Fundamental Studies on the Interaction between Moisture and Textiles:
PART X. Moisture Sorption Properties of Wool and Hair Fibers.*

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ABSTRACT

The moisture sorption isotherm was determined primarily at 30°C for fifteen kinds of wool and hair fibers from sheep, goat, camel, and rabbit families. The isotherm was analyzed in terms of Brunauer, Emmett and Teller (B. E. T.)'s parameters: C (adsorptive energy factor), \( v_m \) (maximum volume of adsorbed water in monolayer per gram of dry material), and \( n_{\text{max}} \) (maximum number of layers in multilayer adsorption), in order to discuss the moisture sorption properties in relation to structural feature of the materials.

Despite of wide variety of the wool and hair fibers, the values of the parameters were found to be almost equal to each other; i.e., C ranging from 9.40 to 11.7, \( v_m \) from 0.0574 to 0.0718 and \( n_{\text{max}} \) from 5 to 6. The X-ray crystallinity, \( X_x \), was estimated by Ruland method as ranging from 24.2 to 30.9% in association with the value of lattice imperfection of around 5. The plots of \( v_m \) against the degree of noncrystallinity, \( 1-X_x \), exhibited roughly a linear relation passing through origin with a slope of 0.0927 for a series of wool specimens, but deviated from the linear relation toward larger \( v_m \) side for particular specimens having the medulla structure.

The moisture sorption process was also investigated by thermodynamic means as a function of moisture regain of the specimen from dryness up to saturation. Namely, the differential heat of moisture sorption, \( Q_L \) (enthalpy difference of the sorbed water in reference to liquid water), and the excess energy, \( T \Delta S \) (entropy difference of the sorbed water also in reference to liquid water), were determined to conclude that the sorbed water is in highly ordered state at dryness and is still in a little more ordered state than in liquid state at saturation.

1. INTRODUCTION

Recent developments in protein chemistry have revealed not only the primary structure of wool keratin in terms of heptapeptide sequential arrangement of amino acid residues\(^{1-3}\), but also the secondary structure of the keratin molecules in relation to a \( (7/2) \) \( \alpha \)-helix conformation of the heptapeptide sequence\(^4,5\), proto-fibril, and micro-fibril. As schematized by Dobb et al.\(^6\) in 1961 and by Fraser et al.\(^7\) in 1985, the fiber structure of a single wool fiber has been successfully understood in terms of structural units of different molecular and supermolecular levels as well as of different kinds of cell structure, such as cuticle, cortex, and cell membrane complex.

Strictly speaking, however, there has been a most fundamental problem unsolved yet. That is, whether the proto-fibril is constituted of double or of triple helix (coiled-coil) of keratin molecules and, consequently, the micro-fibril is composed of nine member ring and two member core of the proto-fibrils (triple helix), as suggested in most of textbooks of biochemistry\(^8,9\), or of nine member ring and three member core of the proto-fibrils (double or triple helix)\(^10-12\). Recently, Woods and Gruen have

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proposed a new structural unit composed of two of the double helix\textsuperscript{13)}.

When one arranges a single low sulfur keratin molecule in the (7/2) helix conformation, it reveals that about one third of the helix surface is covered by hydrophobic groups to form hydrophobic region and two thirds of the helix surface is covered by hydrophilic groups to form hydrophilic region. This has been believed to be a driving force of packing three helicies to form the proto-fibril by occluding the hydrophobic regions within the fibril and exposing the hydrophilic regions at outside of the fibril during development of the keratin molecules in aqueous medium in the follicle at the growth of hair\textsuperscript{14,15)}.

If this is the case, cysteine groups appear at particular three-fold-symmetric positions in cross-section of the proto-fibril. Basing on this particular arrangement of the cysteine groups, Kondo\textsuperscript{15)} explained the formation of micro-fibril in terms of the most stable disulfide bond between the cystein groups; i.e., cystine linkage between the proto-fibrils. This model explains reasonably the formation of micro-fibril in terms of the nine member ring formation of the proto-fibrils occluding two more proto-fibrils within the ring, observed by electron microscopy for a porcupine quill\textsuperscript{16)}.

