



A Study of Adsorption of Water Vapour on Wool under Static and Dynamic Conditions

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Abstract. Adsorption of water vapour on wool provides not only textile comfort, but also convenience in transportation due to increase in its bulk density. The adsorption and desorption isotherms of water vapour for wool were determined by both volumetric technique using a Coulter Omnisorp 100CX instrument and gravimetric method employing a Cahn 2000 electronic microbalance. Adsorption isotherm fitting to B.E.T. model and hysteresis on desorption was observed. The average effective diffusion coefficient of water in wool was found to be $8.4 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ at 25°C from gravimetric data. The effects of packing height and air velocity on the breakthrough curves were also investigated in the wool packed columns. For pseudo first order model, k values changing between $0.33 \times 10^{-6} - 69 \times 10^{-6} \text{ s}^{-1}$ was obtained for $2.2\text{--}6.4 \text{ cm s}^{-1}$ air velocity and $0.05\text{--}0.20 \text{ m}$ packing height ranges.

Keywords: wool, water vapour, adsorption, diffusion, column dynamics

Introduction

Wool is a textile material which is consumed at a rate of 3×10^6 tons per year (IWS, 1989). Wool fibers are sulphur containing proteins and they consist of parts with different morphologies; cuticle, ortho and para cortex and medulla. The physicochemical properties of such as crystallinity, α -keratin and β -keratin fractions and metal cation uptake capacity wool change with race, sex, age and nutrition of the sheep they are taken (Balköse, 1977).

Wool water vapour interactions had been studied by previous workers in detail. It is generally accepted that

the polar groups present in the wool structure, namely the amino, carboxylic acid and OH functional groups interact with water by hydrogen bonding at low relative humidities (Fukuda et al., 1990; Leeder and Watt, 1965). The water vapour is adsorbed on wool in multilayers approximately six such layers have been cited by Miyagawa et al. (1987). The water vapour adsorption on wool is an exothermic process and wool garments are perceived warmer compared to garments made out of other materials such as acrylic (Stuart et al., 1989). On the other hand, the heat-setting of base wool under pressure along with adequate moisture can produce dimensionally stable cylindrical particles with

bulk densities in excess of the highly compressed wool. Packaging of wool without using contaminating materials such as jute and polyethylene is therefore possible with this technique which also reduces the transport costs (Pearson and Warner, 1983). The wrinkling behaviour of wool fabric is also related to the changes in equilibrium water content and the adsorption rate of water vapour (Menefee et al., 1982).

The adsorption isotherms of water vapour on wool were found to be different for different types of wool in studies with quartz spring balance in controlled vacuum chamber (Wlochowicz and Bujok, 1987; Leeder and Watt, 1965). Watt and McMahon (1966) showed that the mass of the sample, packing density of the fiber assembly, the dimensions of the sorption vessel in gravimetric adsorption system affected the rate of approach to the equilibrium values. The heat of adsorption of water vapour in wool was shown to be dependent on moisture of wool (Alexander and Hudson, 1945; Watt and McMahon, 1966; Walker et al., 1970). The diffusion rates of water vapour in wool were effected by both the heat of adsorption and the moisture in wool (Watt and McMahon, 1966; Walker et al., 1970).

It was reported that the quantity of water adsorbed at a given partial pressure was variable and dependent on the previous history of the fiber. The hysteresis phenomenon on wool is of considerable commercial importance. Since the relative humidity of the storage of wool does not determine the water content, buying of "conditioned wool" is not an unchanging criterion. Higher moisture contents are obtained when equilibrium pressure is approached via desorption rather than via adsorption (Alexander and Hudson, 1954).

There are controversial data about the diffusivity of water vapour in wool fabrics, in the voidage between the fibers and in the fibers. The diffusivity of water vapour in wool at 25°C was reported to be $1.19 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ and $5.96 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ at wool moisture ranges of 0–3% and 13–17% respectively (Armstrong and Stannett, 1966). Nordon et al. (1970) reported 6–16 times greater diffusivity values than those obtained by gravimetric methods, for example, in order of $10^{-11} \text{ m}^2 \text{ s}^{-1}$ for corridaele wool by measuring moisture in wool with a vibroscope. The rate of diffusion of water vapour in the voidage between fibres during desorption of bound water from wool was demonstrated to be dependent on bulk density of wool and it was in the order of $10^{-9} \text{ m}^2 \text{ s}^{-1}$ in the 80–160°C temperature range (Walker et al., 1970). David and Nordon (1968) used the diffusion coefficient of water in the interfiber

spaces of a textile bed to be 50–90% of the value in still air in prediction of moisture adsorption in wool bales for a step change in environmental humidity. On the other hand the diffusivity of water vapour in wool fabrics was reported to have a value of $0.42 \text{ cm}^2 \text{ s}^{-1}$ (Menefee et al., 1982).

Coupled heat and moisture diffusion in wool beds was analyzed in terms of conservation of mass and heat and unsteady state diffusion equations; and satisfactory agreement was obtained between the prediction of the model and experimental observations (David and Nordon, 1966).

Mass transfer of water vapour in a bed of wool fibers under forced convection was also modelled and it was concluded that increasing air velocity or decreasing packing height would have the same effect on uptake versus time curves (Nordon, 1965a). Nordon (1965b), showed that all the qualitative features which were observed experimentally, were predicted by the model. Dispersion of air flow on the bed due to packing irregularities caused deviation of experimental data from the theory which was based on the behaviour of single fibers in the bed. Studies with the adsorption unit packed with fiber balls showed that the adsorbed amount was inversely proportional to fiber diameter (Morooka et al., 1991).

