A ^{13}C n.m.r. and X-ray study of the relationship between the distribution of nitrate ester groups and interchain *d*(110) spacings in a series of cellulose nitrates

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An investigation has been made of the *d*(110) lattice spacing for a series of nitrocelluloses prepared by both nitration and denitration. ^{13}C n.m.r. spectra have been analysed to provide a statistical model of the sequence distribution in these nitrated and denitrated materials. These data provide a basis for the interpretation of the lattice parameters.

Keywords Cellulose nitrates; interchain spacings; ^{13}C nuclear magnetic resonance; X-ray spectroscopy; nitrate ester; sequence distribution

INTRODUCTION

Soon after the discovery of the diffraction of X-rays by crystalline materials the technique was applied to cellulosic materials and in particular cellulose nitrates. Miles[1] has reviewed much of this early work which concentrated on the measurement of the mean interchain spacing *d*(110) which is a particularly strong reflection in the X-ray powder diagram of cellulose nitrates. Miles[1] has reported that if cellulose is nitrated, then in general, the interchain distance increases with degree of substitution (*DOS*) with the possibility of a plateau between 12–13% nitrogen content (corresponding on average to 2.26–2.58 nitrate ester groups per glucose residue) up to a limiting value for the 'trinitrate'† of ~7.3 Å. For comparison purposes the typical spacing in unnitrated material is ~6.6 Å††. On denitration of cellulose trinitrate however the spacing of the trinitrate is maintained over a significant *DOS* range even down to a nitrogen content of 11% (*DOS* 1.97). Hence cellulosic nitrates of the same degree of substitution (*DOS*) may have quite different mean interchain spacings depending on the method of preparation. This phenomenon has been further investigated by Trommel[2] who came to the conclusion that this difference could be explained in terms of a different distribution of nitrate groups in nitrated and denitrated material however sufficiently sensitive techniques had not been developed at that time to allow this hypothesis to be subjected to detailed scrutiny. Nitrated cellulose, according to the Trommel argument[2] had uniform distributions of nitrate ester groups along the cellulose chains due to the nitrating acid penetrating all areas of the cellulose. On denitration however, it was assumed that the acid did not readily penetrate the highly crystalline trinitrated areas of the chain and denitration was far more likely at sites adjacent to lower nitrated residues. The final product therefore in this model would have large areas of relatively unsubstituted residues alongside regions of trinitrated material which were assumed to hold the chains apart despite the loss of nitrate groups from other regions. This extreme model however has recently been shown to be untenable by recent e.s.c.a. studies[3] reported from this laboratory and from ^{13}C n.m.r. distribution data[4] of a range of denitrated materials (prepared in nitric acid water mixes identical to those used by Trommel). In this previous work[4] we showed that no unsubstituted residues were present even down to a *DOS* of 2.0 for denitrated materials. However limited sequence distribution data available from this work also suggested that there is a greater tendency for the 3,6-disubstituted residues for example in a denitrated sample, (*DOS* 2.31), to be adjacent to a β-d-glucopyranose residue of low *DOS* rather than a trinitrated residue. In other words the distribution of groups sequentially along a given chain is non-random.

Clearly the mean interchain distance in cellulose nitrates must reflect the detailed differences in microstructure in terms of distribution of nitrate groups both around a single residue and along a chain (sequence distribution) and it is only recently (with our full assignment of the ^{13}C n.m.r. spectra of cellulose nitrates)[4] that a comparison of mean interchain spacing and distribution of nitrate groups has become feasible. In this paper we present such a comparison for a range of celluloses nitrated in nitric-sulphuric mixes and for a high *DOS* (2.8) material denitrated in a series of nitric-acid water mixes.

EXPERIMENTAL

The nitrated materials (using paper linters) used in this study were prepared in mixed acids by methods described in previous publications[3]. The denitrated material was prepared from 2.8 *DOS* cellulose nitrate denitrated in nitric acid/water mixes similar to those used by Trommel[2].

