

The Distribution of Dye and Inorganic Ions Between Cellulose Films and Aqueous Solutions

Some results of immediate interest have been obtained in studies of the equilibrium distributions of sodium, chloride, and dye ions (C.I. Direct Yellow 12) between aqueous solutions and cellulose films at 90°C. After equilibration, samples of film were removed together with some adhering solution and the total ion concentrations in the films + adhering solution were determined. Sodium ions and chloride ions were determined by neutron activation analysis, which proved to have advantages over the use of flame photometry and of specific ion electrodes. The dye ions were determined spectrophotometrically, with due precautions in view of the phototropic nature of the dye.

The procedures previously reported¹ make it possible to calculate the ion concentrations in the films ($[Na^i]$, $[Cl^i]$; g ions/kg of dry film) for any given assumption about the specific solvent content of the films at equilibrium (V , kg/kg of dry cellulose). All data in this note are given with 95% confidence limits. The water retention of the film used was 1.014 ± 0.026 (kg/kg of dry film; centrifugation for 5 min at 500 g). Figure 1 shows data for 0.03M NaCl solutions at 90°C and pH 6.0, on the assumption that $V = 1.0$. The 95% confidence limits on the smooth curves are shown. When the electrical neutrality condition is used to calculate the apparent concentration of ionized acidic groups (presumably $[COONa + COO^-]$) in the films, a value of $(40.0 \pm 5.0) \times 10^{-3}$ equiv/kg is obtained, which agrees well with independent measurements of the acidic group content (42.7 ± 4.0 meq/kg).

If $[Na^s]$ and $[Cl^s]$ are the molal concentrations in solution, the distribution coefficient (K_{NaCl}^V)¹

$$K_{NaCl}^V = \frac{[Na^i][Cl^i]}{V^2[Na^s][Cl^s]} \quad (1)$$

can be used to describe the equilibrium distribution of the NaCl between the aqueous solution and the water-swollen film.² Figure 2 shows that the values calculated for K_{NaCl}^V are not particularly sensitive to small errors in V in these experiments, if V is taken to be the water retained after centrifugation.

The data in Figure 2 can also be interpreted in the light of the conventional, simple Donnan membrane theories of cellulose dyeing. These theories postulate the existence of an internal solution of the inorganic ions in the water in the substrate. This internal solution is considered to have exactly the same properties as the external solution, so that the distribution of the inorganic ions should be characterized by the theoretical condition $K_{NaCl}^V = 1$. There has been extensive controversy over the correct assignment

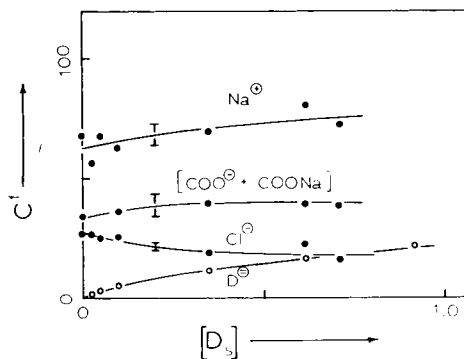


Fig. 1. Equilibrium ion distributions: ordinate, ion concentration in cellulose (meq/kg); abscissa, dye concentration in solution $[D^s]$ (moles/l. $\times 10^3$).

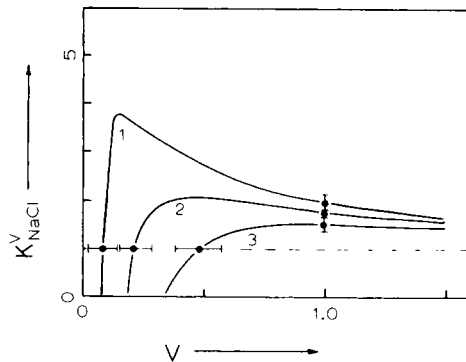


Fig. 2. Experimental dependence of K_{NaCl}^V on V : (1) no dye; (2) $[D^*] = 0.1$ mmole/l.; (3) $[D^*] = 0.7$ mmole/l.

of the volume term V which describes the "volume" of the internal solution in the substrate, and for regenerated celluloses values of $V = 0.45$ l./kg of dry cellulose occur most frequently.^{3,4} The solutions used here are dilute, and it is sufficient for our purposes to assume that the solvent water in both phases has unit density. More detailed studies must take account of the density changes noted by Hermans.⁵

Subject to this assumption, we can now regard Figure 2 as showing the dependence of the volume-based distribution coefficient K_{NaCl}^V on the assumptions made about the volume V of the internal solution in these theories. In particular, we can use Figure 2 to determine the "correct" volume term $V = V_D$, for which $K_{\text{NaCl}}^V = 1$.

In doing this, we are not assuming that these simple theories can provide a "correct" description of the ionic distributions; we are merely attempting to find out if these theories can be applied in a self-consistent manner and whether or not the conventional assignment of $V_D = 0.45$ l./kg is consistent with our data.

If the ionic concentrations and K_{NaCl}^V are measured for some given assumption about V , then

$$V_D = V \cdot \left\{ \frac{R_{\text{Cl}} + R_{\text{Na}}^*}{R_{\text{Cl}} + R_{\text{Na}}} \right\} \quad (2)$$

where

$$R_{\text{Cl}} = ([\text{Cl}^f]/V[\text{Cl}^*]) - 1 \quad (3)$$

$$R_{\text{Na}} = ([\text{Na}^f]/V[\text{Na}^*]) - 1 \quad (4)$$

$$R_{\text{Na}}^* = ([\text{Na}^f]/V[\text{Na}^*]) - K_{\text{NaCl}}^V \quad (5)$$

Figures 2 and 3 show an experimental dependence of V_D upon dye concentration (95% confidence limits on V_D are shown) which cannot be explained on existing theories. At the higher dye concentrations, the experimental values of V_D are, however, quite close to the commonly accepted value of $V_D = 0.45$ l./kg.