Column dynamics was studied for different types of adsorbents. While simultaneous external mass transfer and diffusion in solid are the controlling parameters in some of the models (Rosen, 1954; Carter, 1979; Rasmuson, 1985; Balköse et al., 1990; Ülkü et al., 1992); good fits of the experimental data with fluid to particle mass transfer controlling models were obtained in other studies (Park and Knaebel, 1992; Tudge, 1961). A model based on simultaneous rates of chemical reaction and external mass transfer model for a fibrous ball packed column was suggested for the estimation of design parameters of the column (Morooka et al., 1991). Ruthven (1984), reviewed the mass transfer models for packed columns.

Rasmuson (1985), showed that if the area-to-volume ratio of the slabs, cylinders and spheres is the same, identical breakthrough curves are produced for the short and long contact times.

The aims of the present work are therefore: to study the water vapour adsorption behaviour of merino wool under both static and dynamic conditions, to obtain data at different air rates and packing heights in the column and to fit experimental breakthrough curves to the column dynamics models.

Experimental

Chopped merino wool samples, having an average diameter of 17μ and 1–3 mm length, that have been extracted with petroleum ether were used in the experiments. Wool samples were outgassed under 10^{-3} mbar vacuum at 100°C for 2 hours. The volumetric adsorption measurements were carried out by the Coulter Omnisorb 100CX. A static vapour dose method (Coulter, 1991) was used in the experiments. 112 mg dry wool was moistened by sending water vapour in very small doses from a manifold with 30 cm^3 volume to the sample chamber having 15 cm^3 volume. The dosing pressure, which is the pressure difference between the manifold and sample chamber that are connected to each other by a Nupro valve, was chosen to be 6.5 mbar and 26.5 mbar on adsorption. After each water vapour dosing, the pressure of the system was continuously monitored at 10 second intervals. When the difference between the two subsequent pressure measurements was less than 0.4%, it was generally accepted that the system reached the equilibrium state. The helium evacuation time during this operation was taken to be 40 minutes. Adsorption isotherms were determined at 25°C . Desorption isotherm of wool was determined by using desorbate dose of 26.5 mbar and desorption cut of relative pressure of 0.001.

The Cahn Gravimetric adsorption apparatus shown schematically in Fig. 1 was used in the gravimetric adsorption experiments. The gravimetric set-up consisted of a recording electronic microbalance (Cahn

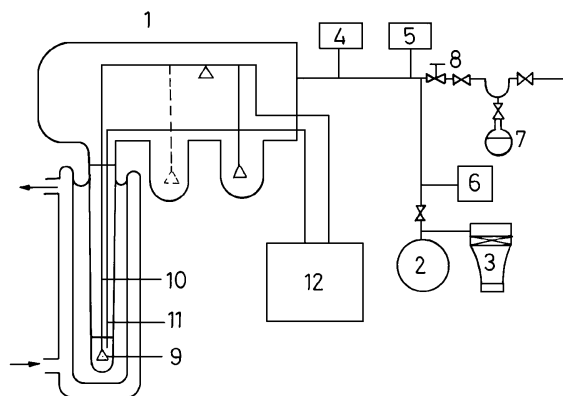


Figure 1. 1-Cahn 2000, 2-Edwards E2M2 oil rotary vacuum pump 3-Edwards Diffstak 250, 4-MKS 0–2 mbar pressure gauge, 5-Penning gauge 10^{-2} – 10^{-7} mbar, 6-EMV 251 0–1000 mbar pressure gauge, 7-water reservoir, 8-BRY 10 kg needle valve, 9-wool sample, 10-nicrome wire, 11-thermocouple, 12-recorder.

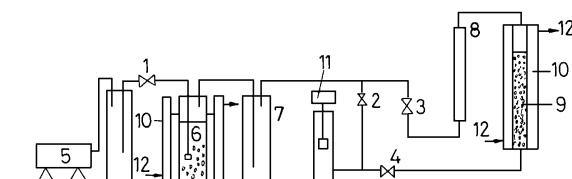


Figure 2. 1,2,3,4-valves, 5-air pump, 6-saturator, 7-mist trap, 8-flowmeter, 9-wool packed column, 10-water jacket, 11-Ebro hygrothermometer, 12-circulating water.

2000), a rotary vacuum pump (Edwards E2M2), an oil diffusion pump (Edwards Diffstak 250), pressure gauges (Edwards Penning for 10^{-2} – 10^{-7} mbar range, MKS for 0–2 mbar range, EMV 251 for 0–1000 mbar range), a PID temperature controlled furnace and a water bath. 45 mg dry wool was used in these experiments. Water vapour was let into the system having 5.5 dm^3 volume, as pulses through an Edwards BRV-10K needle valve. The equilibrium state was achieved when the weight of the sample no longer changed at each pressure level. The adsorption isotherms were obtained at 15°C and 25°C . The desorption isotherm of wool was determined by decreasing the pressure of the system in steps by opening the vacuum valve for short periods.

Figure 2 illustrates the set up for the packed column experiments. A jacketed-glass column of 1.4 cm in diameter and 30 cm in length was used. Water at 25°C was circulated in the jacket. Air was introduced into the column at a constant rate, after passing through a saturator containing 75% H_2SO_4 . The relative humidity of the inlet and the exit stream along with the temperature of the column were monitored by an Ebro hygrothermometer. Wool was dried at 100°C for 2 hours in a constant temperature oven before each run. The parameters for the packed column experiments are listed in Table 1.

Table 1. Parameters of the packed column experiments.