The moisture sorption properties of wool were investigated by Hedges\textsuperscript{17)} as early as in 1926 and by Speakman and Cooper\textsuperscript{18)} in 1936. Speakman\textsuperscript{19)} modified a two-phase adsorption model, which was proposed by Pierce\textsuperscript{20)}, by adding the third form of water in capillary condensation for isotherm of wool fiber; i.e., a three-phase adsorption model. Bull\textsuperscript{21)} applied Brunauer, Emmett and Teller (B. E. T.)'s multilayer adsorption model\textsuperscript{22)} to the moisture sorption data of many proteins including silk and wool in order to characterize the moisture sorption properties in terms of B. E. T.'s parameters. Rowen and Blaine\textsuperscript{23)} also analyzed the moisture sorption isotherms of six kinds of hydrophilic textile fiber including silk, wool, and nylon fiber in terms of the B. E. T.'s parameters.

In 1950, an isotherm theory derived by Bradley\textsuperscript{24)} was applied by Hoover and Mellon\textsuperscript{25)} to experimental data for ovalbumin, silk, and wool over wide ranges of relative humidities from 5 to 95% and of temperatures from 35 to 100°C. The theory was a sort of multilayer theory similar to the B. E. T.'s theory, but took into account the change in adsorptive energy with the number of layers. For a few decades since 1960, the effect of chemical modifications, such as esterification, deamination, grafting and/or deposition of vinyl polymers, upon the moisture sorption properties of wool was studied by several authors\textsuperscript{26–31)}.

In 1970, D'Arcy and Watt proposed a composite isotherm equation composed of monolayer adsorptions by strongly binding sites of type i, monolayer adsorption by weakly binding sites, and multilayer adsorption of cluster formation, and examined the equation for various kinds of protein including silk and wool\textsuperscript{32)}. The stoichiometry of water sorption by proteins, which was studied by Pauling as early as in 1945\textsuperscript{33)}, was further discussed by Leeder and Watt\textsuperscript{34,35)}. Recently, Watt and D'Arcy have reviewed the hydration of biopolymers, especially of wool keratin, with emphasis that hysteresis water, if any, is not associated with specific polar sites but results from conformational changes in the substrate\textsuperscript{36)}. They have also reviewed the most detailed investigation of moisture sorption isotherm of wool over a wide range of temperature from 20 to 100°C for a series of wools from different sources and for other forms of keratin\textsuperscript{37)}.

In a previous paper of this series\textsuperscript{38)}, the moisture sorption isotherms of natural polypeptide fibers (silk and wool) and synthetic aliphatic and aromatic polyamide fibers were investigated at 30°C to discuss the stoichiometry of water sorption by peptide group. It has been concluded that the denser the distribution of the peptide groups along the back-bone chain, the larger is the water accessibility of the group, with an exception of wool, for which the moisture sorption behavior deviates from the conclusion possibly due to the presence of side-chain polar groups. In this paper, the study is extended to a wide variety of wool and hair fibers to examine the moisture sorption properties of the keratin fibers in relation to their structural features. The stoichiometry of water sorbed by wool keratin will be investigated in successive papers by chemical modifications of the materials and by calorimetry of moisture sorption.

2. TEST SPECIMENS AND EXPERIMENTAL PROCEDURES

2.1 Preparation of Test Specimens

Fifteen kinds of wool and other animal hair fibers from sheep, goat, camel and rabbit families, as specified in Table 1, were prepared for measuring the moisture
sorption isotherms.

Two kinds of biochemically descaled wool by a proteolysis using pronase\textsuperscript{39}, one being in laboratory scale for Merino 64's wool and the other being in industrial scale for New Zealand Luster 48's wool, were included to examine the effect of descaling upon the moisture sorption behavior.

