a quartet above ca. 40 °C; i.e., the normal splitting pattern of H_4, with couplings to H_5 and H_6, is restored at high temperatures.[6] Along with these changes, the H_6 signal becomes narrower and distinctly unsymmetrical; at 40 °C, it consists of a doublet (after resolution enhancement) with different line widths. This asymmetry in the H_6 signal is seen at 500 MHz but is absent at 200 MHz, thus showing that T_2 CSA relaxation is important for H_6 and that the CSA and the intramolecular H_5–H_6 DD relaxation mechanisms interfere with one another.[7]

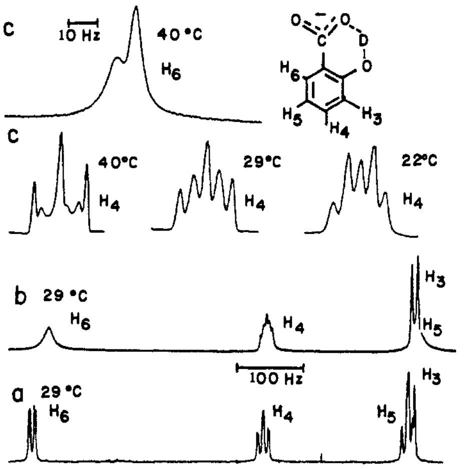

Figure 1. NMR spectra (500 MHz ^1H, Bruker AM500) of the salicylate ion in 10 mM CTAB: (a) 4 mM Nasal (mobile), (b) 10 mM Nasal (viscoelastic), and (c) expanded signals of 10 mM Nasal (viscoelastic or, at 40 °C, viscous), processed with −2 Hz (40 °C) or −3 Hz (22 and 29 °C) resolution enhancements.

Table I. ^1H Line Widths, T_1, and NOE Data for the Salicylate Ion at 500 MHz

solution (D_2O) (29 °C)	$\Delta\nu_{1/2} = 1/\pi T_2$, Hz						
	H_3	H_4	H_5	H_6	T_1[a]	$\eta(H_4)$[b]	$\eta(H_6)$[b]
10 mM Nasal	<0.6	<0.6	<0.6	<0.6	>8	+ve	+ve
4 mM Nasal–CTAB[c]	1	1	1	1	1.5	0.0	−0.3
10 mM Nasal–CTAB[d]	6	6	16[e]	>15[f]	1.4	−0.3	−0.9

[a] Apparent average T_1 (s) measured with a nonselective π–τ–$\pi/2$ sequence. [b] For H_2 and H_5 saturated. [c] Mobile solution, 10 mM in CTAB. [d] Viscoelastic solution, 10 mM in CTAB. [e] 20 Hz at 200 MHz. [f] Overlaps with the H_3 signal.

Table II. Rotational Diffusion Rates (s^{-1}) for the Salicylate Ion

solution	R_X[a]	$(R_Y R_Z)^{1/2}$
10 mM Nasal[b]	$\sim 3 \times 10^9$	$\sim 3 \times 10^9$
4 mM Nasal–CTAB	$\geq 2 \times 10^9$	2.5×10^8
10 mM Nasal–CTAB	$\geq 5 \times 10^8$	1.7×10^6

[a] The X axis is parallel to C_1–C_4. [b] $\tau_c = 1/6R = 5 \times 10^{-11}$ s.

The large negative NOE enhancement (η) of H_6 resulting from the saturation of H_5 supports the largely intramolecular DD relaxation of these nuclei and shows that the correlation time (τ) for tumbling of the H_5–H_6 vector makes $\tau\omega > 1$, where ω is the ^1H frequency in radians/second.[8] At 29 °C and 200 MHz (where CSA effects can be neglected), the H_6 line width of 20 Hz corresponds to $\tau = 10^{-7}$ s, so that $\tau\omega >> 1$ and the DD mechanism causes only transitions between the $\alpha\beta$ and $\beta\alpha$ spin states of H_5 and H_6.[8] When these transitions are fast enough,[9] H_4 is decoupled

