

FRONTAL CHROMATOGRAPHY OF WATER VAPOUR ON CELLULOSE FIBRE*

By

Gy. RÁCZ, Gy. SZÉKELY and K. HUSZÁR

Department of Physical Chemistry, Technical University Budapest

Received July 11, 1975

Presented by Prof. Dr. Gy. Varsányi

Cellulose fibre or fabrics processed at high temperature release or take up water (vapour). Adequate knowledge on the equilibrium of sorption and on the kinetics of sorption-desorption is fundamental planning up-to-date cellulose processing methods. Information on the interaction of cellulose and water may prove useful also in the quality control of cellulose.

An account will be given on experiments with frontal chromatography in which water vapour chromatograms were taken in a column filled with cellulose fibres and on conclusions drawn there from the extent of equilibrium of sorption could be established from the time lag of the front and the characteristics of sorption rate from its shape.

Experimental

Apparatus

Our tests were made with a Pye-Unicam 104 chromatograph equipped with a katharometer cell. A bundle of regenerated cellulose fibres** was introduced in a U-tube of 500 mm length and 4 mm internal diameter, a standard accessory to the chromatograph. Carrier gas entered into the U-tube through a two-way cock, either dry or saturated with water vapour. The mole fraction of the vapour was calculated from the inlet pressure and water vapour pressure at saturation temperature. Turning of the cock produced on error less than 1 cm³ in the determination of the carrier gas volume. After a sorption-desorption cycle the base line returned to its initial position within 1 per cent of the full displacement obtained with saturated water vapour. Using hydrogen as carrier gas the response of the detector was linear which implies that the non-linearity of the detector was smaller than the reproducibility of saturation water concentration (less than ± 2 per cent). When nitrogen was applied as carrier gas, the non-linear characteristic of the detector was taken into consideration. The experiments discussed here were performed at 104 ± 0.5 °C. The chromatogram of a full sorption-desorption cycle is shown in Fig. 1.

* Dedicated to Prof. G. Schay on the occasion of his 75th birthday.

** "Crystalline" fibre, made in Austria, 150 Den, elementary fibre 2,5 Den, degree of polymerization 400.

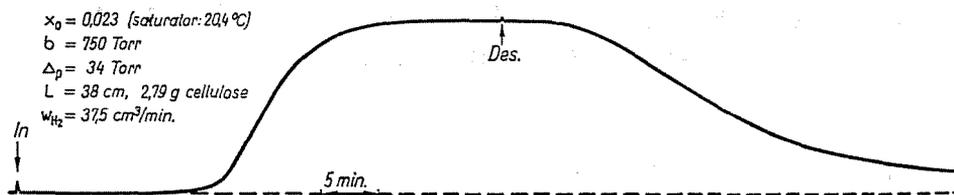


Fig. 1. Frontal chromatogram of water vapour

Stationarity

The examination of the shape of a chromatographic front is considerably simpler in case of a stationary front, i.e. one that does not change its shape during its progress, every point of the front migrates at the same velocity in the column. The column length that produced a stationary front was experimentally determined. Chromatograms were taken with columns of different

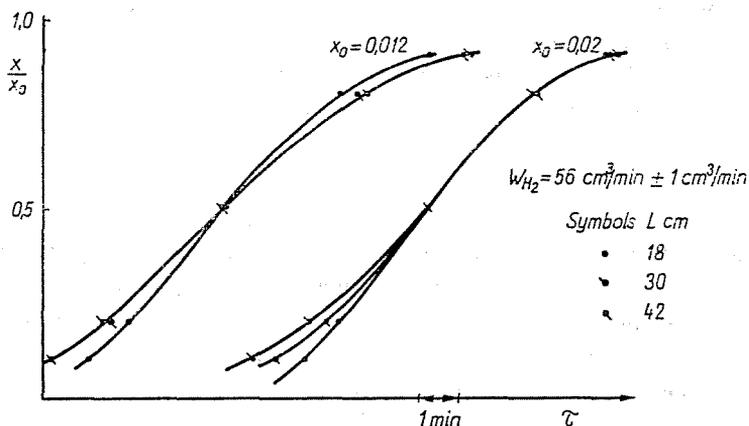


Fig. 2. Variation of shape of front with column length

lengths and superimposed each other. On the horizontal axis a simple time shift was applied, on the vertical axis x/x_0 values (in case of hydrogen carrier the proportionate fractions of the full displacement) are shown. Fig. 2 represents chromatograms taken with carrier gas of two different water vapour concentrations and three column lengths. For an increase of the column length from 18 to 30 cm the chromatogram is seen to still slightly flatten and those taken with columns of 30 cm and 42 cm length to coincide within experimental error.