The X-ray diffractometer used was a Phillips P.W. 1130

† We use the term 'trinitrate' to encompass materials of *DOS* > 2.8 cf. ref. 3

†† Dependent on the origin of the cellulose

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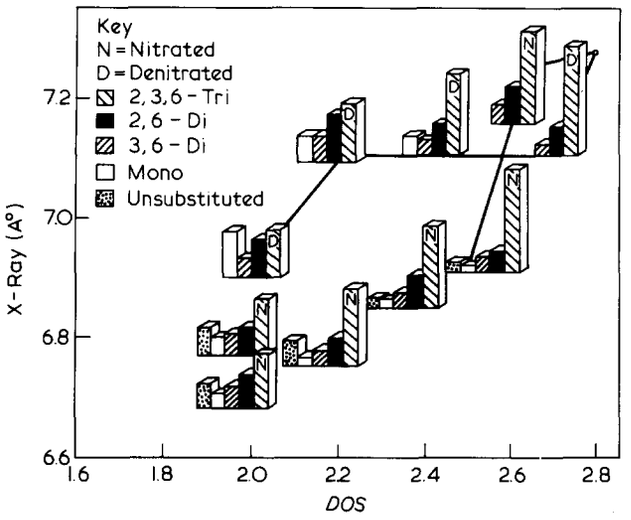


Figure 1 Histogram distribution data for nitrated and denitrated nitrocelluloses plotted *versus d* 110 X-ray spacing. The partial substitution patterns have been determined by ^{13}C n.m.r.

3 kw X-ray generator incorporating a P.W. 1050 diffractometer assembly. (Cu tube operating at approximately 40 kv, 25 ma.) The recordings span from 4° in 2θ to 20° in 2θ and the mean d spacing is taken as the centre of the peak occurring at around 12° in 2θ. The 75.5 MHz ^{13}C n.m.r. spectra were obtained on a Varian associates S.C. 300 spectrometer and the distribution data calculated by methods described in a previous publication[4]. In the particular case of the spectra recorded on nitrated and denitrated material prepared in the same nitrating mix the ^{13}C spectra were recorded on a Varian HL200 spectrometer at the University of Petroleum and Minerals, Dhahran, Saudi Arabia.

RESULTS AND DISCUSSION

The distributions of nitrate groups in the various nitrocelluloses studied are best represented in the form of block histograms set on a X-ray spacing vs. degree of substitution graph as in *Figure 1*. The X-ray spacings of the denitrated material are shown to be consistently higher for the low *DOS* range than those of cellulose nitrates prepared by nitration for comparable *DOS*. It is only in the high *DOS* region that the spacings are comparable and it is interesting to note that in this area the nitrated and denitrated products have comparable distribution patterns. Indeed the distribution patterns of the lower *DOS* materials also reflect the differences in mean interchain spacing, for example the difference between 2.37 nitrated and 2.43 denitrated products is ≈0.2 Å and between 2.14 nitrated and 2.2 denitrated ≈0.35 Å. These changes can only be due to differences in distribution of nitrate groups and in particular to the proportion of unsubstituted residues in the samples. The denitrated nitrocelluloses have no unsubstituted residues and have a correspondingly higher X-ray spacing than their nitrated counterparts.

Improved signal/noise ratios for the ^{13}C n.m.r. spectra compared with previously published work[4] allows a detailed study of the splitting of peaks in the anomeric region which reveals sequence distribution information and it is this data (*Figure 2*) which we shall now consider.

The ^{13}C n.m.r. spectrum in *Figure 2* is for a low *DOS* cellulose nitrate (1.9 *DOS*) prepared by nitration in 53% HNO_3, 20% H_2SO_4 and 27% H_2O. Taking first the lowest field peak at ≈104 p.p.m. due to an anomeric carbon (C1) in a 3,6-disubstituted ring we have previously reported that for denitrated material the splitting of 0.8 p.p.m. observed in this peak is due to the presence or absence of a nitrate group at C3′ in an adjacent ring and that the distribution of nitrate groups along a chain is non-random. In other words the 3,6-disubstituted residues are more likely to be adjacent to other 3,6-disubstituted or to trisubstituted glucopyranose rings. This is again apparent in the spectra for nitrated material shown in *Figure 2*.

The distribution data from the ^{13}C n.m.r. analyses are shown in *Table 1* together with the measured lattice spacings. Considering the data corresponding to the spectra in *Figure 2* the analyses can be simplified approximately in terms of a decad sequence viz the ratio

