Temperature Dependence of the Water-Sorption Isotherms of Wool

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ABSTRACT: Against the background of various other theories, the well-established D'Arcy/Watt model is applied to sorption data of wool between 20 and 100°C to determine its suitability to describe the isotherms and to systematize their temperature dependence. The model contains three components that represent two types of primary adsorption processes (Langmuir- and Henry-type adsorption) and a third one, describing multilayer formation of water molecules. Sorption isotherm data, as taken from the literature, could, in all cases, be fitted extremely well by the model. The temperature dependence of the five parameters of the model, related to the continuous decrease of water regain with increasing temperature for all humidities, reveals a number of inconsistencies. Probably the most important of these is that the Langmuir capacity constant apparently becomes zero at the glass transition temperature of dry wool. This is at variance with the idea of specific molecular sites of water sorption, which is inherent to the model. Other inconsistencies relate to the small van't Hoff enthalpies and possible compensation effects for various parameters. These observations indicate that the D'Arcy/Watt theory, despite its physicochemical plausibility and empirical success, overinterprets the complexity of the mechanisms underlying the sorption behavior of wool and other α -keratin fibers. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1054-1061, 2001

Key words: water sorption; isotherms; wool; D'Arcy-Watt model; temperature

INTRODUCTION

The sorption characteristic of wool for up to approximately 35% water is one of the fundamental properties of this and other α -keratins, which, due to its consequences for fiber and textile processing, has found major interest as a topic for fundamental and applied research. Sorption follows with relative humidity a sigmoid curve that is characteristic of a large and very diverse variety of materials.^{1–3} The most authoritative and

comprehensive review of the sorption properties of wool was provided by Watt. 1

Historically, the continuous description of sorption isotherms has been approached by two main types of models: The oldest approach relates to the well-known theory of Brunauer, Emmett, and Teller (BET theory).⁴ This theory considers the case where water is adsorbed onto a substrate according to a two-stage mechanism. During the first stage, molecules are adsorbed to form a monolayer of the Langmuir type. Onto this layer, further molecules are adsorbed in a multilayer arrangement during the second stage of adsorption. Various older² and newer studies^{5,6} have shown the inadequacies of the BET theory with

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respect to the wool/water system, namely, at higher relative humidities (RH > 50-60%). Staying within the conceptual framework of the BET theory, Le and Ly⁵ modified the theory to allow for defect multilayers of water molecules. This modification, leading to a five-parameter equation, added substantial flexibility to the model and they arrived at excellent fits of the sorption isotherms.

However, the BET theory and its modification, as applied by Le and Ly,⁵ assume the <u>ad</u>sorption of molecules onto the material surface, that is, onto the physical interface between the solid and the environment, including cracks, pores, capillaries, etc. This concept is in contrast to the early observation by Simha and Rowen² that at RHs above approximately 60% the sorption isotherm tends toward a behavior according to the Flory/ Huggins equation, thus demonstrating the polymer/liquid mixture properties of the wool/water system under these conditions. The Flory/Huggins-type behavior of the sorption isotherms for high humidities and the modification of the theory for lower humidities was addressed by Rosenbaum⁷ and more recently again by Pierlot.⁸ It is interesting to note that the validity range of the Flory/Huggins equation for the wool/water system is temperature-dependent and limited toward lower humidities by the humidity-dependent glass transition temperature.^{8,9}

An alternative approach to analyze the watersorption isotherms was proposed by D'Arcy and Watt¹⁰ against the background of earlier theories by Speakman¹¹ and Windle.¹² Their model is based on absorption, which, classically,¹³ is essentially regarded as a process in which surfacelike adsorption occurs in the interior of the substrate with sorbate molecules being bound by physical sites within the interior of the substrate. The equation for the D'Arcy/Watt model for the description of the sorption isotherm contains three terms with five adjustable parameters. The terms correspond to adsorption of water through strongly and weakly hydrophilic sites, respectively, and to the formation of water multilayers at RHs above approximately 50%. Excellent fits of the data for complete wool-sorption isotherms were obtained,¹⁰ modeling the near BET-type character at low humidities as well as the Flory/ Huggins-type behavior at higher water content.