All of these specimens were purified, at first, by soaking in a mixture of one to one volume ratio of ethanol and benzene for several days at room temperature, and then by Soxhlet extraction with ethyl ether several times in order to remove oil or fatty materials, if any, contaminating the received specimens from factories. The purified specimens were further soaked several times in a distilled water adjusted at pH value of about 5 by a dilute HCl, air-dried, and stored in a P\textsubscript{2}O\textsubscript{5} desiccator as test specimens.

The bulk density of the test specimen, as listed in the second column in Table I, was determined by means of the density-gradient-column method using mixture of n-heptane with CCl\textsubscript{4} at 30.0°C after the specimen being dried in vacuum. The fiber thickness in diameter and the number of scales per unit length of fiber in the third and fourth columns in Table I, respectively, were determined as average values by scanning electron microscopy. It is seen, in general, that the thinner the fibers, the denser the scale density.

The ratio of ortho-cortex, para-cortex, and medulla in the fifth column in Table I was determined mostly by optical microscopy and supplementally by transmission electron microscopy by staining the cross section of the specimen with a basic dye of methylene blue and osmic acid, respectively. Some specimen, such as South Africa Adult Mohair, has coaxial distribution of the ortho- and para-cortices, instead of bi-lateral distribution, and the ortho- and para-cortices can not be distinguished for some specimens, such as camel hair and Angora rabbit.

### 2.2 X-ray Diffraction Measurements for Determining the Degree of Crystallinity

The degree of crystallinity was determined in weight

<table>
<thead>
<tr>
<th>Specification</th>
<th>Density in bulk (gr/cc)*</th>
<th>Thickness in diameter (μm)</th>
<th>Scale density (mm(^{-1}))</th>
<th>Ortho/para/medulla ratio (%)**</th>
<th>X-ray crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australian Merino 66's wool</td>
<td>1.308\textsubscript{5}</td>
<td>25</td>
<td>80</td>
<td>63/37/0</td>
<td>25.2</td>
</tr>
<tr>
<td>Australian Merino 64's (descaled)</td>
<td>1.311\textsubscript{1}</td>
<td>25</td>
<td>(90)</td>
<td>68/32/0</td>
<td></td>
</tr>
<tr>
<td>Australian Merino 60's wool</td>
<td>1.307\textsubscript{1}</td>
<td>35</td>
<td>88</td>
<td>66/34/0</td>
<td>27.1</td>
</tr>
<tr>
<td>Argentine X-bred 56's wool</td>
<td>1.300\textsubscript{0}</td>
<td>35</td>
<td>90</td>
<td>71/29/0</td>
<td>26.6</td>
</tr>
<tr>
<td>Argentine Luster wool</td>
<td>1.292\textsubscript{2}</td>
<td>50</td>
<td>57</td>
<td>76/20/4</td>
<td>30.9</td>
</tr>
<tr>
<td>New Zealand Luster 48's wool</td>
<td>1.306\textsubscript{2}</td>
<td>35</td>
<td>84</td>
<td>70/30/0</td>
<td>25.9</td>
</tr>
<tr>
<td>New Zealand Luster 48's (descaled)</td>
<td>1.308\textsubscript{0}</td>
<td>35</td>
<td>(84)</td>
<td>67/33/0</td>
<td>28.9</td>
</tr>
<tr>
<td>Lincoln wool</td>
<td>1.296\textsubscript{2}</td>
<td>45</td>
<td>50</td>
<td>69/31/0</td>
<td>29.0</td>
</tr>
<tr>
<td>Cashmere wool (white)</td>
<td>1.308\textsubscript{4}</td>
<td>20</td>
<td>64</td>
<td>62/38/0</td>
<td>25.5</td>
</tr>
<tr>
<td>Cashmere wool (brown)</td>
<td>1.311\textsubscript{0}</td>
<td>20</td>
<td>66</td>
<td>67/33/0</td>
<td></td>
</tr>
<tr>
<td>South Africa Adult Mohair</td>
<td>1.305\textsubscript{5}</td>
<td>50</td>
<td>57</td>
<td>71/29/0*</td>
<td>24.3</td>
</tr>
<tr>
<td>Camel hair</td>
<td>1.306\textsubscript{6}</td>
<td>20</td>
<td>56</td>
<td>indistinguishable</td>
<td>24.2</td>
</tr>
<tr>
<td>Alpaca hair</td>
<td>1.280\textsubscript{0}</td>
<td>33</td>
<td>120</td>
<td>53/38/9</td>
<td>25.1</td>
</tr>
<tr>
<td>Llama hair</td>
<td>1.277\textsubscript{3}</td>
<td>44</td>
<td>110</td>
<td>50/43/7</td>
<td>28.7</td>
</tr>
<tr>
<td>Angora Rabbit</td>
<td>1.258\textsubscript{7}</td>
<td>20</td>
<td>120</td>
<td>87/13(M)\textsuperscript{*}</td>
<td>28.5</td>
</tr>
</tbody>
</table>