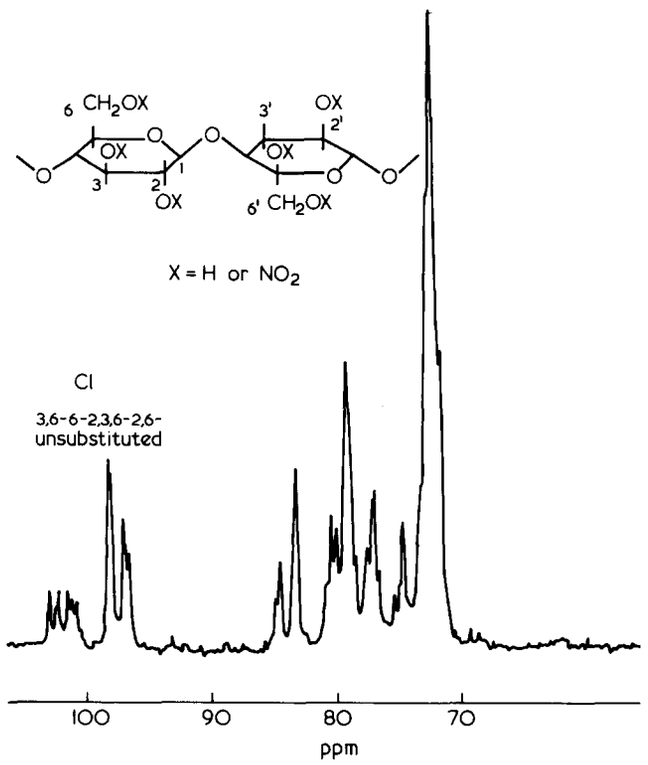
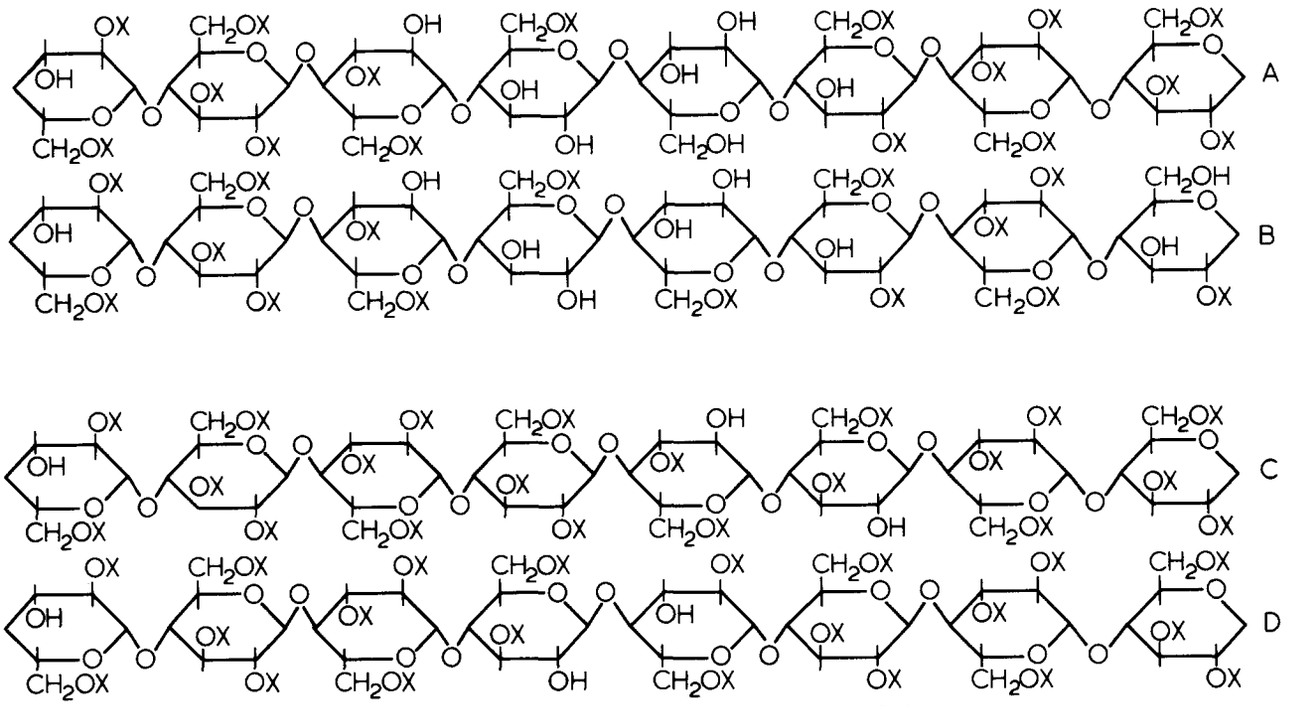


Figure 2 ^{13}C n.m.r. spectrum for 1.9 *DOS* cellulose nitrate prepared by nitration in 53% HNO_3, 20% H_2SO_4 and 27% H_2O nitrating mix