Factors influencing front shape

Carrier gas

The shape of a chromatographic front essentially depends on two effects: diffusion, in the first line longitudinal, taking place under the effect of the concentration gradient, and sorption rate.

Both effects tend to flatten the front.

When sorption is too rapid, only the effect of diffusion appears, and the steepness of the front is inversely proportionate to the diffusivity of the sor-

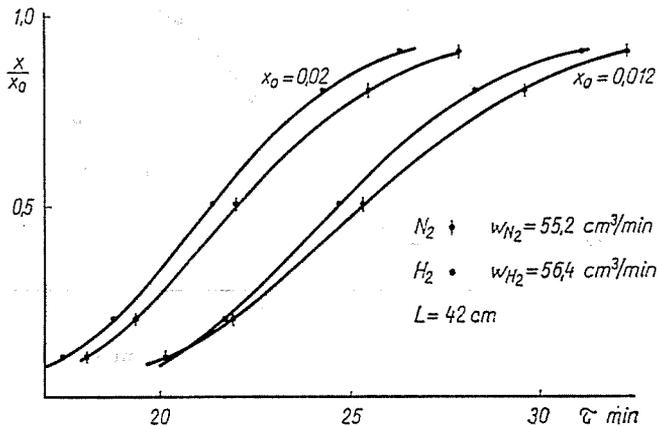


Fig. 3. Effect of quality of carrier gas on front shape

bate [1]. The hydrogen to nitrogen ration of diffusivity of water vapour is 1 to 3, thus the steepness of the front in hydrogen ought to be one third of that in nitrogen. According to the experiments, the steepness of the front little depends on the quality of carrier gas (Fig. 3) and, contrary to the effect discussed above, the front is steeper in hydrogen carrier gas. From this the conclusion was drawn that in nitrogen carrier gas transversal (pore) diffusion takes a small part, that is to say, sorption is retarded by diffusion to the surface. In hydrogen, this effect seems to be negligible, and therefore the shape of the front in hydrogen carrier is felt to be determined by sorption kinetics alone.

Effect of carrier gas velocity

As the velocity of carrier gas increases the chromatographic fronts become steeper.

The steepnesses of three chromatograms taken in a 38 cm long column, compared in Fig. 4 have changed by less than 10 per cent while gas velocity

doubled. According to theory [2] the shape of the stationary front is independent of gas velocity, provided the shape of the front is determined by sorption kinetics, free from the disturbing effect of diffusion; on the other hand, the steepness of the front should be proportionate to the second power of the carrier gas velocity, if the shape of the front depended on longitudinal diffusion alone.

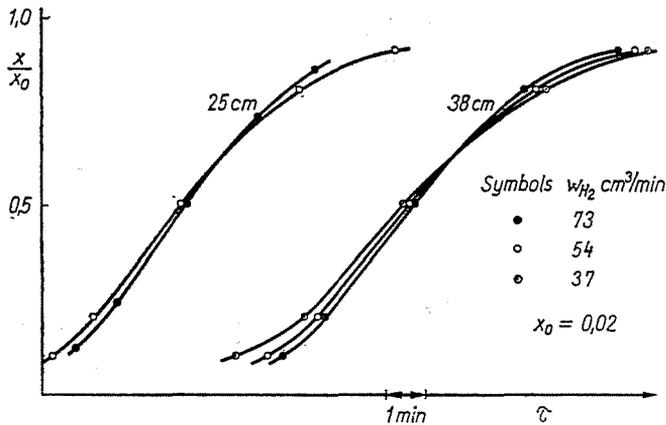


Fig. 4. Effect of carrier gas velocity on front shape

In our case the slight dependence on velocity seems to indicate the presence of a front formed by sorption kinetics. At low velocity rates, however, also diffusion contributes to the development of the front, whereas at high velocity rates formation of a stationary state is questionable.