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(5) For 10 mM Nasal in D_2O at 29 °C, $J_{3,4} = 8.23$, $J_{4,5} = 7.29$, $J_{5,6} = 7.81$, $J_{3,5} = 1.16$, $J_{4,6} = 1.78$, and $J_{3,6} = 0.46$ Hz. The CTAB used was Eastman Kodak technical grade which contains lower homologues of the hexadecyl group and requires a higher concentration of Nasal to induce viscoelasticity than does pure CTAB. The 10 mM Nasal–10 mM CTAB solution was viscoelastic up to about 32 °C and still rather viscous at 50 °C. Purer CTAB (98%, Sigma) (10 mM)–Nasal (5 mM), which is viscoelastic up to about 40 °C, gave similar NMR effects but is less convenient for the present purpose because of the lower Nasal concentration.

(6) A spin $^1/_2$ nucleus coupled to a spin $>^1/_2$ nucleus is often decoupled by quadrupolar relaxation at low temperatures, but not in a strongly spin-selective fashion.[7]

(7) For a review of relaxation in coupled spin systems, see: Vold, R. L.; Vold, R. R. *Prog. Nucl. Magn. Reson. Spectrosc.* **1978**, *12*, 79–133. For interference between the DD and CSA mechanisms, see: Shimuzu, H. *J. Chem. Phys.* **1964**, *40*, 3357–3364. Goldman, M. *J. Magn. Reson.* **1984**, *60*, 437–452. Such effects have been found in (a) the ^{19}F–H system (Mackor, E. L.; Maclean, C. *Prog. Nucl. Magn. Reson. Spectrosc.* **1967**, *3*, 129–157), (b) the ^{31}P–^{19}F system (Withers, S. G.; Madsen, N. B.; Sykes, B. D. *J. Magn Reson.* **1985**, *61*, 545–549. Farrar, T. C.; Quintero-Arcaya, R. A. *Chem. Phys. Lett.* **1985**, *122*, 41–45), (c) the ^{13}C–^1H system (Farrar, T. C., paper presented at the 27th Experimental NMR Conference, Baltimore, April, 1986), and (d) the ^{15}N–^1H system (Guēron, M.; Leroy, J. L.; Griffey, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 7262–7266) but have not been previously reported for the ^1H–^1H system. The CSA of H_6 is possibly induced by the nearby carboxylate group; see also: Ryan, L. M.; Wilson, R. C.; Gerstein, B. C. *J. Chem. Phys.* **1977**, *67*, 4310–4311.

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(9) The line separation is $J_{4,5} - J_{4,6}$ (5.5 Hz) and the rate constant for exchange is twice the nonsecular part of the DD $1/T_2$, i.e., $2/(5T_2)$ of H_5: Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, 1983; p 85.

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from H_5 and H_6; the remaining coupling of H_4 to H_3 gives rise to a doublet (J_{34} = 8.3 Hz). The long-lived H_5–H_6 spin states ($\alpha\alpha$ and $\beta\beta$) cause H_4 to be split into a 1:1 doublet with a separation of $J_{45} + J_{46}$ (8.0 Hz); the additional coupling to H_3 (8.3 Hz) then gives an apparent triplet. The temperature dependence of the H_4 signal is reproduced by line-shape calculations.[9] The "fractional-decoupling" effect apparently has not been previously observed.[6]

Since H_3 and H_4 give relatively sharp signals, the salicylate ion in the viscoelastic solutions must tumble much faster about an axis more or less parallel to C_1–C_4 than about perpendicular axes, as expected for an ion on the surface of a micelle. Since the H_3–H_4 and the H_4–H_5 vectors make angles of about 60° with respect to the fast rotation axis, DD relaxation is inefficient.[10,11]

Rotational diffusion rates for the salicylate ion in the various environments given in Table I were calculated by means of Woessner's equations[12] and are shown in Table II.

The present work shows that salicylate ions have very different tumbling motions in the mobile and viscoelastic micellar solutions, and therefore the suggestion[3] that the latter solutions contain linked spherical micelles is not supported by the present NMR relaxation evidence.

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Registry No. Sodium salicylate, 54-21-7.

