

SURFACE STUDIES OF FIBRE-WATER SYSTEMS BY GAS CHROMATOGRAPHY

**D. G. GRAY, Pulp & Paper Research Institute of Canada,
Montreal, Canada**

THE surface and interfacial properties of fibres and paper are important in the production and end-use of paper and board, and much attention has been paid to the nature of the interface between water-swollen cellulose fibres and the aqueous suspension medium. Much less attention has been paid to the equally important interface between fibres containing water and the atmosphere. The properties of this interface must range from those characteristic of a dry fibre to those of pure water, corresponding to water contents ranging from a fraction of a monolayer up to the fibre saturation value.

In the intermediate range of water contents, where the fibres are in equilibrium with atmospheres ranging from 1 to >95 per cent relative humidity, little is known about the nature of the surface. Yet it is this surface which plays an important role in processes such as printing and airforming. Is the water content at the surface the same as in the bulk? If not, which component is in excess? How does the external surface area of a fibre or sheet change with moisture content? Many of the methods of surface chemistry, such as the classical nitrogen adsorption methods and the more modern instrumental surface techniques, require exposure of the samples to a high vacuum, and thus direct application to wet cellulose surfaces is impossible. In principle, vapour and liquid permeation methods⁽¹⁾ and dynamic wetting measurements⁽²⁾ should be adaptable to surface area or surface roughness measurements on fibres containing water, but information on the surface chemistry is not easily deduced. Recently gas chromatography (GC), with the fibres or paper packed inside the column as the stationary phase, has been used to study the adsorption of non-swelling organic vapours on cellulose.^(3,4) Adsorption isotherms, surface areas, and the thermodynamics of adsorption as a function of surface coverage were determined. This method requires only ambient temperatures and pressures and is thus also applicable to studies on

Under the chairmanship of Dr H. Corte

moist cellulose and fibre surfaces.⁽⁵⁾ Some preliminary results on moist cellulose fibres will be outlined in this contribution.

The basics of gas chromatography are described in several texts.⁽⁶⁾ Reviews on physical measurements by GC⁽⁷⁾ and on applications to polymeric stationary phases^(8, 9) have been published. In the work reported here, the adsorption isotherms on cellulose fibres were measured using the 'elution by characteristic point' method of finite concentration GC.⁽¹⁰⁾ The relevant equations are presented in References 3–10. The steps in measuring and interpreting the data may be summarised as follows. (I) The variation in GC retention times for different vapour phase concentrations of probe vapour first gives the shape of the adsorption isotherms with the amount adsorbed expressed per unit weight of stationary phase. (II) The monolayer coverage Γ_m is derived from the isotherm shape using the Brunauer–Emmett–Teller (BET) equation (11). (III) The surface area is derived from the coverage by assuming a value for the area occupied on the surface by a probe molecule. (IV) The adsorption isotherms are recalculated with adsorption expressed per unit surface area. (V) A comparison of adsorption isotherms at different relative humidities indicates the relative affinities of moist cellulose for the probe vapour.

Results and discussion

THE retention of n-decane on cellulose surfaces alters markedly when the cellulose is moist. Three series of chromatographic peaks for decane on Whatman filter paper fibres conditioned at different relative humidities are shown in Fig. 1. It is evident that for moderate amounts of decane the retention time on the moist substrate is less than on the dry cellulose. Similar results are obtained on bleached kraft fibres. These results reflect either a lower affinity of the wet cellulose for n-decane, or a decrease in the surface area of the cellulose, or some combination of both factors. The crux of the problem is to determine separately these two contributions to the change in GC retention.

The problems in measuring the surface area of moist fibres are first considered. In principle, the BET treatment⁽¹¹⁾ of the isotherm data should give the amount of adsorbed vapour required to form a monolayer, independent of the nature of the surface or of the vapour. For isotherms which do not show a distinct knee (Type III, or Type II with low values for the BET constant C , according to the usual classification⁽¹¹⁾), it has been suggested that monolayer coverages are untrustworthy,⁽¹²⁾ although this has been disputed.⁽¹³⁾ Assuming that valid values for the monolayer coverage may be derived from 'weak-kneed' isotherms using the BET equation, there remains the problem of converting monolayer coverage to surface area. This requires knowledge of the

