31. Complex Formation between Sugars and the Sodium Cation in Non-Aqueous Solvents

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Summary

In low dielectric solvents such as pyridine or isopropylamine, sodium perchlorate interacts strongly with a variety of sugars. The interaction is best described as non-specific, with close proximity of the ionic partners maintained, as in a sugar-shared ion pair.

1. Introduction. – ^{23}Na-NMR. linewidths reflect the electrostatic field gradient at the quadrupolar nucleus: taking advantage of this principle, we have shown that ^{23}Na-NMR. is a valuable tool for study of Na$^+$-sugar complexes, in which the sodium cation coordinates on one face to oxygen atoms from the sugar, and on the other with nitrogen atoms from pyridine as the solvent [1]. In such a solvent as pyridine, does the sugar-sodium cation interaction display a similar specificity as in water solution, where *Angyal* [2] has shown that an *axial-equatorial-axial* sequence of OH groups is the favored disposition?

2. Experimental Part. – The spectra are obtained with vacuum-sealed tubes, as described previously [3]. Analysis of the data proceeds according to the published protocol [1]. NaClO$_4$ (2.10^{-2}–$1.5.10^{-1}$M) is co-dissolved with various sugars carefully dried, (3.10^{-2} M) in pyridine or in isopropylamine, re-distilled and dried prior to use. The quoted error limits are taken as three standard deviations in order to allow for the systematic errors. The IR. spectra have been recorded with a *Perkin Elmer* 125 spectrophotometer.

3. Results and discussion. – Formation constants K and linewidths characteristic of sugar-bound sodium are presented in Table.

The conclusions are as follows: 1) in order for the interaction to be detectable by this method, a nitrogen containing solvent is required. No line broadening is observed with sorbose in DMSO- or in 2-methoxyethanol-solution, neither with methyl-β-D-ribopyranoside in ethylacetate or in acetone solution. In water, only *myo* inositol gives a significant sodium-line broadening [4]. This agrees with our original idea of using a nitrogen-containing solvent to create a sizable electric field dissymmetry at the

Characteristics of sugar-sodium cation complexes at 290 K

Sugar/solvent	$K\ [M^{-1}]$	$\Delta\nu^{a}_{\frac{1}{2}}$ [Hz]
Sorbose/pyridine	7.2 ± 2.2	800 ± 150
Sorbose/isopropylamine	19.0 ± 4.0	$500 \pm\ \ 50$
Methyl-β-D-ribopyranoside/pyridine	5.5 ± 0.6	$730 \pm\ \ 70$
Methyl-β-D-ribopyranoside/isopropylamine	12.7 ± 1.4	$580 \pm\ \ 60$
Ribose/pyridine	6.8 ± 1.3	850 ± 120
p-Methoxy-phenyl-β-D-galactopyranoside/pyridine	13.3 ± 1.8	$500 \pm\ \ 80$
Sorbitol/pyridine	11.2 ± 2.1	830 ± 150
Lactose/pyridine	8.0 ± 1.6	2000 ± 400

sodium, which interacts with the sugar oxygen atoms at the same time; 2) hydroxy groups on the sugar are necessary: whereas methyl-β-D-ribopyranoside interacts strongly with Na$^+$, the fully acetylated tetraacetyl-β-D-ribopyranoside shows no interaction; 3) of the molecules listed in Table, only methyl-β-D-ribopyranoside possesses the *axial-equatorial-axial* sequence of OH groups conductive to strong interaction in water solution [2]. The studies by *Suggett & Franks* [5] have implicated, as an explanation, the predominant involvement of equatorial hydroxyl groups in stabilizing the water structure. However, this proposition has been disputed [6] since each OH group in a sugar appears to form two strong hydrogen bonds with water molecules irrespective of its *axial* or *equatorial* position. In pyridine solution, this *axial-equatorial-axial* interaction does not appear to be particularly favored. Provided three or more OH groups are present in the molecule, a relatively strong complex is formed. Its structure is very similar with most sugars, as witnessed by the $\Delta\nu^{a}_{\frac{1}{2}}$ values (Table), all equal except for lactose, with a correlation time approximately doubled for this disaccharide; 4) the non-specific character of the interaction in amine solvents is also suggested by comparison of the results in pyridine ($\varepsilon = 12.3$) and in isopropylamine ($\varepsilon = 6.0$). Formation constants in these two solvents and in water ($\varepsilon = 80$, and $K < 1$ for the examples in Table) increase as the inverse of the dielectric constant, as would befit a predominantly-electrostatic interaction; 5) plotting the ^{23}Na reduced linewidth $\Delta\nu_{1/2}.\eta^{-1}$, where η is the viscosity measured for the solution, for NaClO$_4$ as a function of concentration in pyridine, we find a straight line of positive slope 68.8 Hz.cP^{-1} · mol^{-1} and 47 Hz.cP^{-1} intercept: relaxation is effected, in part, through the proximity of the ClO$_4^-$ counter-ion [7]. We have obtained additional evidence that, in pyridine solution, sodium perchlorate indeed exists partly as loose, solvent-separated ion pairs, and partly in dissociated form.

In DMF solution, the ClO$_4^-$ anion shows an infrared band at 624 cm^{-1}, attributed to the T$_2$ mode for the fully symmetric T$_d$ ion [8]. By contrast, in the lower dielectric pyridine solution, an additional band is present at 611 cm^{-1}: A$_1$ mode of a unidentate C$_{3v}$-symmetric, or B$_1$(B$_2$) mode of a bidentate C$_{2v}$-symmetric ClO$_4^-$ anion [8]. Introduction of a sodium complexant such as dibenzo-18-crown-6, or sorbose, shifts the

equilibrium towards the dissociated form: the intensity of the band at 611 cm^{-1} drops correspondingly.

A similar shift from the dissociated to solvent-separated ion pairs, as the dielectric constant of the solvent is reduced, is obvious from the ^{35}Cl linewidth for the perchlorate anion [9] [10]: it increases from *ca.* 2 Hz in DMSO-solution – a low value indicative of T_d symmetry – to *ca.* 17 Hz in pyridine-solution, consistent with proximity of the sodium counter-ion. In agreement with the infrared results, addition of three equivalents of sorbose reduces slightly the ^{35}Cl linewidth, to 13 Hz. Thus, with $NaClO_4$ in pyridine-solution, these Na^+-sugar complexes appear to be sugar-bridged ion pairs.

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