* Determined by a density gradient column method of n-heptane/CCl\textsubscript{4} at 30.0±0.1°C.

** Optical microscopy staining by methylene blue.

* Co-axial distribution of ortho and para cortices, instead of bi-lateral distribution.

** Ortho and para cortices can not be distinguished.
fraction by an X-ray diffraction photometry using a random assembly of shortly chopped fibers of each specimen. The X-ray crystallinity, $X_c$, was evaluated by a method proposed by Ruland\(^{40}\), i.e.,

$$
X_c = \frac{\int_0^\infty s^2 I_{\text{cry}}(s) \, ds}{\int_0^\infty s^2 I(s) \, ds} K
$$

(1)

where $I(s)$ is the scattering intensity at the end of the reciprocal space vector $s$, $I_{\text{cry}}$ and $I$ are the crystalline and total coherent scatterings, respectively, and $K$ is a term for lattice imperfection defined as

$$
K = \frac{\int_0^\infty s^2 \langle f^2 \rangle \, ds}{\int_0^\infty s^2 \langle f^2 \rangle \, D ds}
$$

(2)

where $\langle f^2 \rangle$ is the mean square atomic scattering factor, and $D$ is a disorder function approximated as

$$
D = \exp(-ks^2)
$$

(3)

where $k$ is a factor of lattice imperfection including thermal effects as well as the first and second kinds of lattice imperfection.

The X-ray diffraction measurements were performed over an angular range of twice the Bragg angle, $2\theta$, from 5 to 70° at room temperature by a diffractometer, Rigaku Rotaflex RU200, with Cu-Kα radiation of wavelength $\lambda = 1.541\text{Å}$. After corrections for air-scattering, polarization and absorption, the scattered intensity distribution, $I(2\theta)$, was converted to that of $I(s)$ by $|s| = s = (2/\lambda)\sin\theta$, as shown in the upper-half in Fig. 1, for example, for Australian Merino 60’s wool. In the figure, the contributions of incoherent scattering were already eliminated by calculating first the mean square atomic scattering factors and then intensity distribution of the incoherent scattering both as a function of $s$ using the equations in literatures\(^{41,42}\).

The corrected intensity distribution, $I(s)$, was resolved into crystalline contributions from the $j$-th crystal planes, $I_{\text{cry},j}(s)$, as well as noncrystalline contribution, $I_{\text{am}}(s)$, by a nonlinear least square method of curve fitting on assuming each crystalline contribution to be represented by Lorentzian function, as illustrated also in the upper-half in Fig. 1. The shape of $I_{\text{am}}(s)$ was, however, found to be a little asymmetric with respect to $s$ to give the best fit. Some numerical results of the resolution are listed in Table II for two kinds of Australian Merino

![Fig. 1 X-ray diffraction intensity distribution from random assembly of short-chopped fibers of Australian Merino 60's wool.](image1)

![Fig. 2 X-ray diffraction intensity distributions from a bundle of Australian Merino 60's wool as functions of twice the Bragg angle, $2\theta$, and azimuthal angle, $\phi$. $\phi = 0^\circ$: equatorial and $\phi = 90^\circ$: meridional direction.](image2)
Table II Numerical Analysis of X-ray Diffraction Intensity Distribution into Crystalline and Noncrystalline Components for Australian Merino 60 and 66's Wools*.