Effect of water vapour concentration

Fig. 5 shows the comparison of chromatograms taken with three different water vapour concentration. The kinetic equation of sorption has to involve the concentration dependence of the chromatograms.

Water vapour sorption at equilibrium

The total quantity of water vapour from the break-through point of the inert gas to the full saturation of the column was determined from the area before the front. The sorbed quantities have been represented as a function of partial water vapour pressure (Fig. 6). To calculate partial pressure, the arithmetical mean of the measured inlet and outlet pressures was multiplied by the mole fraction set in the water vapour saturator.

It should be mentioned here that, if equilibrium of sorption settled at any instant, the entire isotherm could be calculated from the desorption part of the chromatogram. In our case, calculation gives a curve running above the isotherm. This is another proof of no-equilibrium sorption.

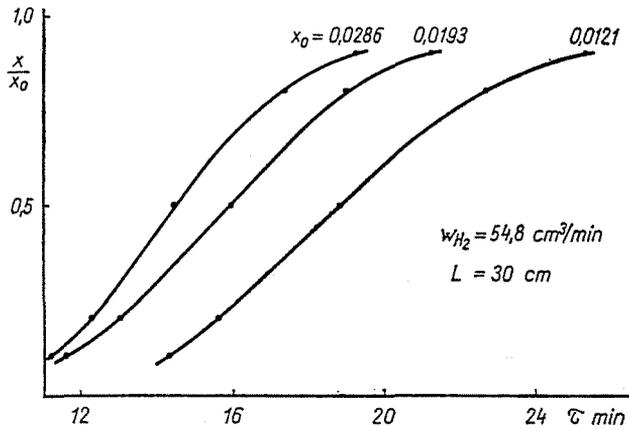


Fig. 5. Influence of water vapour concentration

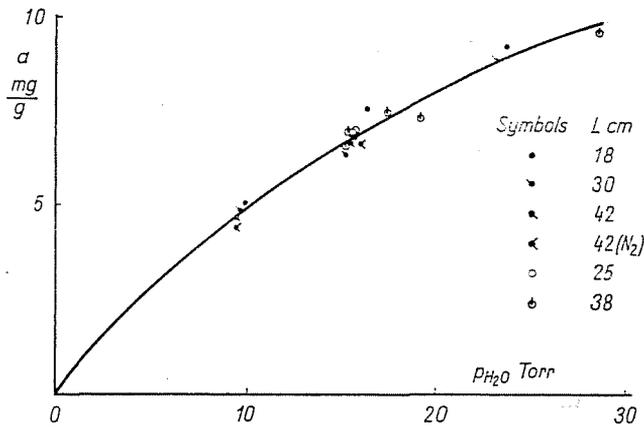


Fig. 6. Sorption isotherm

Kinetic equation of sorption

The kinetic equation of sorption is the relationship between sorption velocity and the concentrations of gas phase and of sorbent in contact. This relationship can be established from the chromatogram. Pressure at the outlet

end being constant, mole fraction may replace partial water vapour pressure, and the relationship may be written in the form:

$$\left(\frac{da}{d\tau}\right)_L = f(x, a)$$

or, replacing gas-phase water mole fraction by the quantity of sorbate at equilibrium:

$$\left(\frac{da}{d\tau}\right)_L = f(a_e, a),$$

In case of linear kinetics:

$$\left(\frac{da}{d\tau}\right)_L = k(a_e - a),$$

The adsorbed quantity increases in time if equilibrium sorption is higher than actual sorption.

At the end of the column water vapour concentration x and its time derivative $\left(\frac{dx}{d\tau}\right)_L$ can be determined and so can be the value a_e belonging to the water vapour concentration from the sorption isotherm. The data for the kinetic equation are calculated from the fundamental differential equation of chromatography, that is the equation of continuity of water vapour:

$$\frac{m}{s} \left(\frac{\partial a}{\partial \tau}\right)_z + \left(\frac{\partial \rho_{H_2O}}{\partial \tau}\right)_z = \left(\frac{\partial n_{H_2O}}{\partial z}\right)_\tau \quad (1)$$

where:

- m — packing density, [g/cm]
- a — sorbed quantity, [g/g]
- s — free cross-section, [cm²]
- τ — time [min]
- z — distance along the column [cm]
- ρ_{H_2O} — water concentration, [g/cm³]
- n_{H_2O} — flow density of water, including convective and diffusion flows [g/cm²min].

