Since the oxidation of ethylene and methanol gives rise to formaldehyde directly, we consider that large quantities of hydrogen peroxide should be formed in suitably conditioned reaction vessels when these substances are oxidized. Recently we have found a 20 per cent conversion of ethylene to hydrogen peroxide at 320° C in a matured quartz vessel. It seems probable that with flow methods even higher yields of hydrogen peroxide may be possible.

R. G. W. NORRISH
J. M. THOMAS

Department of Physical Chemistry,
University of Cambridge.

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Factors affecting the Mobilities of Anions in Nylon

It has been reported^{1,2} that the diffusion coefficients of anions in nylon rapidly increase with increasing internal concentration. In the case of the trisulphonic dye naphthalene scarlet 4R, McGregor, Peters and Petropolous² attributed this result to a proportionality between the diffusion coefficient and some power of the activity coefficient of the anion. Atherton and Peters³ modified the Gilbert-Rideal theory⁴ (originally developed to explain the sorption of inorganic acids by wool) so as to cover polyvalent dyes in nylon; they obtained anion activity coefficients of the form $[1/(1-\theta_A)]$, where θ is the fraction of occupied amine sites.

We wish to direct attention to the importance of distinguishing between the influence on diffusion of direct interactions between anion and substrate, and interactions involving the accompanying cations (usually protons). These associate with specific sites in the nylon so that the proton activity coefficient takes the form $1/(1-\theta_H)$; if coupled bulk transport of dye acid occurs, proton activity variation leads to relationships between diffusion coefficient and concentration of the type **observed**. This effect can only be satisfactorily eliminated by using radiotracers, which enable anion mobilities to be measured. Even when this is done, there remains the possibility that anion mobility can be increased by co-operative interaction with mobile cations. Such effects have been observed in keratin⁵. For acid sorption, the number of free protons is $\theta_H/(1-\theta_H)$, so proliferation occurs near the site-saturation point, and gives rise to a similar experimental result.

The following tracer experiments illustrate these points. The ions investigated were a simple inorganic ion, Br⁻, and a monosulphonic dye anion, naphthalene orange G (NOG, C.I. acid orange 7).

The internal concentration range investigated was the so-called 'amine-dyeing' region. The amine end group content, 0.028 m.equiv./g, was obtained by dissolving the nylon in 70:30 per cent phenol: methanol solution and titrating with N/20 hydrochloric acid solution using thymol blue as the indicator. The titration curve of each acid has a shoulder at approximately 0.026 m.equiv./g (at the temperature at which the diffusion runs were carried out), before rapidly rising at low pH's due to acid sorption on the amide sites.

It can be seen from Fig. 1A that the diffusion coefficient of the inorganic ion in the amine-dyeing region varies only slightly with internal concentration; it is impossible to explain in this case the variation of diffusion coefficient with concentration merely in terms of an idealized activity

coefficient of the form $\frac{1}{(1-\theta)}$.

Two curves are shown for the NOG anion. Fig. 1B, curve b, at internal concentrations less than 0.02

Fig. 1

m.equiv./g, was obtained using buffered solutions (buffer concentration M/100 mixed phosphate) whereas curve a was obtained under free acid conditions. Free acid points could not be obtained for internal concentration < 0.01 m.equiv./g since these correspond to external free acid concentrations of 10^{-6} N and lower. The general effect of the use of buffer is to produce a pronounced peak at an internal concentration of about 0.012 m.equiv./g.

In the absence of buffer, the height of the peak is reduced. It has been shown previously that the presence of inorganic electrolytes accelerates NOG in keratin and that even more pronounced effects are observed with polyvalent ions. The pronounced peak in the presence of buffer may well have a similar cause and it is, therefore, of considerable importance to exclude all ions other than those of the free dye acid from the system in investigations of this kind. After allowing for possible ion-acceleration effects, there remains the residual negative slope on curve a in the intermediate internal concentration range; such an effect was previously observed in keratin also⁶, and was attributed to internal agglomeration. In view

of this complex behaviour the $\frac{1}{(1-\theta)}$ term is inadequate at intermediate concentrations.

The dye self-diffusion coefficient increases rapidly with increasing concentration as the available amine sites become saturated ($\theta \rightarrow 1$), as was observed by Peters *et al.*² with naphthalene scarlet 4R. It remains to be seen whether this is solely due to interactions between the anion and the fixed positive sites, or whether interactions with the hydrogen ions also play a part, analogous to the salt acceleration effect already described.

J. MARSHALL
J. A. MEDLEY

Wool Industries Research Association,
Torridon, Headingley Lane, Leeds, 6.

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