This investigation was conducted to study the applicability of the D'Arcy/Watt equation to fit the literature data of sorption isotherms of wool in the temperature range of $20-100^{\circ}C^{14}$ and the

temperature-dependent performance of the various components of the model. The results provide further insight into the nature of keratin/water interactions and reveal major inconsistencies of the widely accepted D'Arcy/Watt model.

Theory and Data Analysis

Against the background of earlier concepts for the nature of the water sorption of wool by Speakman,¹¹ Windle,¹² and Hailwood et al.¹⁵ and following thermodynamic considerations, D'Arcy and Watt proposed the following equation to describe the sorption isotherm of wool, but applicable also for other α -keratin fibers such as human hair:

$$w_{1}/w_{2} = K' \frac{Kp/p_{0}}{1 + Kp/p_{0}} + Cp/p_{0} + k' \frac{kp/p_{0}}{1 - kp/p_{0}}$$
(1)

where w_1 and w_2 are the weight fractions of water and dry wool, respectively. Their ratio w_1/w_2 is commonly referred to as water *regain* in the wool literature. p/p_0 is the relative vapor pressure, that is, the RH. K', K, C, k', and k constitute a set of five adjustable parameters, which have defined meanings in the context of the underlying sorption processes, as discussed below.

The right-hand side of eq. (1) contains three components, where the first two describe two types of primary processes related to monolayer adsorption, and the third one, a secondary process, describing multilayer formation. The first term has the form of a Langmuir isotherm and describes the adsorption onto a variety of molecular sites, summarized into a group classified as "strongly adsorbing." The second term has the form of Henry's law of mixing and describes adsorption onto the group of weakly adsorbing sites. These two terms together give the familiar dualmode sorption model for polymer/water systems at low regains, that is, below their glass transition.^{3,16} The third term describes multilayer formation by water molecules. Comparison with the first term shows that it is formally a modified Langmuir-type expression, which was introduced by Hailwood and Horrobin¹⁵ to describe "liquidlike" water in wool. However, as Watt explicitly pointed out,¹ water molecules in the multilayer are not to be equated with liquid water since



Figure 1 Sorption isotherms as $regain (w_1/w_2)$ versus $RH (p/p_0)$ at different temperatures as line plots. Experimental data are marked for 20°C. The isotherms relate to the order of temperatures as given in Table I.

there is a diffuse residual attraction from the substrate which is not present in liquid water.

In view of recent general criticism of sorption models by Pierlot,⁸ it appears to be necessary to point out that neither the D'Arcy/Watt¹⁰ nor the dual-mode sorption model¹⁶ imply a classification of the state of the adsorbed water molecules into distinct groups. Namely, the D'Arcy/Watt model is built on the observation that the principal nature of the wide variety of molecular adsorption mechanisms in wool and in a variety of other proteins^{10,17} can be well summarized by the three terms of eq. (1). All three mechanisms are simultaneously and continuously contributing to the overall process of water sorption and to the state of the water molecules at all vapor pressures.^{1,16}

This investigation is based on data given by Watt and D'Arcy¹⁴ for sorption isotherms for me-

rino wool for temperatures between 20 and 100°C. For temperatures below 50°C, the isotherms were determined by stepwise changes of humidity, and above 50°C, by integral sorption steps. Figure 1 summarizes graphically the data taken from ref. 14. All curves show the familiar sigmoid form, which is typical for the water-sorption isotherms of glassy polymers.³

Equation (1) was fitted to the data using STA-TISTICA (StatSoft Inc.) with nonlinear optimization on the basis of the program specific Quasi-Newton algorithm,¹⁸ minimizing by iteration the sum of the squared errors. Correlation coefficients well beyond r = 0.999 were achieved in all cases, which are generally related to residuals of less than 2×10^{-3} for all regain data. The quality of the fits provided no basis to introduce weights for the minimization procedure, as proposed by D'Arcy and Watt.¹⁷ Table I summarizes the values for the five parameters and their standard errors obtained in this way for each of the temperatures, as well as the overall means and 95% ranges ($q_{95\%}$).