According to Eq. (1), the flow velocity of water changes because of the variation of sorption and of concentration at the given place. Eq. (1) has to be transformed so as to contain measured quantities.

If the effect of diffusion is negligible, flow densities of water vapour

to hydrogen are related as their mass fractions:

$$\frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2}} = \frac{\omega_{\text{H}_2\text{O}}}{\omega_{\text{H}_2}} \quad (2)$$

Consider the gas mixture as perfect. If so:

$$\rho_{\text{H}_2\text{O}} = x \frac{18p}{RT} = \alpha x \quad (3)$$

$$n_{\text{H}_2} = \frac{w}{s} \frac{2p_r}{RT_r} = \frac{w}{9s} \beta \quad (4)$$

In the equations α denotes the term $18p/RT$ under the conditions of the chromatographic column; β the same term under the conditions of gas volumetry; x the mole fraction of water vapour; w the volume flow rate of hydrogen. Substituting (2), (3) and (4) into (1):

$$\frac{m}{s} \left(\frac{\partial a}{\partial \tau} \right)_z = - \left(\frac{\partial x}{\partial \tau} \right)_z \alpha - \frac{\beta}{s} \frac{w}{(1-x)^2} \left(\frac{\partial x}{\partial z} \right)_z \quad (5)$$

The partial derivatives of the mole fraction of water vapour are related as:

$$\left(\frac{\partial x}{\partial z} \right)_z = - \frac{1}{u_x} \left(\frac{\partial x}{\partial \tau} \right)_z \quad (6)$$

where u_x is the rate of propagation of a zone of constant mole fraction x . Substituting Eq. (6) into (5):

$$\left(\frac{\partial a}{\partial \tau} \right)_z = \frac{s}{m} \left[\alpha + \beta \frac{1}{(1-x)^2} \frac{w}{u_x s} \right] \left(\frac{\partial x}{\partial \tau} \right)_z \quad (7)$$

This equation is suitable for the determination of sorption velocity. In our case the value of the quotient $w/u_x s$ is about 500, thus the first term in square brackets is negligible as compared to the second. Pressure drop in the column is slight, thus β may be considered as constant.

Eq. (7) can further be reduced by introducing the relationship for the rate of propagation of the stationary front expressing that water vapour fed in unit time saturates a length u_x of the column:

$$\frac{\beta w x_0}{1 - x_0} = u_x m a \quad (8)$$

where

x_0 — mole fraction of water vapour in the feed,

a_0 — mass fraction of water vapour in the water saturated cellulose.

(8) omits the accumulation of water vapour in the gas space.

Substituting (8) into (7) results in a relationship for the calculation of adsorption velocity:

$$\left(\frac{da}{d\tau}\right)_L = \frac{a_0}{x_0} \frac{1-x_0}{(1-x)^2} \left(\frac{dx}{d\tau}\right)_L \quad (9)$$

Integrating Eq. (9) from a time where no water vapour leaves the column yet (i.e. $x = 0$ and $a = 0$) to a time where a mole fraction x of the water in the gas leaves the column, and the mass fraction of water in the cellulose at the column end is a :

$$a = \frac{a_0}{x_0} \frac{1-x_0}{1-x} x \quad (10)$$

Eq. (10) gives the third parameter needed for determining the kinetic relationship: the water mass fraction a in the sorbent in contact with the gas phase of composition x .

Table I

Calculation of sorption velocity
 Experimental conditions: $L = 30$ cm, $m = 0.065$ g/cm, $x_0 = 0.0286$
 Pressure drop in column: $\Delta p = 26$ Torr, $w_{H_2} = 54.6$ cm³/min

$x \cdot 10^2$	τ	$\frac{dx}{d\tau} \cdot 10^2$	p_{H_2O}	$\frac{da}{d\tau}$	a_e	a	$a_e - a$
—	min	min ⁻¹	Torr	mg g ⁻¹ min ⁻¹	—	mg g ⁻¹	—
2.86	11.3	2.4	2.25	0.70	1.5	0.83	0.67
5.72	12.3	3.4	4.50	1.00	2.55	1.66	0.89
14.3	14.5	4.05	11.35	1.20	5.3	4.18	1.12
22.9	17.4	1.96	18.00	0.59	7.3	6.75	0.55
25.8	19.2	1.1	20.3	0.33	8.0	7.65	0.35
28.6	—	—	22.5	—	8.5	—	—