<table>
<thead>
<tr>
<th></th>
<th>Relative peak height **</th>
<th>Peak position in twice the Bragg angle $2\theta$ (°) and in (s)</th>
<th>Peak half-width in twice the Bragg angle $2\theta$ (°) and in (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Merino 60's</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>peak 1</td>
<td>1.00</td>
<td>9.00 (0.102)</td>
<td>3.48 (0.039)</td>
</tr>
<tr>
<td>peak 2</td>
<td>0.467</td>
<td>18.3 (0.206)</td>
<td>3.26 (0.036)</td>
</tr>
<tr>
<td>peak 3</td>
<td>0.563</td>
<td>21.9 (0.247)</td>
<td>6.22 (0.070)</td>
</tr>
<tr>
<td>peak 4</td>
<td>0.266</td>
<td>42.0 (0.465)</td>
<td>9.76 (0.110)</td>
</tr>
<tr>
<td>amorphous</td>
<td>1.23</td>
<td>23.0 (0.259)</td>
<td>21.1 (0.238) + 31.4 (0.351) ++</td>
</tr>
<tr>
<td>Merino 66's</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>peak 1</td>
<td>1.00</td>
<td>8.98 (0.102)</td>
<td>3.66 (0.041)</td>
</tr>
<tr>
<td>peak 2</td>
<td>0.587</td>
<td>18.2 (0.205)</td>
<td>3.28 (0.037)</td>
</tr>
<tr>
<td>peak 3</td>
<td>0.806</td>
<td>21.9 (0.247)</td>
<td>5.68 (0.064)</td>
</tr>
<tr>
<td>peak 4</td>
<td>0.342</td>
<td>42.0 (0.465)</td>
<td>7.45 (0.084)</td>
</tr>
<tr>
<td>amorphous</td>
<td>1.60</td>
<td>22.5 (0.253)</td>
<td>20.6 (0.232) ++ 37.4 (0.416) ++</td>
</tr>
</tbody>
</table>

* By assuming each peak to be represented by Lorentzian function.
** Normalized by the peak height of peak 1.
+ Left-half and ++ right-half of the amorphous peak.

wool, 60, and 66's. As can be seen in the table, four crystalline peaks, peak 1 through peak 4 in the order of ascending Bragg angle, and a broad and asymmetric amorphous peak are separated from each other.

According to the photometric measurements of diffraction intensity distributions of the fiber pattern, as shown in Fig. 2 for the Merino 60's wool as functions of twice the Bragg angle, $2\theta$, as well as of azimuthal angle, $\phi$, the peak 1 could be assigned to an equatorial reflection with peak position $(2\theta \phi)$ of 9.0° and lattice spacing of 9.82Å, while the peak 2 to a meridian reflection with $2\theta \phi$ of 18.3° and lattice spacing of 4.85Å. The lattice spacing of 4.85Å is, however, considerably smaller than value of 5.14Å, which can be evaluated from the meridional reflection, as indicated by the arrows in Fig. 3 for photographic fiber patterns of the Australian Merino 66's wool and a Lincoln wool. Actually, the value of 5.14Å has been accepted for explaining the fiber period of wool keratin molecule in crystal lattice in terms of its folded conformation by Astbury, and or coiled-coil conformation of $\alpha$-helix by Pauling et al. and by Crick.