Exp. no.	Mass, g	z, cm	T , $^\circ\text{C}$	c_0 , g g^{-1}	v , cm s^{-1}
1	2	5.5	18	0.0090	2.2
2	4	11.0	18	0.0090	2.2
3	6	19.0	18	0.0090	2.2
4	8	20.0	18	0.0090	2.2
5	2	5.5	16	0.0081	6.4
6	4	11.0	18	0.0095	6.4
7	6	19.0	25	0.0135	6.4
8	8	19.0	19	0.0100	6.4
9	8	20.0	18	0.0090	5.1
10	8	20.0	18	0.0090	3.8

Experimental Results and Discussion

Adsorption Isotherms

The adsorption isotherms of water on wool are given in Fig. 3 which displays the measurements carried out both by the Coulter Omnisorp 100CX and by Cahn 2000 under static conditions. Only representative points from 2000 data points have been shown for the volumetric system in Fig. 3(a).

With reference to the adsorption isotherm obtained by Coulter Omnisorp 100CX at 25°C, wool seems to adsorb more water when the dosing pressure was

increased from 6.5 to 26.5 mbar. It was possible for the system to approach the equilibrium state closer if the pressure difference between the manifold and the adsorption vessel was high, due to the higher rate of mass transfer of water vapour through the valve that isolated the sample chamber and the manifold.

The adsorption isotherm resulting from the Cahn 2000 measurements at 25°C indicated that wool adsorbed much more water at all relative humidities than those recorded by the Omnisorp 100CX at the same temperature. This shows that equilibrium probably was not attained by the Omnisorp 100CX. The adsorption of water vapour was realised from a large water vapour volume in the case of the Cahn 2000 experiments, and equilibrium was considered to be attained when the sample weight became constant.

It was not possible to measure the adsorption isotherms with the same incremental pressure changes in both volumetric and gravimetric methods, due to manual control of the gravimetric system. The moisture of the wool was changed in infinitesimal incremental steps and in large steps in the volumetric and gravimetric systems respectively. This gave rise to different time dependent relaxation phenomena in wool fibers (Nordon et al., 1970) in the volumetric and gravimetric systems.

Adsorption occurs from variable surface concentration and from constant surface concentration in the Omnisorp 100CX and Cahn 2000, respectively. Although the adsorption isotherms obtained by both the volumetric (Omnisorp) and the gravimetric (Cahn 2000) methods display similar trends, it has been observed that a closer approach to equilibrium was possible with the Cahn 2000 regardless of the fact that wool-water adsorption equilibrium was only attainable after a long period of time in both methods. The adsorption isotherm describes equilibrium behaviour and only one adsorption isotherm exists at one temperature provided that no change occurs on the structure of adsorbent with adsorption. However, only a close approach to equilibrium is possible for commercial instruments operating at a fast rate, if the rate of adsorption is high. For example, Wesson (1984) used continuous volumetric and gravimetric methods in obtaining adsorption isotherms of nitrogen and argon on Chabosil that adsorbed at a fast rate. Nearly the same isotherms were obtained by using both methods. On the contrary for wool, even with our static dosing method, different isotherms were obtained due to the slow rate of approach to equilibrium.

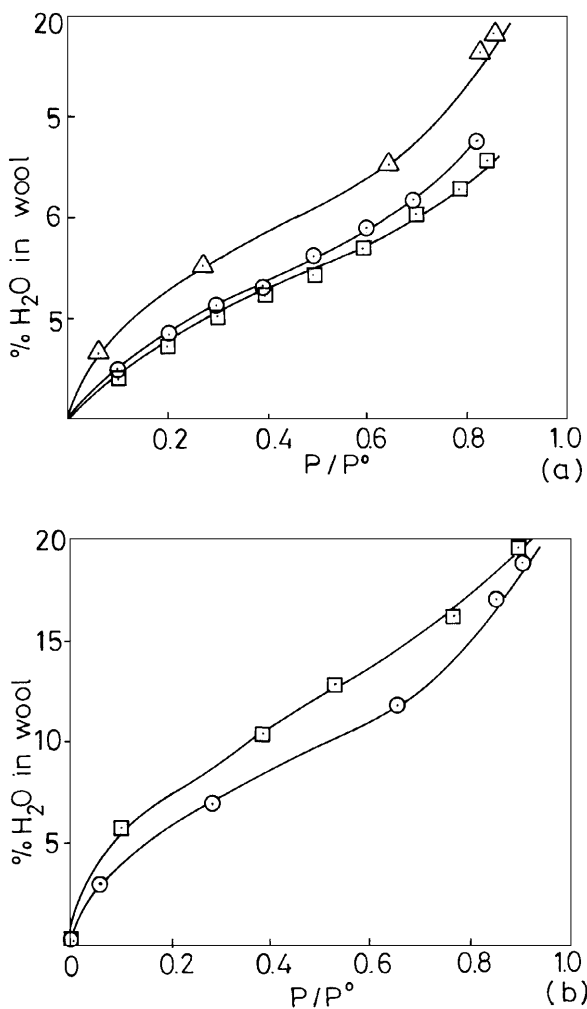


Figure 3. (a) Adsorption isotherm of water vapour on wool at 25°C at Cahn 2000, Δ ; at Omnisorp 100CX for dose pressure 6.5 mbar, \square ; 26.5 mbar, \circ ; (b) Adsorption isotherm of water vapour on wool at Cahn 2000 at 25°C, \square ; at 15°C, Δ .

Table 2. BET constants for adsorption isotherm of water vapour in wool.

Method	c	$V_m, \text{cm}^3 \text{g}^{-1}$	Regression coefficient
Volumetric, 6.5 mbar dose	6.35	64.3	0.9991
Volumetric, 26.5 mbar dose	8.30	64.3	0.9994
Gravimetric	7.33	90.9	0.99

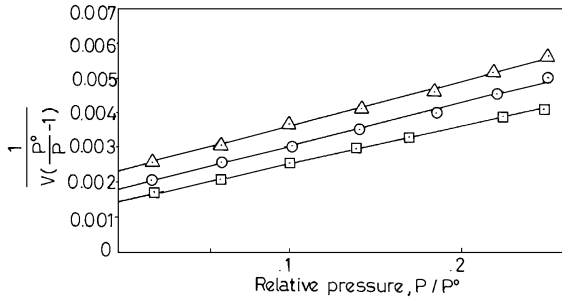


Figure 4. BET isotherms for Cahn 2000, \square ; Omnisorp 100CX at 6.5 mbar, Δ ; 26.5 mbar, \circ ; dose pressure at 25°C.