Table 1 Nitrated material

N.m.r. *DOS*	Tri	2,6	3,6	Mono	Unsubstituted	X-ray *d*(101) spacing (Å)
1.9	38	19	14	12	18	6.81
1.9†	36	23	14	10	17	6.66
2.1	50	18	10	5	17	–
2.14	53	17	8	6	16	6.73
2.37	55	22	11	6	6	6.90
2.50	58	14	9	4	5	6.93
2.62	62	25	13	–	–	7.25
2.53	65	16	11	4	4	7.08
2.67	71	16	9	4	–	7.13
2.83	83	11	6	–	–	7.28

† Corresponds to the spectra displayed in *Figure 2*. The other sample of *DOS* 1.9 was prepared in a nitrating mix of slightly different composition



A *DOS* 1.9 Nitrated sequence 2,6-2,3,6-3,6-6-unsub. 2,6-2,3,6-2,3,6

B *DOS* 2.0 Denitrated sequence 2,6-2,3,6-3,6-6-6mono-2,6-2,3,6-2,6

C *DOS* 2.62 Nitrated sequence 2,6-2,3,6-2,3,6-2,3,6-3,6-2,6-2,3,6-2,3,6

D *DOS* 2.74 Denitrated sequence 2,6-2,3,6-2,3,6-3,6-2,6-2,3,6-2,3,6-2,3,6

Figure 3 Statistically calculated decad sequence for nitrocellulose of *DOS* 1.9, 2.0, 2.62 and 2.74 for nitrated and denitrated materials

of tri:2,6 di:3,6 di:6 mono:unsubst. is approximately partitioned 4:2:1:1:2. On the basis of a random substitution pattern one would predict a probability of 0.5 (5/10) that a 3,6-disubstituted residue in this material would be adjacent to another 3,6- or trisubstituted residue (viz have a nitrate ester group in the 3′ position). The integrated area ratios available for the spectrum in *Figure 2* however reveal a probability close to 0.25. Repeating the calculation for the peak at highest field in the anomeric region (~98 p.p.m.) due to C1 in 2,6-disubstituted residues we would expect a probability of ~0.5 (on the basis of random substitution) that a 2,6-disubstituted would have an adjacent 3′ substituted residue (either 3,6 or 2,3,6 substituted). It is difficult to quantify the data for this region of the spectrum however it is clear that there is a very much higher probability (~0.8) that a 2,6-disubstituted residue has a 3′ substituted residue adjacent to it. For the major component of the C1 region at ~(99.7) p.p.m. a random model would give an equal probability of a 2,3,6-trisubstituted residue having a 3′ substituted residue adjacent to it and the spectra indeed suggest two components of roughly equal intensity. We have previously commented on possible long range effects influencing the splitting pattern for the remaining component associated with unsubstituted and 6-mono substituted residues. The foregoing analysis allows a rough model to be constructed of a likely structure for a decad sequence for the nitrocellulose of *DOS* 1.9 and this is indicated schematically in *Figure 3*. A similar analysis has been made of a sample corresponding to a higher *DOS* (2.6) and the results are also displayed in *Figure 3*.

The conclusion from this is that far from being random the nitrate ester equilibrium favours short blocks of fully substituted residues with short blocks of lower *DOS* residues. This is not unreasonable since we have previously argued[4] that the rate constants for nitrate ester formation at a given site in a glucose residue must increase as the *DOS* increases in that residue. By the same token substitution in adjacent residues may well therefore increase the rate of nitration such that a block structure develops. In a previous paper[4] we have considered partial *DOS* for denitrated materials and the striking difference with respect to nitrated materials of the same *DOS* (>2) is the absence of unsubstituted residues. For comparison purposes we also include in *Figure 4* typical sequence information inferred from the ^{13}C n.m.r. data, for nitrated material 2.14 *DOS* and denitrated material 2.2 *DOS*. Despite only a small difference in nitrogen content the sequence analysis for the most probable decad in each case reveals significant differences in sequence patterns along a given chain. This is reflected in a large change (0.35 Å) in the *d*(110) spacings (cf. *Figure 1*) whereas similar comparisons of sequence patterns drawn between materials of relatively high *DOS* (2.6) and very low *DOS* 1.9 (where the difference in *d*(110) spacings for nitrated and denitrated materials is small (cf. *Figure 1*), show strong similarities the only differences being in the number of mono- and unsubstituted residues present (cf. *Figure 3*). To conclude this discussion on the sequence information it should be stressed that the models presented in *Figures 3* and *4* are very much simplified and ideally require computer modelling similar to that presented by Atkins[5] to determine nearest neighbour distances between chains, although it is clear that the large differences in sequence patterns between nitrated and denitrated materials (*Figure 4*) must give rise to local

