Electron Spin Resonance Studies of Valinomycin Na^+–$TCNE^-$ Ion Pairs

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Summary The existence of a valinomycin Na^+–$TCNE^-$ tight ion-pair complex in benzene solutions is demonstrated by e.s.r. spectroscopy and possible conformational changes in the antibiotic complex are detected.

Crown ethers and a number of naturally occurring antibiotics such as valinomycin (VM) and the macrotetralide actins have been shown to act as charge carriers for ions across cell membranes.[1] These substances generally form 1:1 complexes with cations in which the cation is surrounded by the lipophilic complexing agent. In the lipid bilayer the positive charged complex presumably forms ion pairs with available anions.

VM has been shown in a variety of studies to be a very effective charge carrier in liquid-like bilayers.[2] Recently it has been shown that crown ethers solubilize alkali-metal salts of tetracyanoethylene (MTCNE) in low dielectric constant solvents and that the complexes formed exist as tight ion pairs.[3] We report here that VM forms similar tight ion pair complexes and that the e.s.r. spectrum of these ion pairs provides information on anion–cation interactions in the antibiotic complex.

The e.s.r. spectrum of the VMNa$^+$–TCNE$^-$ complex is characterized by a temperature-independent splitting due to four equivalent nitrogens in the TCNE$^-$ radical (1·57 G), a temperature-dependent ^{23}Na hyperfine splitting (Figure), and linewidths of *ca.* 30 mG. The lines in the ^{23}Na quartets exhibit a temperature-dependent linewidth effect characteristic of a situation in which two or more ion pair forms are in rapid equilibrium.[4]

Previously published work suggests that VM can exist in more than one conformational form when complexing Na$^+$.[5,6] Thus, it is possible that conformational changes in VM are responsible for the two or more VMNa$^+$–TCNE$^-$ ion-pair forms. Studies of VMK$^+$–TCNE$^-$ and VMCs$^+$–TCNE$^-$ in benzene over the temperature range investigated for VMNa$^+$–TCNE$^-$ show no evidence for more than one ion-pair form. N.m.r. studies have indicated that VMK$^+$ in methanol is a stable complex over the temperature range −35 to 74 °C.[6]

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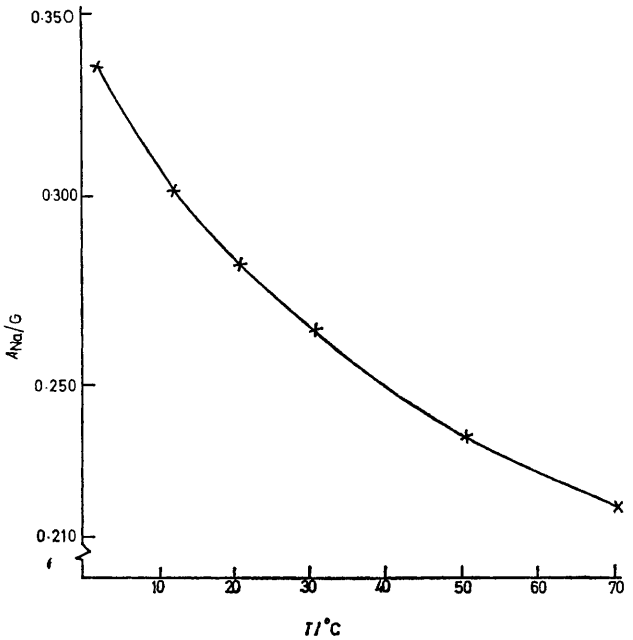

Figure. The ^{23}Na hyperfine splitting for the VMNa$^+$–TCNE$^-$ complex in benzene as a function of temperature.

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