The adsorption isotherms of water vapour on wool obtained by the gravimetric method at 15°C and 25°C, Fig. 3(b), were similar to those isotherms reported by previous workers (Alexander and Hudson, 1945; Leeder and Watt, 1965; Wlochowitz and Bujok, 1987; Nordon, 1970) for different wool types.

The adsorption isotherm data obtained in both our volumetric and gravimetric instruments were fitted to the BET isotherm with correlation coefficients of at least 99% as shown in Fig. 4 and Table 2. Higher monolayer capacities found using the Cahn data probably indicate a closer approach to equilibrium.

For practical purposes in industrial applications, the equilibrium isotherm of wool obtained by Cahn 2000 at 25°C, could be roughly represented by a straight line with correlation coefficient of 0.95 and represented by Eq. (1) as follows;

$$q = Kc \quad (1)$$

where q is the moisture in wool and c is the humidity of air. q and c are both in g cm^{-3} . The slope of the straight line in Fig. 5, K , is found to be 15000.

Heat of Adsorption

Net heats of adsorption at different wool moisture values were calculated from the adsorption isotherms measured at 15°C and 25°C with the Cahn 2000

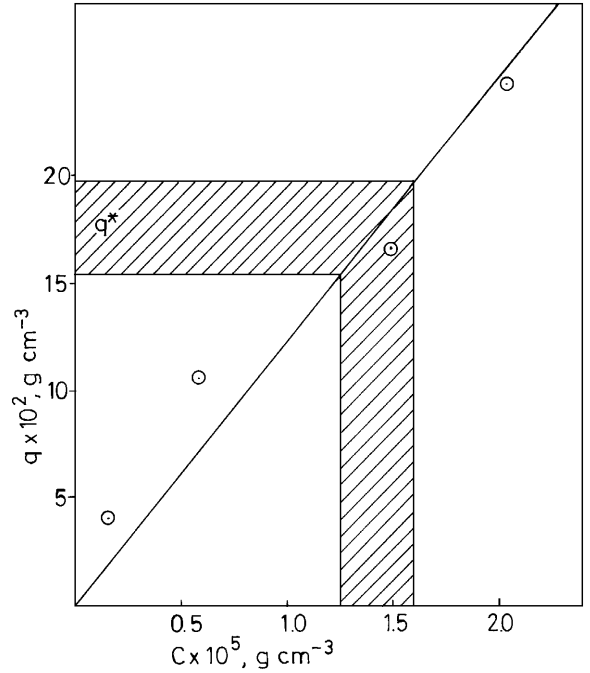


Figure 5. Adsorption isotherm of water vapour on wool at 25°C at Cahn 2000 in concentration unit g cm^{-3} . Crosshatched area represents inlet concentration range to the column.

(Fig. 3(b)) and using Eq. (2) (Gregg and Sing, 1982)

$$\ln \left(\frac{P_1/P_1^0}{P_2/P_2^0} \right) = ((q_{st} - q_l)/R)(1/T_1 - 1/T_2) \quad (2)$$

where P_1 and P_2 are pressures at temperatures T_1 and T_2 , P_1^0 and P_2^0 are saturation vapour pressures at T_1 and T_2 , q_{st} is isosteric heat of adsorption and q_l is the latent heat of condensation. Isosteric heat of adsorption values have been found by adding the latent heat of condensation of water at 25°C (2445 J g^{-1}) to the calculated net heat of adsorption values ($q_{st} - q_l$), and shown in Table 3 together with the data from the works of Alexander and Hudson (1945), Nordon (1965) and Armstrong and Stannet (1966). Isosteric heat of adsorption in the present study decreases with moisture of wool as observed by previous workers. As surface coverage of the monolayer increases, a continuous reduction in heat of adsorption has been observed for other adsorbate-adsorbent pairs. The isosteric heat of adsorption falls to a level only slightly above the molar heat of condensation in the vicinity of monolayer coverage of the surface with the adsorbate. Adsorption sites in wool have different energies and ones with the highest energy will interact with water vapour at first. The

Table 3. Isosteric heat of adsorption of water vapour in wool as a function of wool moisture, J g^{-1} .

Moisture in wool, %	6	9	12	15
Present study	3704	3683	3426	2601
Alexander and Hudson (1945)	2984	2888	2845	2697
Nordon (1965)	3050	2911	2780	2697
Armstrong and Stannet (1966)	2765	2549	2528	2466

polar NH_3^+ , COO^- and $-\text{OH}$ groups have heat of hydration values of 16.8, 7.4 and 5.7 kcal mol^{-1} , respectively. At low relative humidities, water is first sorbed onto amino groups, then onto carboxyl and hydroxyl groups as the water content of the system increases (Leeder and Watt, 1965). This explains the decrease of isosteric heat of adsorption as the water content in wool increases.

Hysteresis in Wool

Figure 6 shows that hysteresis exists in wool. The low pressure region of the desorption isotherm obtained by the volumetric method (Fig. 6(a)) does not describe the actual adsorption behaviour of the wool. Since the pressure difference between the sample chamber and the manifold was very small at low pressures, the rate of mass transfer through the valve between them became very slow and equilibrium was not attained in a reasonable time. As seen in Fig. 6(a), when the relative pressure was close to zero, wool seems to contain $65 \text{ cm}^3 \text{ g}^{-1}$ or 5.2% water on desorption. On the other hand the gravimetric method (Fig. 6(b)) shows that it returns to its original dry weight on desorption. Since there is no constriction for mass transfer in the gravimetric system, it provided more accurate measure of the equilibrium state of wool, both on adsorption and desorption.