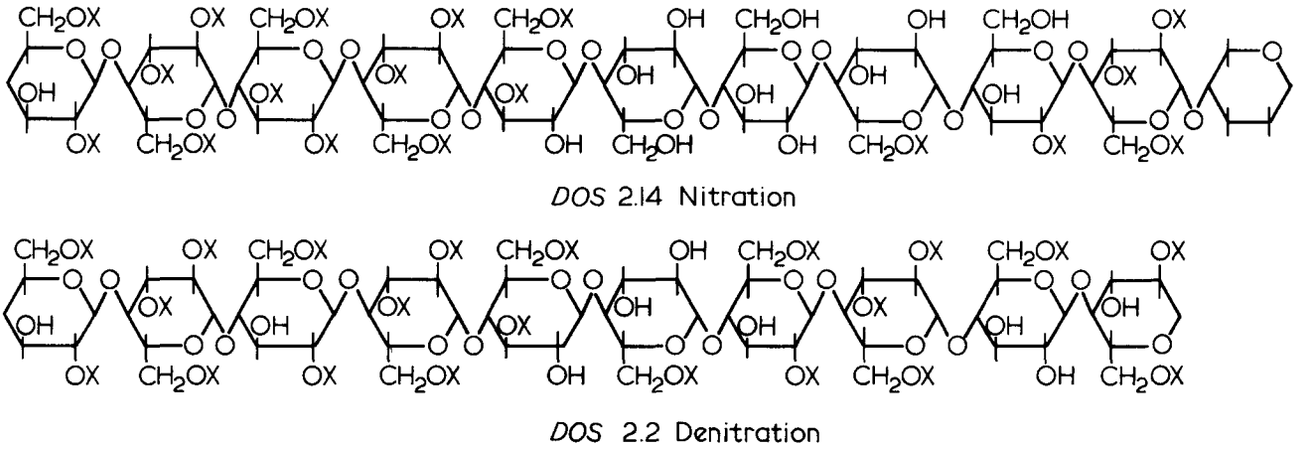


Figure 4 Statistically calculated sequences for nitrated and denitrated nitrocelluloses of *DOS* 2.14 and 2.2 respectively

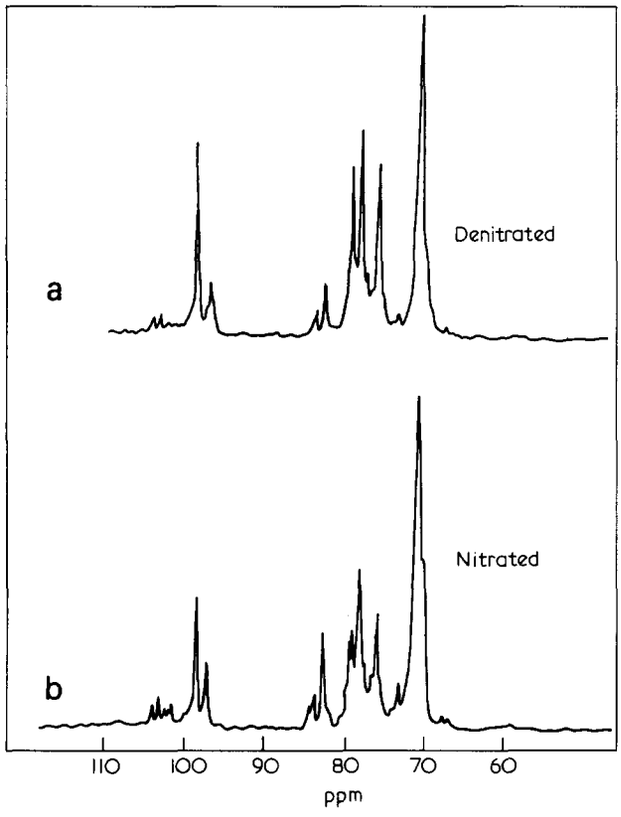


Figure 5 ^{13}C n.m.r. (75.5 MHz proton decoupled) spectra of cellulose nitrates prepared by (a) denitration and (b) nitration in the same mix

differences in hydrogen bonding systems and indirectly to interchain spacings. The work considered here, however, has essentially dealt with nitration and denitration in different media. With respect to the important question of equilibria it would be extremely interesting to investigate materials prepared by nitration and denitration in the same medium.