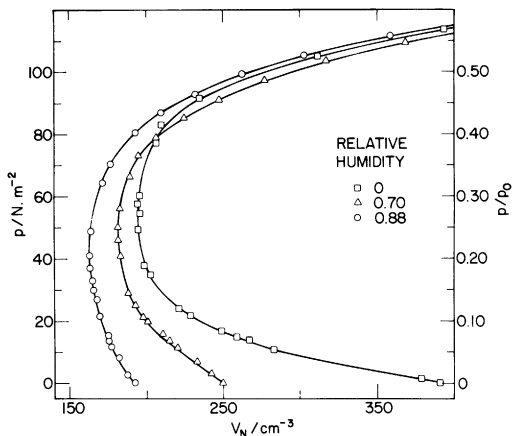


Fig. 1—Gas chromatographic retention data at 25° C for n-decane on Whatman filter paper fibres with different water contents. The points indicate the individual GC peak maxima, and the lines thus represent the variation of peak retention volume with peak height, expressed as partial pressure of n-decane

area occupied by each adsorbate molecule, which is often estimated from the equation

$$A_m = 1.09(M/\rho N)^{2/3} \times 10^{14}$$

where A_m ($\text{nm}^2/\text{molecule}$) is the area occupied by each molecule, ρ (g/cm^{-3}) is the density of the liquid adsorbate, M is its molecular weight and N is Avogadro's number. This equation gives the time-honoured value of 0.162 nm^2 for the area occupied by a N_2 molecule at 77 K. On dry cellulose, this formula gave good agreement for surface areas measured with n-alkanes, n-butanol and dioxan, although, not unexpectedly, long chain normal alcohols were found to give divergent results.⁽⁴⁾ The agreement in surface areas for a range of adsorbents, despite the simplistic assumptions of the model, and despite isotherms with BET C values as low as 4, suggests that the method may remain valid for moist fibres, at least at lower relative humidities.

The results for surface area measurements, calculated on cotton fibres making these assumptions are summarised in Fig. 2. After exposure to 40 per cent RH, the surface area of the moist fibre has decreased irreversibly; when redried the surface area is essentially the same as when moist. The decrease is attributed to the fibre preparation process, where the fibres, dried from a dilute aqueous suspension by evaporation on a ceramic plate, become torn

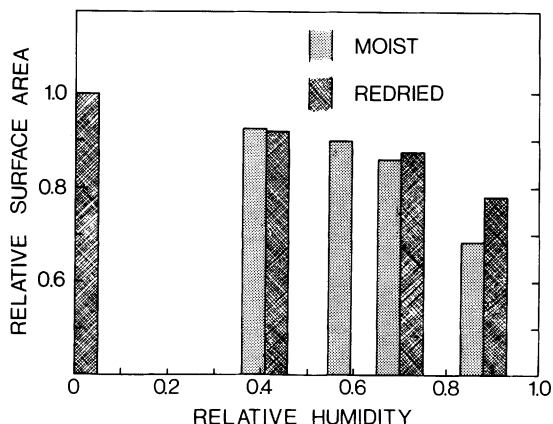


Fig. 2—The surface area (relative to the initial dry area) of moist and redried fibres from Whatman filter paper, on equilibration at the indicated relative humidities. The surface areas were measured in both moist and redried states as indicated. The sequence of measurements runs from left to right

and fibrillated when scraped off. In the column, the surface area decreases on exposure to humid air because the fibrils relax (and possibly also because of surface pore filling and fibre-fibre bonding at higher relative humidities). In contrast to the cotton fibres, bleached kraft fibres and samples of paper show the expected slight increase in surface area at lower relative humidities. Above about 75° RH, a decrease in the surface area of all samples become apparent, but a substantial component of the decrease is reversible, i.e., on drying the surface area increases again. The reversible portion of the change in surface area is tentatively attributed to an increase in the area A_m occupied by a decane molecule at monolayer coverage as more water is adsorbed on the surface. It may be noted that above 75 per cent RH, the isotherm knee becomes nonexistent, $C \rightarrow 2$, and the reliability of BET surface areas is questionable.⁽¹²⁾ Thus, although the monolayer capacities may be reduced, the surface area measurements at high relative humidities require caution in interpretation.

If the surface area can be estimated by GC or by other means, then the adsorption isotherms from steps I and II may be recalculated on the basis of adsorption per unit surface area. Some isotherms for cellulose at different relative humidities are compared in Fig. 3 with an isotherm for n-decane on liquid water, which was estimated from literature data⁽¹⁴⁾ for hydrocarbons on a water-coated GC support. It is evident that n-decane is adsorbed onto

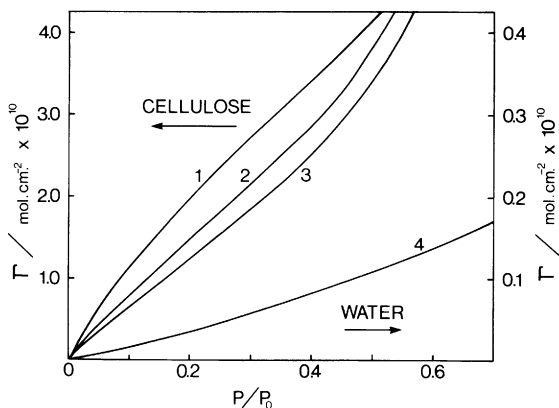


Fig. 3—The adsorption isotherms for n-decane on the surface of cellulose at 29° C and 0 per cent RH (1), 70 per cent RH (2), and 88 per cent RH (3). The estimated adsorption at 12.1° C of n-decane on a water surface is also shown in curve (4); note the expanded vertical scale