Diffusivity of Water Vapour in Wool and Pseudo First Order Rate Constant

The diffusivity of water vapour in wool has been calculated from experimental uptake data and Eq. (3).

$$\frac{M_t}{M_\infty} = 1 - \frac{(4\alpha \cdot (1 + \alpha)) / (4 + 4\alpha + \alpha^2 q_n^2)}{\sum \exp(-Dq_n^2 t / r^2)} \quad (3)$$

where M_t and M_∞ are moisture adsorbed at time t and at equilibrium, r is the fibre radius, α is the ratio of the

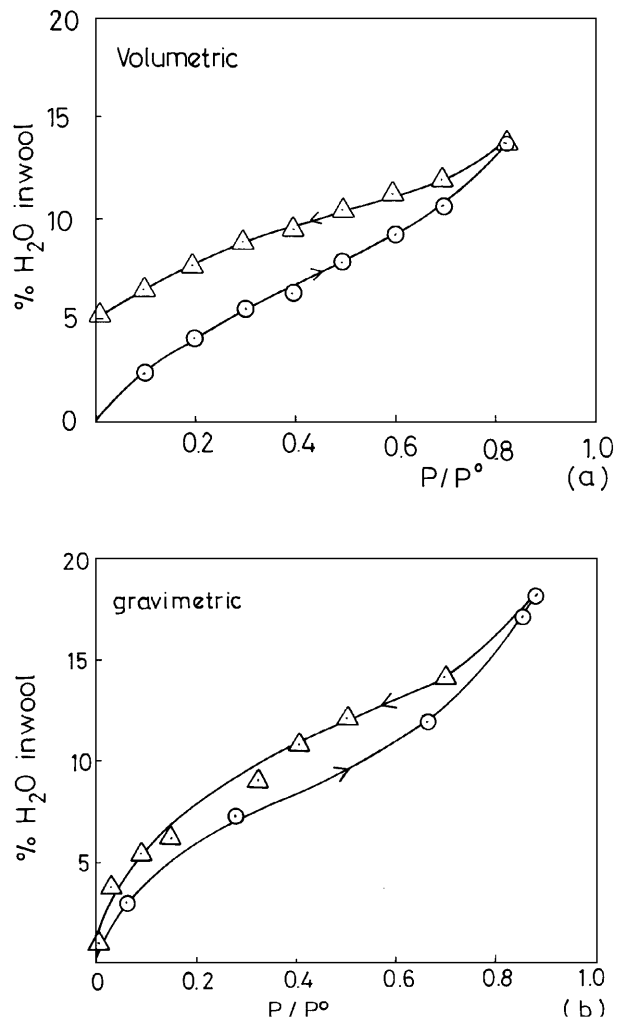


Figure 6. (a) Hysteresis of water vapour adsorption on wool determined at 25°C at Omnisorp 100CX; (b) at Cahn 2000 adsorption, \odot ; desorption, \triangle .

volume of the solution and volume of the solid. q_n 's are the positive roots of

$$\alpha q_n J_0(q_n) + 2J_1(q_n) = 0 \quad (4)$$

where J_0 and J_1 are the zero and the first order Bessel functions.

Using the first sixth roots of Eq. (4) for α equals ∞ , given in Crank (1975), the average diffusion coefficient of water vapour in wool has been found as $8.5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$. This value is close to Armstrong and Stannet's (1966) value and smaller by an order of hundred from Nordon et al.'s (1970) value. Correction of diffusivities

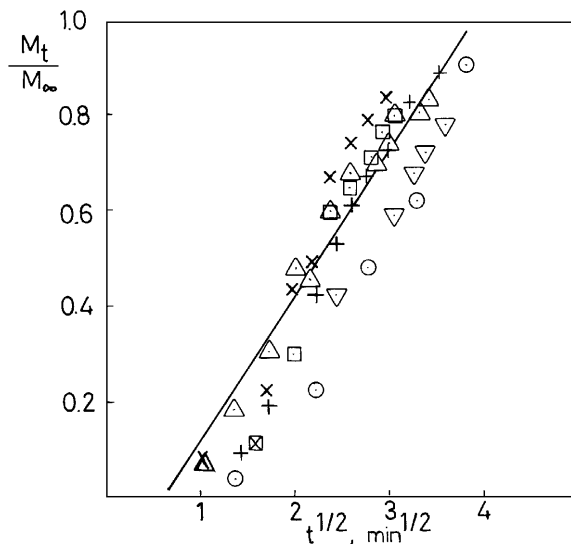


Figure 7. Fractional uptake of water vapour to wool at different pressure steps versus square root of time, initial and equilibrium moisture of wool 0 and 3%, \square ; 2.6% and 7%, ∇ ; 6.2% and 13.75%, \times ; 11% and 19%, $+$; 15% and 19.0%, Δ ; 0 and 19.0%, \circ , respectively.

due to change in temperature of wool with adsorbed water should be made as Armstrong and Stannet (1966) did. The heat of adsorption can be dissipated by radiation to the surroundings and by conduction through aluminium sample pan and nichrome weighing wire (10 in Fig. 1). Heat transfer by convection is negligible due to existence of high vacuum. No change in temperature of the vapour phase could be detected by the thermocouple (11 in Fig. 1) in the vicinity of wool fibers during adsorption. Thus, it was not possible to make a temperature correction.