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(10) The 60° angle is close to the "magic angle", where $3\cos^2\theta - 1 = 0$, (Levy, G. C.; Cargioli, J. D.; Anet, F. A. L. *J. Am. Chem. Soc.* **1973**, *95*, 1527–1535). Anisotropic motions of aromatic rings in micelles have been studied by ^{13}C relaxation: Menger, F. M.; Jerkunica, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 688–691. Stark, R. E.; Storrs, R. W.; Kasakevich, M. L. *J. Phys. Chem.* **1985**, *89*, 272–277.

(11) Intermolecular DD relaxation via the CTAB protons should lead to some broadening in the salicylate protons, especially in the narrow signals of H_3 and H_4. It probably largely determines the apparent T_1's of the salicylate protons, as observed by nonselective pulse sequences.

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Metal Atom Reactions with Methane. Boron, Aluminum, Gallium, and Indium Atoms and Dimers

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The group 13[1] metal atoms B, Al, Ga, and In possess very high intrinsic chemical reactivity under low-temperature conditions.[2-11] Thus, recall that Al atoms react spontaneously with alkyl halides (CH_3X)[2] and water even at as low at 10 K.[9] Under the same conditions, Ga atoms also react with CH_3X but less efficiently than Al.[2] Reactions of Al atoms with CH_4 have also been reported,[10] although there is some controversy about whether photoactivation is necessary or if Al clusters are necessary.[11]

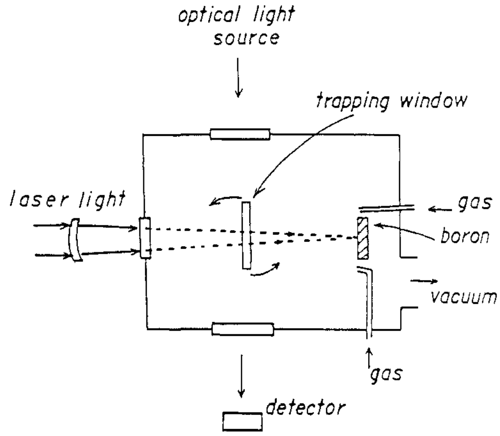

Figure 1. Schematic diagram of a matrix isolation reaction chamber with a laser evaporation source.

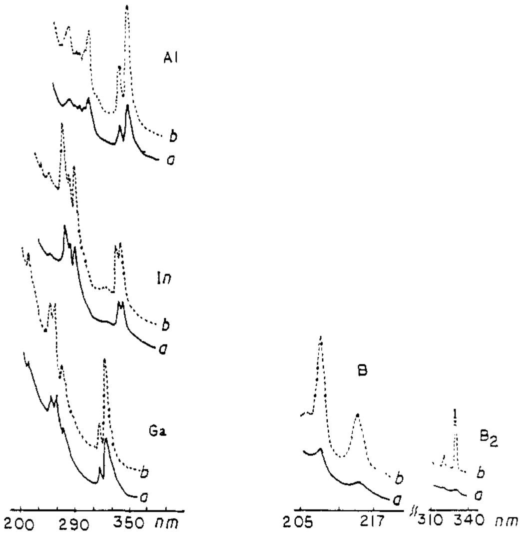

Figure 2. UV absorption spectra of B, Al, Ga, and In evaporated by XeCl excimer laser isolated in Ar matrix at 10 K: (a) in 5% CH_4/Ar matrix, evaporation time, 10 min; (b) in pure Ar matrix, evaporated an additional 10 min after (a).

Theoretical support for the low activation barrier for $CH_4 + M \rightarrow CH_3MH$ has been found, especially for B and Al atoms and for the B anion.[12] A partially filled p-shell appears to be very important so that an empty p-lobe can interact with the C–H σ^* orbital.[12]

To gain further understanding of the C–H bond-breaking process on single atoms, we have extended our studies to B atoms and have compared these with Al, Ga, and In atoms. In order to study all of these systems under similar conditions we have designed a matrix-isolation unit that utilizes an excimer laser as a heat source for evaporation of bulk B, Al, Ga, and In. The basic matrix unit is similar to what we have described earlier. However, the laser beam (75 mJ/pulse and about 5 pulses/s) is directed through the center of the cold window (a hole in the window) onto the target, which is vaporized (Figure 1), and as the laser beam bores a hole in the target the exiting vapor is directed back along the laser beam path and onto the window.[13,14] This design allows

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