Short Communication

Low-frequency (30 – 400 cm⁻¹) Raman Spectra of Water in Cellulose Gels

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In a recent paper we studied the structure of water in aqueous agarose and κ-carageenan gels by means of Raman spectroscopy.[1] A transformation of the scattered light called $R(\bar{v})$-representation was used.[2] We found this technique powerful in a number of investigations of low frequency Raman spectra,[2–12] where a serious problem is the high intensity of the central Rayleigh line. The $R(\bar{v})$-representation and similar representations have been used to avoid this problem or for a comparison with far-IR spectra as discussed in Refs. 1, 2, 11, 13, 14 and references cited therein. In our studies of water,[4] aqueous solutions[5–12] and gels,[1] we found it useful to use a background correction, because these samples always showed an inevitable small fluorescence. This paper presents results on water-swollen cellulose gels. The fluorescence from these gels was intense and consequently a new type of background correction was necessary.

The structure of water near the cellulose interface has been a controversial subject for many years.[15–17] Models proposing both a structuring[16] and a destructuring[15] of water at the phase boundary have been proposed. Goring[16] analyzed the water structure in terms of the cluster model for water[18] and concluded that the cellulose surface reduced the water structure in a layer of water adjacent to the surface, whereas Caulfield[17] proposed a long-range structuring of the water.

There is considerable evidence,[15] mainly from studies on the differential heat of water sorption and

investigations on the specific volume and density of moist cellulose, that the first strongly adsorbed water with a high density exhibits properties that are different from those of the rest of the water. In Goring's investigation the high density of the first adsorbed water was interpreted as a perturbation of the water structure rather than as compression or adsorption.

Investigations on the thermoelasticity of the same cellulose gels as used in the present study have previously shown[19] that the enthalpic component (χ_H) of the Flory-Huggins interactive parameter was negative, but that the entropic component (χ_S) was positive (negative residual partial molar entropy of water) thus indicating a structuring of the water absorbed into the cellulose. In these cellulose gels the partial specific volume has been found to be 0.87 cm³/g for the first 13 % of the sorbed water and 1.00 cm³/g for the remainder. This suggests that the first 13 % can be classified as bound water, whereas any water in excess of this quantity appears to be normal water. The present investigation was undertaken in order to see whether any long-range ordering of this water can be detected or whether the water should be classified as "normal".

The cellulose gels used here were synthesized by heating cellulose xanthate (viscose) solutions until gelation of the viscose took place, after which regeneration and appropriate washing procedures were employed as previously reported.[19] The gels correspond to the gels denoted O – B for which characteristics and properties have previously been published.[19] The highly swollen (water content: 85 %) gels thus obtained were slowly dried to a range of different water contents and then sealed in glass tubes until used. All results refer to gels in deionized water. A glucose solution was prepared from 1 g D(+)-glucose, H_2O (Riedel-de Haen) and 3 ml redistilled water.

Instrumental details were previously described.[1] The spectral slit width was 4 cm⁻¹ and the recording speed 25 cm⁻¹ per min. Spectra were obtained from 30 – 400 cm⁻¹. A filter with 10A bandwidth and ca. 60 % transmission was used in the laser beam (400 mV, 514.5 nm) to prevent the appearance of laser emission lines in the spectrum. Cylindrical high quality 4 mm (i.d.) NMR tubes were used as cells.

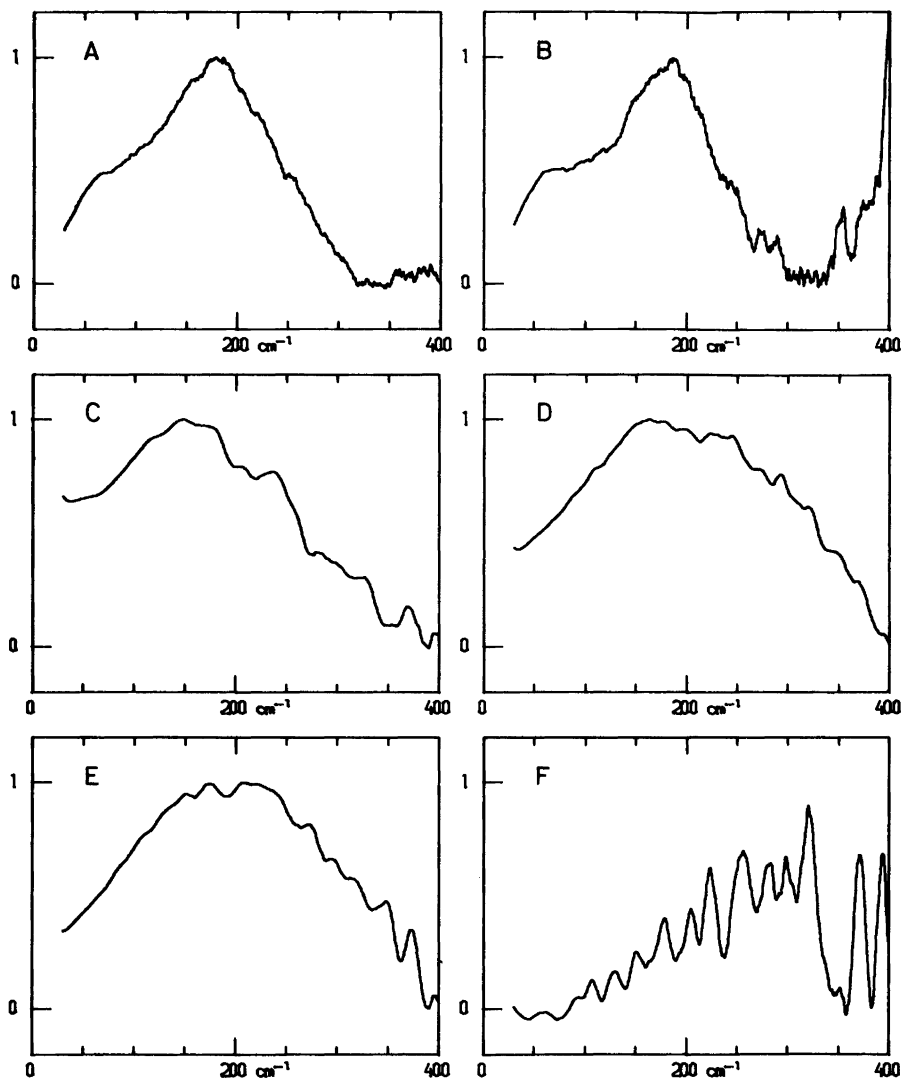$$R(\bar{v}) \propto \bar{v}[1 - \exp(-h\bar{v}c/kT)]I(\bar{v}) \qquad (1)$$