The relation between fractional uptake versus square root of time, as shown in Fig. 7, confirms that Fickian diffusion occurs after an initial slow adsorption period for each step increase in pressure. This initial period could be explained by relaxation of the wool structure due to penetration by moisture.

Rate of Adsorption Versus Rate of Desorption

Experiments were conducted with wool initially having 18% moisture for a step change of pressure from 20 mbar to 10^{-2} mbar. In those tests the fraction of desorbed water from wool changed linearly with square root of time for the initial period of desorption as shown in Fig. 8. On the other hand, fraction of adsorbed amount by dry wool for a step change of the pressure from 10^{-2} to 30 mbar versus square

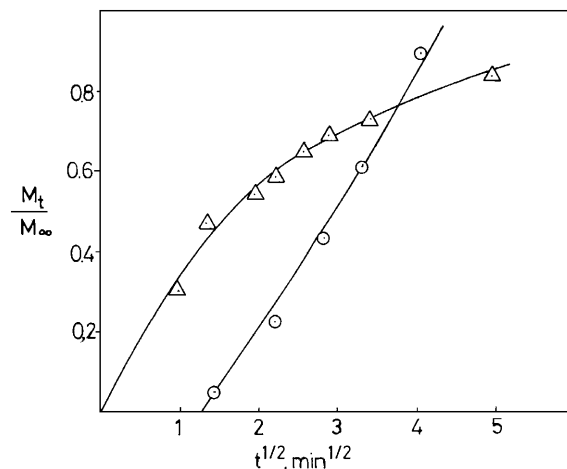


Figure 8. Fractional adsorbed, \circ ; or desorbed amount, Δ ; of water vapour onto or from wool versus square root of time.

root of time was linear after a slow period of adsorption for the initial 3 minutes. The difference between adsorption and desorption rates can be explained as: while desorption occurs from swollen fiber, adsorption is onto unswollen fiber. On desorption, water vapour is removed in a shorter time as the fiber returns to its unswollen state. Thus, desorption is faster than adsorption, as also observed by Nordon (1965b).

The experimental uptake data were also analyzed for the linear rate of transfer model

$$dq/dt = k(q - q^*) \quad (5)$$

where k is the pseudo first order rate constant or mass transfer constant, q is the moisture in wool, q^* is the moisture content of wool in equilibrium with water vapour in the gas phase. k values around $2.3 \times 10^{-4} \text{ s}^{-1}$ was obtained by analysis of uptake data for 5 to 10 minutes for each step change in pressure.

Dynamic Column Experiments

Since no difference was detected between the temperatures of inlet and outlet gas streams it was concluded that the column operated isothermally.

The flow in the column was analysed for axial dispersion in terms of Peclet numbers, Pe , for each run. The longitudinal diffusion coefficient, D_L and Pe were calculated from Eqs. (6) and (7) respectively.

$$D_L = 0.7D_{\text{H}_2\text{O}/\text{air}} + bv \quad (6)$$

$$Pe = zv/D_L \quad (7)$$

Table 4. Mass transfer coefficient, longitudinal diffusivity, Peclet number, Biot number, Reynold's number and pseudo first order rate constant for each run.

Exp. no.	$K_f \times 10^2$ ms^{-1}	$D_L \times 10^5$	Pe	Bi $\times 10^{-8}$	Re $\times 10^5$	$k \times 10^{-6}$ s^{-1}
1	1.2	1.8	67	3.7	0.44	4.80
2	1.2	1.8	134	3.7	0.44	0.88
3	1.2	1.8	232	3.7	0.44	5.00
4	1.2	1.8	244	3.7	0.44	0.33
5	2.2	1.8	195	6.8	1.28	21.00
6	2.2	1.8	310	6.8	1.28	69.00
7	2.2	1.8	675	6.8	1.28	17.00
8	2.2	1.8	675	6.8	1.28	20.00
9	1.9	1.8	566	5.8	1.02	19.30
10	1.6	1.8	422	4.9	0.76	13.00

where $D_{\text{H}_2\text{O}/\text{air}}$ is the diffusivity of water vapour in air, $0.256 \text{ cm}^2 \text{ s}^{-1}$ at 25°C (Faust et al., 1960), z is the packing height and v is the linear velocity in the column. The small D_L values and the high Pe numbers as seen in Table 4 indicate the axial dispersion in the column can be neglected.

The controlling parameter of mass transfer in the column was determined by Biot number, Bi. From the analysis of commercial scale applications, high values of Bi (Bi > 3) indicate intraparticle mass transfer resistance controls the mass transfer rate (Ülkü et al., 1992). Using the following equations Bi number for each run was calculated.

$$\text{Bi} = K_f r / 3D \quad (8)$$

where K_f is the gas phase mass transfer coefficient.

$$\text{Sh} = 2K_f r / D_{\text{H}_2\text{O}/\text{air}} = 1.17(\text{Re})^{0.585}(\text{Sc})^{1/3} \quad (9)$$

is applicable to packed columns with cylindrical packing, and the diameter of the cylinder should be used in the Re and Sh numbers (McCabe et al., 1988).

$$\text{Sc} = \mu / \rho D_{\text{H}_2\text{O}/\text{air}} \quad (10)$$

$$\text{Re} = 2rv\rho/\mu \quad (11)$$

where μ and ρ are viscosity and density, respectively. The following physical properties were used in calculating K_f

$$\mu = 0.2 \text{ Pa} \cdot \text{s for air at } 25^\circ\text{C}$$

$$\rho = 1.18 \text{ kg m}^{-3} \text{ at } 25^\circ\text{C and 1 Bar}$$

(from Foust et al., 1960).