RESULTS AND DISCUSSION

Figure 2 gives the data points for the 20°C isotherm as taken from ref. 14. Equation (1) is fitted through the points on the basis of the parameter values given in Table I, yielding the various component sorption curves as given by the three terms of the D'Arcy/Watt equation. In view of the high correlation coefficients obtained through the fitting procedure (r > 0.999), fits of similar quality are obtained at all temperatures.

Temperature (°C)	Parameter \pm Std. Err.				
	K'	K	С	k'	k
20	0.0515 ± 0.00729	13.3 ± 3.42	0.103 ± 0.0136	0.0284 ± 0.00299	0.878 ± 0.0074
35	0.0441 ± 0.00563	14.9 ± 3.64	$0.106 \ \pm 0.0107$	0.0256 ± 0.00223	0.8839 ± 0.0058
50	0.0372 ± 0.00654	17.4 ± 6.50	$0.111 \ \pm 0.0127$	0.0219 ± 0.00254	0.8935 ± 0.0075
65	0.0353 ± 0.00232	16.9 ± 2.27	0.1005 ± 0.00467	0.0237 ± 0.00104	0.8843 ± 0.0030
80	0.0327 ± 0.00358	17.0 ± 3.76	0.0878 ± 0.00770	0.0274 ± 0.00204	0.8684 ± 0.0057
100	0.0259 ± 0.00560	$23 \hspace{0.1in} \pm \hspace{0.1in} 11.9 \hspace{0.1in}$	$0.085 \ \pm 0.0135$	0.0272 ± 0.00392	$0.867 \ \pm 0.0113$
Mean	0.0378	17.1	0.099	0.0257	0.879
$q_{95\%}$	0.09941	3.47	0.0109	0.00262	0.0106

Table I Values of the Five Parameters of the D'Arcy-Watt Model for Various Temperatures, with their Standard Errors (Std. Err.), Arithmetic Means (Mean), and 95% Confidence Ranges ($q_{95\%}$)



Figure 2 (**•**) Data for the sorption isotherm at 20°C and the $(-\cdot -)$ 1.term (Langmuir) of eq. (1), (-- -) 2.term (Henry), and $(\cdot \cdot \cdot)$ 3.term (multilayer), respectively. The solid line (—) represents eq. (1) fitted through the data points, from which the contributions of the various terms are determined.

The Langmuir term (1.term) contributes to the sorption at lower values of RH, approaching an equilibrium value of 5% regain at humidities beyond approximately 20%. The Henry term (2.term) exceeds in importance the Langmuir adsorption at humidities beyond approximately 40%, approaching a limiting value of 10% regain at saturation. Multilayer formation (3.term) gains importance at humidities beyond 50–60%, which coincides with the range where the BET theory loses its empirical validity.² It leads to a sharp upturn of sorption at humidities beyond 80%, which corresponds to the regain-dependent glass transition at 20°C.¹⁹

Langmuir Term

The Langmuir term contains two parameters, namely, K' and K. K' is the so-called *Langmuir capacity constant*:

$$K' = M n_L / N_A \tag{2}$$

where M is the molecular weight of water; n_L , the number of molecular sites that induce the Langmuir isotherm; and N_A , Avogadro's number.