Fig. 1. A, redistilled water. *B*, 1 g D(+)-glucose in 3 ml water. *C*, 3 g water and 1 g cellulose. *D*, 2 g water and 1 g cellulose. *E*, 1.2 g water and 1 g cellulose. *F*, 0.5 g water and 1 g cellulose. The ordinate in each separate figure is the function $R(\bar{v})$ which is calculated as described in the text.

$R(\bar{v})$-curves were as previously constructed from the intensity in the Stoke's side $[I(\bar{v})]$ of the spectrum;[1-12] eqn. (1), where $\bar{v}$ is the Raman shift in cm^{-1}, and the other symbols have their usual meaning.

The gels were not transparent, resulting in a very high intensity of the central line, but even worse was the fact that all gels showed a strong fluorescence. Previously, we made corrections in which a mean intensity value around the lowest intensities for water (*ca.* 300 cm^{-1}) was subtracted from all intensities.[1,4-12] A correction in this way was sufficient for liquid water (Fig. 1A) and for the glucose solution (Fig. 1B). The $R(\bar{v})$-curves in Fig. 1A – 1B were smoothed by a running mean smoothing procedure.[20] The simple background correction mentioned above was not fruitful for the cellulose gels, because of a very intense fluorescence. We assumed the same band shape of the fluorescence for all gels and to compensate for the fluorescence we

then used the following procedure. $I(\bar{v})$-curves from two separate runs for each gel were added and smoothed. The resulting curves are called $I(\bar{v})$-sum curves. The intensity of these curves in a 1 cm^{-1} interval at 400 cm^{-1} was normalized to the same value for all gels. The $I(\bar{v})$-sum curve for the sample with lowest water content (17%) was then subtracted from the $I(\bar{v})$-sum curves of the gels with higher water content. $R(\bar{v})$-curves were calculated according to the equation given above from the resulting $I(\bar{v})$-curves. In the frequency region investigated (30–400 cm^{-1}) liquid water shows a minimum intensity [4,14] at 300–400 cm^{-1}, whereas the broad fluorescence band shows maximum intensity at 400 cm^{-1}. The impurities giving rise to the fluorescence should be identical in all samples and the procedure chosen should thus remove the fluoresence.

Finally, the $R(\bar{v})$-curves were smoothed in the usual way by the smoothing procedure. The results are shown in Fig. 1C – 1F. The subtraction technique makes the $R(\bar{v})$-curves less reliable at higher frequencies and the overall band shapes in Fig. 1C – 1F should not be taken too seriously, but it is evident that the 75% (Fig. 1C), 66.7% (Fig. 1D) and 55% (Fig. 1E) gels show a broad band with a maximum around 200 cm^{-1}, whereas this band was unobservable in a gel containing 33.3% water (Fig. 1F). The low frequency $R(\bar{v})$-curve of the glucose solution (Fig. 1B) is dominated by the broad bands from water with maxima at ca. 180 cm^{-1} (strong) and at ca. 60 cm^{-1} (weak). The spetrum of water in Fig. 1A is included as a reference. The glucose solution in Fig. 1B shows a band at ca. 400 cm^{-1}. This band if present in the gels is too weak to be observed in the $I(\bar{v})$-curves where the fluorescence is dominating, but the present technique should also compensate for this band and remove it from the difference curves shown. It is therefore plausible to assign the broad bands in Fig. 1C – 1E to the most intense water band with a maximum at 180 cm^{-1}. This band depends upon the local water structure,[4,14] and it can thus be concluded that its structure in the gels is similar to that found in liquid water. No water seems detectable in the gel containing 33.3% water (Fig. 1F), but the signal-to-noise ratio is poor for this sample with the lowest water content.

The main conclusion of this work is that the local water structure in cellulose gels, at least at water concentrations higher than 50%, is identical with that found in liquid water. This result is in accordance with our previous investigations of other polysaccharide gels.[1] Unfortunately no quantitative estimations could be performed due to the very strong fluorescence of the cellulose gels.

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