The Bi numbers reported in Table 4 are at the order of 10^8 indicating diffusion in the solid controls the mass transfer rate in the column. For this reason, a solid diffusion controlling model which neglects the film resistance and axial dispersion, was selected to predict the breakthrough curves. For designing a process to operate within flexible conditions, approximate breakthrough curves may be sufficient. Since analytical solutions do not exist for inflecting isotherms with intraparticle diffusion, our system has been approximated by a linear isotherm as indicated in Eq. (1) and Fig. 5. The breakthrough curve of each run can therefore be predicted by using Rosen's (1954) analytical solution (Eqs. (12) and (13)).

$$U = 1/2 + \psi/\pi \quad (12)$$

$$\psi = \int_0^\infty e^{-xH_1} \cdot \sin[\gamma\beta - xH_2] \cdot \frac{d\beta}{\beta} \quad (13)$$

where $U = c/c_0$, c = outlet concentration, c_0 = inlet concentration

$$x = \frac{3DKz}{mVr^2} \quad (14)$$

$$y = 2D \left(t - \frac{z}{v} \right) / r^2 \quad (15)$$

The variables in the above equations are: m is the void volume/solid particle volume, r is the radius of the spherical particles, z is the packing height, and H_1 and H_2 are as described in (Ülkü et al., 1992).

Although the model represented by Eq. (12) was developed for spherical particles, it was applied for the wool packed column with cylindrical particles. Thus, it gives just an idea about the column dynamics. For the present study, r in the Eqs. (14) and (15) was taken to be the radius of the sphere which has equivalent surface area with the fibers considering Rasmusson's (1985) observations on the effect of particle shape on breakthrough curves. The independently measured values of diffusivity of $8.4 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ and K of 15000 were used. The tables that give the solution of Eq. (12) as parameters of x and y in Rosen's (1954) article was used.

The problem can also be analysed by using the pseudo first order rate expression (Ruthven, 1984)

$$U = (1/2)\text{erfc}(\xi^{1/2} - \tau^{1/2}) - (1/8)\xi^{1/2} - (1/8)\tau^{1/2} \quad (16)$$

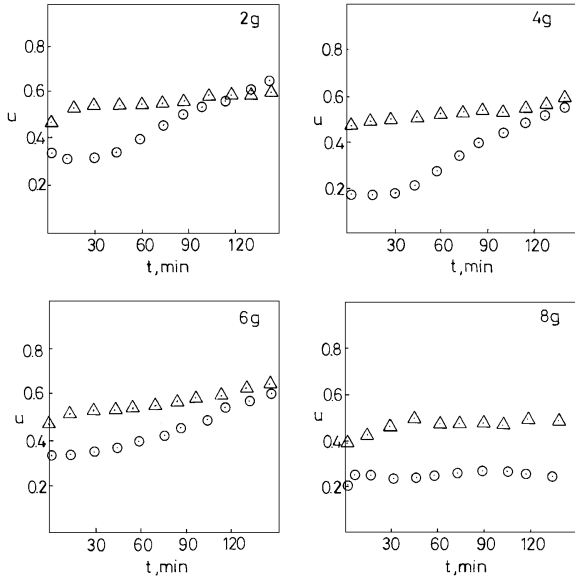


Figure 9. Experimental, \odot ; and predicted, \triangle ; breakthrough curves for 2.2 cm^{-1} air rate: amount of wool is the parameter.

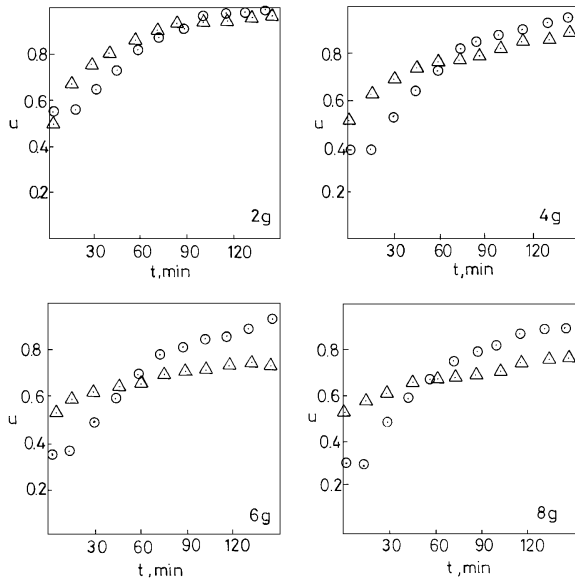


Figure 10. Experimental, \odot ; and predicted, \triangle ; breakthrough curves for 6.4 cm^{-1} air velocity: amount of wool is the parameter.

where

$$\tau = k(t - z/v) \quad (17)$$

$$\xi = kKz/vm. \quad (18)$$

The experimental breakthrough curves are shown in Figs. 9, 10, and 11 considering amount of the wool

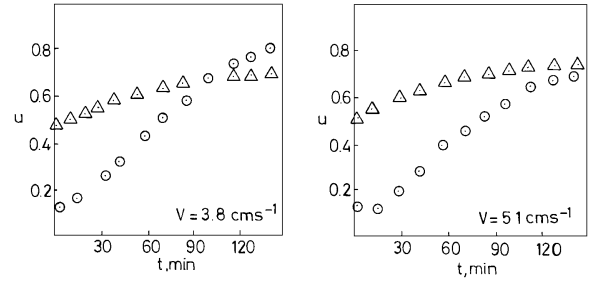


Figure 11. Experimental, \odot ; and predicted, \triangle ; breakthrough curves for 8 g wool: air velocity is the parameter.

and air velocity as the parameters. The shape of the breakthrough curves did not have dual shock waves as observed by Park and Knaebel (1992) for inflecting isotherms. As shown in Fig. 5 and Table 1 inlet concentration of the runs changes in a small range. Maybe dispersion occurs due to channelling between the wool fiber agglomerates. A well developed mass transfer zone could not be formed due to small packing heights.