water very much less strongly than onto cellulose. This is in line with the decrease in BET C parameter. The magnitude of the phenomenon may be illustrated as follows. Consider the adsorption of very low concentrations of n-decane, where decane-decane interactions are essentially eliminated. The retention volume V_N for n-decane on dry cellulose, as the partial pressure of decane approaches zero, is 390 ml (Fig. 1). The retention volume on water may be estimated to be at least two orders of magnitude less, and so is ~ 0 , within experimental error. Reduced to unit surface area, the retention volume at 72 per cent RH is 0.74 of the dry retention volume. (In other words, at this humidity, which corresponds to 10 per cent water regain, the real surface behaves towards n-decane *as if* it were an imaginary surface of 74 per cent dry cellulose and 26 per cent ordinary water.) A similar picture emerges from the isotherms in Fig. 3. Thus the GC method may be used to quantify the interaction of moist cellulose with water-insoluble materials such as hydrocarbons. Conversely, the surface treatment of hydrocarbon polymer fibres may be followed using GC with water as the probe vapour;⁽¹⁵⁾ this seems relevant to measuring the hydrophilicity of synthetic polyolefin pulps.

Conclusions

- (i) Adsorption of non-swelling, water-immiscible organic compounds on moist cellulose surfaces is readily determined by gas chromatography.

- (ii) Surface areas obtained from such adsorption isotherms for n-decane below about 90 per cent RH appear reliable. Moisture uptake causes a decrease in surface area, and factors other than swelling must be operative.
- (iii) Above 90 per cent RH, the surface areas decrease markedly, but further work is necessary to ensure that at least part of the decrease is not due to an increase in the area occupied by the n-decane molecule at monolayer coverage.
- (iv) The affinity of moist cellulose for n-decane decreases with water content.

References

1. See for example Corte, H., *Fundamentals of Papermaking Fibres*, Ed. F. Bolam (Technical Section, British Paper and Board Makers' Association, London 1958), 301-331
2. Bendure, R. L., *J. Colloid Interface Sci.*, 1973, **42** (1), 137-144
3. Mohlin, U.-B. and Gray, D. G., *J. Colloid Interface Sci.*, 1974, **47** (1), 747-753
4. Tremaine, P. R. and Gray, D. G., *J. C. S. Faraday Trans. I*, 1975, **71**, 2170-2185
5. Tremaine, P. R., Mohlin, U.-B. and Gray, D. G., *J. Colloid Interface Sci.*, 1977, **60** (3), 548-554
6. See for example, Littlewood, A. B., *Gas Chromatography*, 2nd ed. (Academic Press, London, 1970)
7. Conder, J. R. in *Progress in Gas Chromatography*, Ed. J. H. Purnell (Wiley-Interscience, New York, 1968), 209-270
8. Braun, J. -M. and Guillet, J. E., *Advances in Polymer Science*, 1976, **21**, 107-145
9. Gray, D. G. in *Progress in Polymer Science*, Ed., A. D. Jenkins, **5** (Pergamon, London, 1977), 1-60
10. Conder, J. R., *Chromatographia*, 1974, **7**, 387-394
11. See for example, Adamson, A. W., *Physical Chemistry of Surfaces*, 2nd ed. (Interscience, New York, 1967)
12. Young, D. M. and Crowell, A. D., *Physical Adsorption of Gases* (Butterworths, London, 1962), 147-164
13. Brunauer, S., Copeland, L. E. and Kantro, D. L. in *The Solid Gas Interface*, Ed. E. A. Flood, **1** (Marcel Dekker, New York, 1967), 413-429
14. King, J. W., Chatterjee, A. and Karger, B. L., *J. Phys. Chem.*, 1972, **76** (19), 2769-2777
15. Courval, G. J. and Gray, D. G., *J. Polym. Sci., Letters Ed.*, 1976, **14** 1(4), 689-692

Transcription of Discussion

Discussion

Dr A. H. Nissan When you say the surface area decreases do I understand you to say that the surface area seen by decane molecules decreases, not necessarily the total surface area seen by water and decane; or do you mean that in fact the total surface area decreases?

Gray The total surface area of the fibre water system decreases. It decreases not only for decane but for every organic molecule which we tried and we have tried a range of five or six by now. It is not the internal pore surface area. We do not get into the pores. The decane does not dissolve in water.

Nissan Would a glucose molecule see the same area as decane?

Gray No, sir. Because a glucose molecule would dissolve in the water. We chose the probe so that it will stay on the outside. We don't want to get inside.

Under the chairmanship of Dr H. Corte