There are good reasons for believing that these apparent "volume terms" V_D do not, in fact, have the significance usually attributed to them as a "volume" of internal solution within which the inorganic ions dissolve and in which they have the same properties as in the external solution.³ Thus, the present data are quite well represented at the lower dye concentrations by theoretical curves calculated on the assumption that the chloride ion follows a simple Donnan distribution based on a volume term $(V_D)_{\text{Cl}} = 0.9$ (this choice of $(V_D)_{\text{Cl}}$ is not critical) and that the sodium ions participate in ion binding with the acidic groups of the cellulose (Figs. 3 and 4). It is clear from eqs. (2)–(5) that any mechanisms which lead to positive deviations from the condition $K_{\text{NaCl}}^V =$

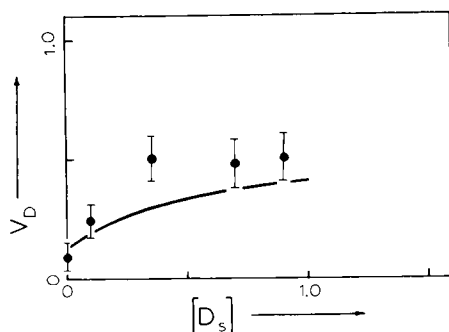


Fig. 3. Experimental dependence of V_D upon $[D^*]$: ordinate, V_D (kg/kg dry cellulose); abscissa, $[D^*]$ mmole/l. The smooth curve is calculated for sodium ion binding (see Fig. 4).

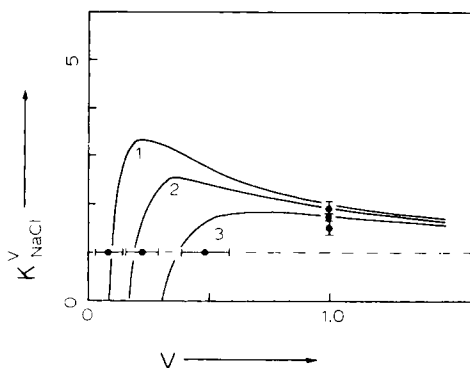


Fig. 4. Theoretical dependence of K_{NaCl}^V on V and on $[D^*]$ for sodium ion binding. The binding parameters were adjusted to fit the data in the absence of dye (curve 1) at $V = 1.0$, and to agree with independent measurements of the acidic group dissociation coefficient K_{COOH}^V for $V = 0.9$ (this choice of V is not critical). The value $K_{COOH}^V = 0.88 \times 10^{-5}$ (equiv/l.) was used, together with $K_{COONa}^V = 0.67 \times 10^{-2}$, and the calculations require about 40–50% of the sodium ion on the film to be "bound" to the acidic groups: only some 10–30% of the acidic groups are predicted to be in the free, ionized form: (1) no dye; (2) $[D^*] = 0.1$ mmole/l.; (3) $[D^*] = 0.7$ mmole/l.

1, at the value of V used as the basis of measurement of the ionic concentrations, will be reflected in similar changes in the apparent "volume term" V_D . As pointed out elsewhere,¹ V_D is unlikely to be a pure volume term.

Figure 2 shows clearly that the central problem of the assignment of a unique value to V when determining the ionic concentrations in these systems is still unresolved. At present, we can do little more than present self-consistent analyses based on clear assumptions about V . Although the use of the water retention W after centrifugation under standard conditions has obvious empirical advantages, this represents an upper bound on V . The extrapolation of water retention data to zero surface tension of the adhering solution gives a limiting water retention W_0 which is about 92% of W in the case of cellulose films.⁴ On this basis, the present films would have $W_0 = 0.93$ (kg/kg of dry cellulose), a value which agrees with estimates of the water content of cellulose model filaments, based on swelling measurements in liquid water.⁵ There is, however, strong evidence that water amounting to some 0.11 to 0.13 kg/kg of dry cellulose is so firmly bound to the cellulose that it acts as "nonsolvent water."⁵ On this basis, a

plausible estimate of V for the films used here is $V = 0.80$ kg/kg of dry cellulose. The sorption data alone do not show any features which clearly confirm this value as a correct choice of V . The data have been analyzed assuming $V = 0.9$, because this corresponds quite closely to the expected total water content of the swollen films. Data calculated for $V = 0.8$ would show essentially the same features.

The material presented in this note was obtained by Mr. K. H. Ezuddin in partial fulfillment of the requirements for the degree of M.S. in Textile Chemistry, North Carolina State University at Raleigh.

The dye was provided by the G. A. F. Company and the cellulose film, by du Pont. The neutron activation analyses were carried out by the activation analysis laboratory at NCSU, Raleigh, and we are indebted to Professor H. A. Rutherford for suggesting this technique.

References

1. R. McGregor, *Text. Res. J.*, **42**, 172 (1972).
2. F. Helfferich, *Ion Exchange*, McGraw Hill, New York, 1962.
3. T. Vickerstaff, *The Physical Chemistry of Dyeing*, 2nd ed., Oliver and Boyd, London, 1954.
4. J. Farrar and S. M. Neale, *J. Colloid Sci.*, **1**, 186 (1952).
5. P. H. Hermans, *Contribution to the Physics of Cellulose Fibres*, Elsevier, Amsterdam, 1946.

R. MCGREGOR
K. H. EZUDDIN

School of Textiles
North Carolina State University
Raleigh, North Carolina 27607

Received June 11, 1973
Revised August 14, 1973