Figure 5 shows the ^{13}C n.m.r. spectra of a cellulose nitrate prepared by nitration in 53.3% H_2SO_4, 20.8% HNO_3, 25.7% H_2O and denitration of a 2.8 *DOS* material in the same mix. The striking feature of the spectra is that the final *DOS* attained in this case is not the same for nitration and denitration†. At first glance this may seem inconsistent with a pure equilibrium nitration reaction and may seem to support an accessibility argument (cf. refs. 1–4). It is appropriate here therefore to review the data presented both here and in previous papers with respect to this important question.

Clearly, the theory of accessibility, which argues for a rate controlled nitration where the final *DOS* is dependent only on the relative accessibility of the cellulose is untenable. It is obvious, for example, that inaccessible regions in this argument should be totally unsubstituted since the nitrating acids cannot penetrate these regions and also that the degree of accessibility may be altered according to the swelling power of the nitrating acids (cf. ref. 1). However the ^{13}C n.m.r. data reveal that over a large *DOS* range of denitrated materials and above a *DOS* of $\simeq 2.5$ in nitrated materials, no unsubstituted residues are present indicating that in all probability acids of some composition reach all parts of the fibre in a standard nitration time of two hours†.

The e.s.c.a. data[3] have also revealed that at the very surface of fibrils even in mixes where the sulphate ester effect is negligible or absent (nitric-phosphoric mixes)[3] total substitution is not attained and the final *DOS* at the surface is dependent on equilibria established at the surface; the final position of equilibrium depending on the acid mix employed. If the top 20–50 Å is to be considered totally accessible at least in comparison to the remaining several microns of a typical macroscopic fibre then the fact that the reaction *never* goes to completion in the surface regions is impossible to explain on the basis of an extreme accessibility theory[1].

The data accumulated to date also reveals that the final *DOS* seems unrelated to the swelling power of the reagent (according to the Miles diagram)[1], in fact it is generally true that mixes which produce a highly swollen cellulose, nitrate to particularly low levels. Whereas according to an accessibility theory increased swelling should be related to increased *DOS*. Again we must assume that under all normal conditions of nitration the acid is able to rapidly penetrate all areas of the fibrils perhaps initially by passing through voids between fibrils reacting rapidly at the surface (within 1 s) and diffusing more slowly into the bulk of the fibrils.

However the other extreme of a pure equilibrium theory also has some anomalies for example one would

† The nitrated material has a *DOS* ~2.0 whilst the denitrated material has a *DOS* ~2.4

† Under the conditions of these nitrating or denitrating reactions ~100 fold excess of reagent was employed

expect in an equilibrium that a cellulose nitrated in a given mix should have the same *DOS* as a high *DOS* cellulose nitrate denitrated in the same mix. In one case ^{13}C n.m.r. data has shown that this is clearly not the case. *Figure 5* shows such experiments and the difference in ^{13}C spectra for such material is clearly evident where the denitrated material clearly has the higher *DOS*. The explanation appears to lie in the heterogeneous nature of the reaction and the importance of what amounts to the lattice energy of disruption consequent upon nitration and denitration. It has been inferred from previous studies[3,4] that the rate constants for nitration at a given site in a β-d-glucopyranose residue increase with the *DOS* of the ring as do those for denitration at a given site. Also the nitration of a given residue is dependent to a large extent on the *DOS* of the adjacent residue and in particular on whether there is a nitrate group at the C'_3 position in an adjacent ring.

Clearly, on a microscopic scale the equilibrium situation is rapidly established at individual sites along a chain but the many factors which determine the final *DOS* on a macroscopic level are such that materials nitrated and denitrated in the same mix need not have the same *DOS**. Indeed as has already been demonstrated in this work nitration and denitration at a given residue will proceed according to the influence of its immediate neighbour giving rise to differences in sequence distribution and ultimately to a difference in average *DOS*. It is worth pointing out that a similar experiment carried out at high *DOS* revealed no difference in *DOS* between materials nitrated and denitrated in the same mix. This is consistent with the theory presented here and inconsistent with an accessibility argument which would suggest a similar difference in *DOS*.

* The important distinction here is that in a heterogeneous process morphological factors are important in determining the reactivity of a given site as well as the short range electronic structure factors

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