A good fit between experimental and predicted breakthrough curves from solid diffusion model, Eq. (12), could not be obtained. The reasons of the lack of fit between experimental and predicted values could be explained as follows:

- (i) Since wool is a resilient material, it is not possible to pack the column in the same manner for each run. Channelling of air occurs in the column.
- (ii) Felting of fiber on handling cause agglomeration of fibers to spheres with 2–3 mm diameter. In such a case, the diffusivity of water vapour in these agglomerates and the corresponding agglomerate particle size would give a closer fit between predicted and experimental data.
- (iii) There is hysteresis of the adsorption-desorption equilibrium. Hence the assumed linear isotherm assumption is not valid.
- (iv) The transport rate of water vapour in wool is time-dependent due to relaxation of wool with moisture.
- (v) The heat of adsorption changes with moisture in wool.
- (vi) Very small changes in room air temperature affect the humidity of the air from humidifier, even when the column is thermostated.
- (vii) The laboratory-scale columns are short. The length of the mass transfer zone of the column

seems to be much longer than the column height for the present case.

- (viii) The fibers have a very small average diameter (3.4×10^{-5} m) compared to their length (1–2 mm).

Thus, the breakthrough curves are studied with a more empirical approach. Taking k value determined in Cahn 2000 as the starting point, k values that give a reasonable fit between experimental and predicted breakthrough curves (Figs. 9, 10, and 11) were found from Eq. (16) by trial and error method. As seen in Table 4, k values changes with air velocity and packing height confirming the data obtained by Park and Knaebel (1992) from silica gel packed columns. k values from packed column experiments were much smaller than the one found from the gravimetric adsorption system, as observed also by Nordon (1965b).

Although the fibers are very small in diameter, the observed slow rate of adsorption prevents achievement of equilibrium in the short columns in the few seconds retention time (z/v 0.9–9.2 s) of the gas. Thus, it was not possible to obtain bone dry air from the columns of the present study and to observe a sharp break point such as obtained with zeolites (Ülkü et al., 1992) and silica gel (Balköse et al., 1990) in the same column operating under the same conditions. Even if wool cannot compete with commercial desiccants, it is worth studying water vapour adsorption in wool since it is consumed in large quantities. The heat of adsorption (Stuart et al., 1989), change in wrinkling behavior with moisture (Menefee et al., 1982), and hysteresis in water vapour adsorption (Alexander and Hudson, 1954) are phenomena with commercial importance in wool trade.

Conclusion

The measurement of adsorption isotherm of wool will certainly be more accurate and precise upon establishing wool-water equilibration. It is obvious that by changing variables such as equilibration time and the dose pressure in Omnisorp 100CX, the equilibrium values obtained in Cahn 2000 can be reached for other adsorbents that does not swell with adsorption. Very long equilibration times should be avoided to prevent the effect of leakage at a very small level.

Water vapour adsorption on wool fits the BET isotherm. Swelling of wool with water vapour adsorption, hysteresis in adsorption and desorption, and

variable heat of adsorption are the main causes of the discrepancy between adsorption isotherms determined by different methods.

Undefined heat transfer characteristics in the Cahn 2000 adsorption rate studies created problems in determination of the diffusivity of water vapour in wool. From the Cahn data, an average D for water vapour in the fibers was found as 8.5×10^{-14} m² s⁻¹. For pseudo first order model, k values varied between 0.33×10^{-6} – 69×10^{-6} s⁻¹ were obtained for 2.2–6.4 cm s⁻¹ air velocity and 0.05–0.20 m packing height ranges.

Empirical results obtained in this study may be utilised to scale up the wool moistening process.

Nomenclature

c	Water vapour concentration at the outlet of the column, g cm ⁻³ , g g ⁻¹ , BET constant
c_0	Water vapour concentration at the inlet of the column, g cm ⁻³ , g g ⁻¹
D	Effective diffusion coefficient of water vapour in wool, m ² s ⁻¹
$D_{H_2O/air}$	Diffusivity of water vapour in air, m ² s ⁻¹
D_L	Longitudinal dispersion coefficient
H_1, H_2	As described in (Rosen, 1954)
K	Equilibrium constant, q/c
K_f	Gas phase mass transfer coefficient
m	Void volume of the column/solid volume in the column
M_t	Mass of adsorbed water by the wool at time t , g
M_∞	Mass of adsorbed water by the wool at time ∞ , g
P	Partial pressure of water vapour in air, bar
P_o	Vapour pressure of water, bar
Pe	Peclet number
q	Water concentration in wool, g cm ⁻³
q^*	Equilibrium water concentration in wool, g cm ⁻³
q_l	Heat of condensation of the water vapour
q_{st}	Isosteric heat of adsorption, J g ⁻¹
r	Radius of the cylinder or sphere
Re	Reynolds number
Sc	Schmidth number
Sh	Sherwood number
t	Time, s
T	Temperature, K or °C
U	c/c_0
x	$3DKz/mvr^2$, dimensionless packing height

y	$2D(t - z/v)/r^2$, dimensionless time parameter
v	Linear gas flow rate, ms^{-1}
V	Water vapour adsorbed as reported in standard temperature and pressure per unit mass of wool, $\text{cm}^3 \text{g}^{-1}$
V_m	Monolayer adsorption capacity as reported volume in standard temperature and pressure per unit mass of wool, $\text{cm}^3 \text{g}^{-1}$
z	Packing height

Greek Letters

α	Volume of solution/volume of solid
β	Variable of integration in Eq. (13)
τ	$k(t - z/v)$
ξ	kKz/vm
ψ	As described in Eq. (13)
ρ	Density, g cm^{-3}
μ	Viscosity, $\text{Pa} \cdot \text{s}$

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