An example for the procedure of computation is given in Table I. Breakthrough times were read at the points marked out at the 0.1, 0.2, 0.5, 0.8 and 0.9 parts of the total deflection and the $\left(\frac{dx}{d\tau}\right)_L$ values were determined by graphic differentiation (Table I, column 3). The partial water vapour pressure in the exit gas was calculated (column 4), and equilibrium sorption

was read from the sorption isotherm (column 6). Sorption velocities calculated from Eq. (9) are compiled in column 5, the momentary sorption values obtained from Eq. (10) in column 7.

Similar calculations have been made for all the chromatograms taken in columns 30 and 42 cm with water concentrations $x = 0.02$ and $x = 0.029$. The sorption rate results are shown in Fig. 7 as a function of the difference of equilibrium and momentary sorption values.

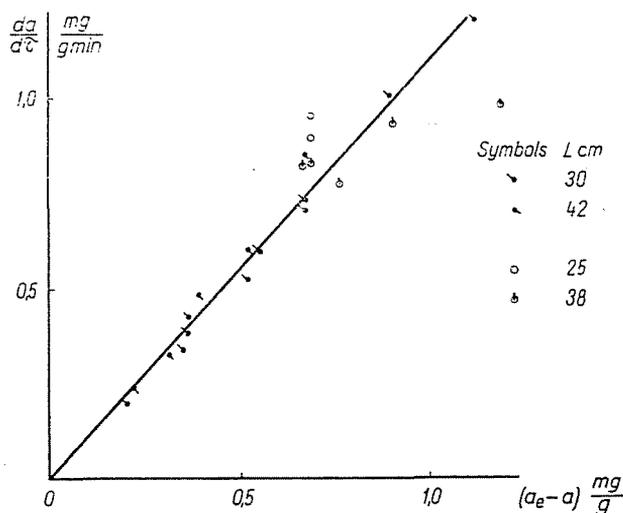


Fig. 7. Dependence of sorption rate on difference between equilibrium and momentary sorption

No calculations have been performed on the chromatograms taken at a water vapour concentration of $x = 0-0.012$ for the way the sorption isotherm is drawn here greatly influences the result.

For chromatograms taken with columns 25 and 38 cm long calculations have been performed at a single point for each. The results are indicated in Fig. 7, with symbols ○ (25 cm) and ⊙ (38 cm). The scatter of the points is not quite random. Results obtained with the shorter column scatter upwards from the straight line, as the derivative $dx/(d\tau)$ (and the resulting value $da/d\tau$) are greater than the stationary value. With a 38 cm long column the values taken at low gas rates scatter slightly downwards from the fitting straight line, probably because in forming the front also gas-phase diffusion has its share.

On the basis of Fig. 7 sorption rate on the examined cellulose fibre at 104 °C can be stated to be in proportion to the difference of the quantities of sorbate at equilibrium condition and that contained momentarily in the fibre. The proportionality factor is 1.1 min^{-1} .

The experiments performed so far yield no conclusion on whether water is adsorbed on the surface of or inside the cellulose fibre. This point is to be cleared up by our next measurements of sorption rate of cellulose fibres of various diameters and specific surfaces.

Authors are greatly indebted to Prof. István Rusznák for having called their attention to the problems of water-vapour-cellulose systems and for the effective support given in the elaboration of the theme.

Summary

Frontal chromatograms were taken in a column filled with a bundle of regenerated cellulose fibres. Investigation of the effects of carrier gas velocity, quality and of column length, showed the shape of the front to be determined by sorption kinetics alone. The effect of longitudinal diffusion in hydrogen was negligible. The sorption rate computed from the chromatogram varied linearly with the differences of equilibrium sorption and momentary sorption values. The rate constant was 1.1 min^{-1} at 104°C .

References

1. SCHAY, G.: Theoretische Grundlagen der Gaschromatographie, DVW, Berlin 1960., p. 110.
2. Ibid. p. 122.

dr. György RÁCZ
dr. György SZÉKELY
dr. Klára HUSZÁR } H-1521 Budapest