Molecular Motion and Interactions in Aqueous Carbohydrate Solutions. 
I. Dielectric-Relaxation Studies

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Dielectric-relaxation studies in the frequency range 200 kHz to 35 GHz are reported for a range of sugars (from mono- to trisaccharides) in aqueous solution. The complex dielectric spectra were analyzed using a weighted least-squares minimization method to resolve the various component relaxations, and the implications of the analyses in terms of the molecular dynamics of solute and solvent and the interactions between solute and solvent are discussed. For the highest concentration studied (ca. 2 M), it was found that the most significant analysis required three discrete relaxation processes, whereas lower concentration samples could usually be satisfactorily fitted with two. Irrespective of any uncertainty in model selection, a number of conclusions regarding the solute–solvent interactions can be made, and it is shown how final quantification of the extents of hydration can be made using the input of information from other techniques.

KEY WORDS: Aqueous; hydration; sugar; carbohydrate; dielectric relaxation; time-domain spectroscopy.

1. INTRODUCTION

In recent years, preliminary studies on sugar–water interactions using the techniques of nuclear magnetic and dielectric relaxation have been described.¹,² Differences in the observed hydration properties have been discussed in terms of a specific hydration model in which the compatibility

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between the spatial orientation of hydroxyl groups around the sugar ring and the long-range order in the aqueous solvent is considered to be a significant influence on the extent of hydration. The earlier dielectric-relaxation studies,\(^{(1)}\) however, were the first applications of the techniques of time-domain spectroscopy\(^{(3)}\) to aqueous problems and employed, in part, a direct time-domain analysis of the experimental data which are now known to be unreliable. The present study, therefore, is a more extensive and both experimentally and statistically more rigorous examination of the dielectric-relaxation properties of aqueous solutions of a number of small sugars (mono-, di-, and trisaccharides) including those previously studied.

In hydration studies of small molecules, both dielectric and nuclear magnetic relaxation methods can individually be extremely powerful. However, it is one of the aims of this series of papers to illustrate not only the power but also the limitations of these methods, and yet still to show how these limitations may be successfully overcome by a judicious combination of the two techniques. The feature of nuclear magnetic relaxation which is particularly attractive for such work is its facility, by suitable choice of relaxing nucleus and isotopic composition of solute and solvent, to monitor the motion of a single chosen component. In contrast, the dielectric-relaxation approach is most useful because it is much less sensitive than NMR to exchange between water molecules hydrating the solute and those in the bulk solvent. Consequently, there is a reasonable probability of resolving individual relaxation properties of the bulk and hydration water. This paper concentrates on the dielectric studies alone, while the paper following deals primarily with NMR aspects.

Despite the power, \textit{in principle}, of dielectric-relaxation methods for hydration studies, there are drawbacks. As every polar component in the system makes a contribution to the total permittivity \(\varepsilon\), the observed spectrum \(\varepsilon(\omega)\) is often complex. For solutions of small molecules in particular, where solute and solvent rotational correlation times may not be very different, there is almost inevitably a curve-fitting problem. Thus, there may not be an unequivocal resolution of the total spectrum but rather one or two alternative models. In this study we have examined the relaxation spectrum of solutions of six sugars in fairly concentrated solution (ca. 2 \(M\) in terms of concentration of monosaccharide units). In this way we can best identify \textit{differences} between the relaxation behavior of these sugars in solution and draw conclusions concerning the molecular motions and interactions which are truly independent of the model selected to fit the data. To this end, we have measured dielectric properties over as wide a frequency range as is available to us (\(~100\) kHz to 35 GHz) using a combination of classical frequency-domain and time-domain spectroscopic methods in order to maximize the chances of a realistic resolution of the spectra.