Figure 3 shows the decrease of the capacity constant K' with temperature, indicating that the number of strongly hydrophilic sites decreases with temperature. With eq. (2), it results from the data in Table I that the number of strongly hydrophilic sites decays by a factor of about 2 from 17.2×10^{20} /g dry wool at 20°C to 8.6×10^{20} /g dry wool at 100°C. On the basis of the data given by

Marshall,²⁰ the weighted mean molecular weight of the amino acid residues in merino wool is calculated as 107 g/mol. On this basis, the number of Langmuir sites per residue is determined as 0.31. Assuming a 1:1 interaction, this would lead to the conclusion that only about one-third of the residues are available as sites for Langmuir adsorption. The value drops to 0.15 at 100°C.

When analyzing glassy polymer/water systems in general³ by the dual-mode sorption model, the Langmuir capacity constant is presumed to be a measure of unrelaxed free volume in the glass that decreases with increasing temperature, approaching zero at the glass transition temperature T_g .²⁴ Recent investigations by Dlubek et al.²¹ of the property of water in local free volumes of a specific, hydrophilic polyimide by positron annihilation lifetime spectroscopy support this view.

A straight line is fitted through the data (see Fig. 3), intersecting with the temperature axis at 185°C. In view of the extrapolation, this value is in good agreement with the glass transition temperature of dry wool, 175°C.^{19,22} This result implies that the group of sites that exhibit strongly hydrophilic properties would vanish above the T_g . Since this is obviously implausible, it appears necessary to look for a less specific mechanism, rather than the adsorption onto specific, molecular sites, for the origin of the Langmuir isotherm. This appears to be in contrast to evidence coming from experiments on chemically modified wool, which apparently supports Watt's site-specific model.²³ It is in agreement, however, with the



Figure 3 Data for the Langmuir capacity constant K' versus temperature T. A straight line is fitted through the data, given by the equation on the graph (correlation coefficient r = 0.98). The 95% confidence limits for K', as taken from Table I, are given by the vertical error bar. The glass transition temperature for dry wool $(T_g^{dry} = 175^{\circ}\text{C})$ is marked.



Figure 4 Data for the Langmuir affinity constant K versus temperature. The arithmetic mean is given by the horizontal line and the 95% confidence limits by the vertical error bar. The broken line gives the van't Hoff equation fit through the data (see text).

observation that chemical modifications, including, namely, hydrolysis, have very little effect on the sorption behavior of wool at low humidities.¹

The second parameter of the Langmuir term, K, is a measure for the attraction of the water molecules by the molecular sites (Langmuir affinity constant). The values for K, as given in Table I, are graphically summarized in Figure 4. They show an apparently continuous increase with temperature, which in comparison to the 95% confidence limits of K, does not appear, however, to be very pronounced.

From thermodynamic considerations, K is related to the molecular partition function for the primarily adsorbed molecules and to their heat of sorption¹⁰ leading with respect to its temperature dependence to the familiar van't Hoff expression²⁴:

$$K = K_0 \exp(-\Delta H_K / RT) \tag{3}$$

where K_0 is the preexponential factor, and ΔH_K , the difference between the enthalpy of the penetrant in the Langmuir-sorbed state compared to that in the vapor phase.²⁴

Nonlinear fitting of eq. (3) to the data of K in Table I (r = 0.898) yields ($\pm 95\%$ confidence limits):

$$K_0 = 125 \pm 298$$

and

$$\Delta H_K = 5.5 \pm 6.7$$
 kJ/mol

In view of the confidence limits, both values are not significant on the 95% level. ΔH_K can, in fact, not plausibly be positive due to the exothermic nature of water adsorption in wool. The estimate of the van't Hoff enthalpy, being, in fact, around zero, is in contrast to values of -49.0 kJ/mol (-11.7 kcal/mol) for the Langmuir absorption of water into PAN²⁴, which is a rather typical value for physisorption.²⁵ This discrepancy together with the specific temperature dependence of K(see above) emphasizes the need to reconsider our current understanding of specific aspects of the sorption mechanisms of water in wool.

The broken line in Figure 4 reflects the fit of eq. (3) to the data for the linear parameter and temperature scale. The lack of significance of both the van't Hoff equation parameters implies that the apparent increase of K with temperature is not significant.

The decrease of the capacity and the only apparent increase of the affinity constant with temperature combine to give from eq. (1) the decrease of the saturation water regain rg^L for the Langmuir isotherm:

$$rg^L = K'K/(1+K) \tag{4}$$

Figure 5 summarizes the values for the Langmuir saturation regain for the various temperatures, showing that the Langmuir saturation regain drops linearly and significantly (r = 0.98) from 5% at 20°C to 2.5% at 100°C.

Henry Term

Parameter C in the second term of eq. (1) (Henry term) is Henry's law solubility coefficient. In the



Figure 5 Equilibrium regains for the three components of eq. (1), as indicated. Straight lines are fitted through the data as guides for the eye.



Figure 6 Henry term constant C in a van't Hoff plot (eq. 5). The horizontal line marks the mean for lower temperatures, and the sloped line, the van't Hoff relationship for higher temperatures, respectively. The transition temperature between the two ranges is marked (see text).

D'Arcy/Watt theory,¹⁰ Henry's law is a linear approximation for the Langmuir isotherm for weakly adsorbing sites. The parameter is expected^{3,24} to follow van't Hoff's law with temperature, so that

$$C = C_0 \exp(-\Delta H_C / RT) \tag{5}$$

The linearizing plot for eq. (5) of $\ln C$ versus 1/T is realized in Figure 6. From this, we propose that C is constant at values larger than $1/T \approx 3.0 \times 10^{-3} \,\mathrm{K}^{-1}$, comprising the last three data points. The horizontal line reflects this concept. For lower values of 1/T, van't Hoff's law is assumed, given by the sloped line for the lower four data points. The data point at $1/T = 3.1 \times 10^{-3} \,\mathrm{K}^{-1}$ (50°C) is included in both groups of data. The horizontal line relates to the arithmetic mean (± standard error, n = 3) $\ln C = -2.238 \pm 0.0218$, so that C = 0.107 for $T \leq 50^{\circ}$ C.

Nonlinear fitting of eq. (5) to the data for $T \ge 50^{\circ}$ C yields (± standard error, n = 4, r = 0.976):

$$C_0 = 0.012 \pm 0.0042$$

and

$$\Delta H_C = -5.9 \pm 0.96 \text{ kJ/mol}$$

The value $\Delta H_C = -5.9$ kJ/mol (-1.4 kcal/mol) is by nearly one order of magnitude smaller than is the analogous value determined by Ranade et al.²⁴ for PAN (-10.3 kcal/mol). The lines in Figure 6 intersect at $1/T = 3.05 \times 10^{-3} \text{ K}^{-1}$, indicating a transition temperature for *C* at 55°C. This agrees with the temperature (50°C) at which the sorption mode to obtain the isotherms had to be changed¹⁴ due to changes of the principal sorption properties of wool. It is interesting to note that this temperature roughly agrees with a transition temperature found in wool fibers in water through mechanical tests by Feughelman et al. (60–70°C),²⁶ which was later on related to sulphydryl–disulphide interchange by Weigmann et al. (70°C).²⁷

With eq. (1), we have for the saturation regain, rg_H , related to the Henry term,

$$rg_H = C \tag{6}$$

The values are plotted in Figure 5 and are roughly approximated by a straight line, as a guide for the eyes. The saturation regain for the Henry term decreases not very strongly from about 10% at 20° C to 8.5% at 100° C.

Multilayer Term

The third term in eq. (1) describes the formation of multilayers of water adsorbed onto the alreadypresent primarily adsorbed water molecules. The term was derived from thermodynamic considerations by Hailwood and Horrobin¹⁵ and adapted by D'Arcy and Watt.¹⁰ In view of the similarity with the expression for the Langmuir term, the parameters k' and k for multilayer adsorption have equivalent meanings¹⁷: k' describes the number of sites available for multilayer adsorption (multilayer capacity constant):

$$k' = M n_{ML} / N_A \tag{7}$$

where $n_{\rm ML}$ is the number of sites available for <u>multilayer</u> adsorption.

Figure 7 shows the data for k' taken from Table I plotted against temperature (left *y*-axis). Since analysis of variance, as part of regression analysis, indicates pronounced homogeneity of the data, we propose k' as being independent of temperature with a mean of $k' = 2.57 \times 10^{-2} \pm 10\%$ (95% confidence limits, see Table I). This yields a value of 8.6×10^{20} multilayer sites/g of dry wool. The value corresponds well to the value for the number of Langmuir sites at 100°C, but is by a factor of 2 smaller than the value of n_L at 20°C. This leads to the conclusion that only a fraction of



Figure 7 Multilayer parameter k' (capacity constant) and k (affinity constant) versus temperature, respectively. The vertical error bars mark the 95% confidence limits. A straight line (- -) is fitted through the data for k (r = 0.6), given by the equation on the graph.

the water molecules, adsorbed in the Langmuir or Henry mode, are available as sites for multilayer formation. The reversible changes of the sorption isotherms of wool after heat treatment, namely, in the region of high regains,¹⁴ indicate that the number of these sites is dependent on the thermal history of the material. The restricted accessibility of primarily adsorbed water molecules for multilayer formation is observed for a wide variety of proteins¹⁰ and is consistent with the concept of "buried water" in proteins.²⁸

The second parameter of the multilayer term k (multilayer affinity constant) is a measure for the attraction of the water molecules onto already present molecules to form the multilayer. The values for k, as given in Table I, are summarized in Figure 7 (right y-axis). Analysis of variance indicates homogeneity of the data, yielding the arithmetic mean ($\pm 95\%$ confidence limits) as $k = 0.879 \pm 12\%$ (see Table I). In view of the expected van't Hoff-type temperature dependence of k, this implies that $\Delta H_k = 0$, similarly as for the Langmuir affinity constant K. The qualitatively inverse course of k with temperature compared to k' (see Fig. 7) indicates the occurrence of compensation effects between the two parameters.

Linear regression, applied for heuristic reasons and represented by the broken line in Figure 7, reveals a small decrease of k with temperature T, which is, however, significant on the 80% level only (r = 0.6). The individual values for k' and kin Table I combine to yield from eq. (1) the equilibrium regain for the multilayer term $rg_{\rm ML}$, plotted in Figure 5:

$$rg_{ML} = k'k/(1-k)$$
 (8)

 $rg_{\rm ML}$ decreases linearly and significantly (r = 0.91), although not very strongly, from 20% at 20°C to 18% at 100%.

CONCLUSIONS

The experimental results for sorption isotherms in the temperature range 20–100°C show that water regain decreases for all humidities continuously with temperature (see Fig. 1). The D'Arcy/ Watt model contains three terms to fit the isotherm over the whole humidity range. The model, containing five adjustable parameters with defined meanings within the framework of the model, leads to excellent fits of the experimental data.

Despite its pronounced physicochemical plausibility and empirical success, the temperature dependence of the parameters reveals a number of inconsistencies of the model. Probably, the most important of these is the observation that the Langmuir capacity constant appears to become zero around the glass transition temperature of dry wool. This is consistent with observations for the water sorption in glassy polymers but certainly inconsistent with the idea of specific molecular sites of water sorption. The second problem with the theory arises from the results that van't Hoff enthalpies derived for the Langmuir and the multilayer affinity constant are zero or very low, which is at variance with the strong affinity of wool for water, expressing itself in the substantial values for the heat of sorption. The third aspect are the generally small changes of a number of the parameters with temperature and the observation of possible compensation effects for the parameters of the multilaver term. This indicates that the D'Arcy/Watt theory overinterprets the complexity of the mechanisms underlying the sorption isotherm. Current investigations aim at the development of simpler models for the analysis of the water-sorption isotherms of wool. which are consistent with the chemical properties of the material as well as with the role of the glass transition for sorption performance.

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