Although more detailed resolution and assignments of the crystalline diffractions appearing at $s = 0.25$ and 0.47 are necessary, let us proceed to the determination of the degree of crystallinity according to Eq. (1). Lower-half in Fig. 1 shows $s^2I_{am}$ (s), $s^2I_{cry}$ (s), and $s^2I$ (s) ($= s^2I_{cry}$ (s) + $s^2I_{am}$ (s)), which are calculated from $I_{am}$ (s) and $I_{cry}$ (s) in the upper-half in Fig. 1. The results of the application of Eqs. (1) - (3) to the determination of the degree of crystallinity are shown in Table III as functions of $k$ and integration interval, $s_o - s_u$. The values of the lattice imperfection, $k$, and consequently the value of the degree of crystallinity, $X_x$, were chosen from the table so as to give the most constant value of $X_x$ irrespective of the integration interval; i.e., $k = 5$. This value of $k = 5$ was adopted for final determination of $X_x$ for all of the test specimens, as listed in the sixth column in Table I.

2.3 Measurements of the Moisture Sorption Isotherm and the Heat of Moisture Sorption

The moisture sorption isotherm was determined primarily at 30°C and supplementally at 15 and 45°C using a weighing bottle method, as described elsewhere. In practice, a weighing bottle containing about 1 gram of dry specimen in a vacuum oven for three days at 90°C was kept in a desiccator to condition the specimen under the given temperature and vapour pressure adjusted by an aqueous solution of sulphuric acid. They were stored in a large constant temperature air-bath thermostated by forced air-flow. Usually it takes more than two weeks until moisture sorption equilibrium is attained. The moisture sorption isotherm was represented by the plots...
Fig. 3 X-ray diffraction patterns of Australian Merino 66’s wool and Lincoln wool, obtained by a flat film camera with camera distance of 50.0 mm. Fiber axis is in vertical direction.

Table III The Degree of Crystallinity of Australian Merino 60 and 66’s Wools as Functions of k and Integration Interval.*

<table>
<thead>
<tr>
<th>Integration interval $a_k$</th>
<th>$k = 0$</th>
<th>$k = 1$</th>
<th>$k = 2$</th>
<th>$k = 3$</th>
<th>$k = 4$</th>
<th>$k = 5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Merino 60’s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.04–0.34</td>
<td>23.9</td>
<td>24.6</td>
<td>25.4</td>
<td>26.2</td>
<td>26.9</td>
<td>27.6</td>
</tr>
<tr>
<td>0.04–0.50</td>
<td>21.6</td>
<td>23.0</td>
<td>24.3</td>
<td>25.5</td>
<td>26.7</td>
<td>27.8</td>
</tr>
<tr>
<td>0.04–0.71</td>
<td>18.1</td>
<td>20.1</td>
<td>21.9</td>
<td>23.4</td>
<td>24.8</td>
<td>26.0</td>
</tr>
<tr>
<td>mean: 27.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Merino 66’s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.04–0.34</td>
<td>23.3</td>
<td>24.0</td>
<td>24.8</td>
<td>25.5</td>
<td>26.2</td>
<td>26.5</td>
</tr>
<tr>
<td>0.04–0.50</td>
<td>19.7</td>
<td>20.9</td>
<td>22.1</td>
<td>23.3</td>
<td>24.3</td>
<td>25.3</td>
</tr>
<tr>
<td>0.04–0.71</td>
<td>17.3</td>
<td>18.8</td>
<td>20.1</td>
<td>21.3</td>
<td>22.4</td>
<td>23.3</td>
</tr>
<tr>
<td>mean: 25.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The degree of crystallinity is in percent.

of percent moisture regain (mass of sorbed water per unit mass of dry material) against relative humidity ranging from dryness up to saturation.

Calorimetry of the moisture sorption process was performed by using a heat transfer type calorimeter (CM-204 S1, Rhesca Co., Tokyo) to measure at first the heat of wetting (integral heat of moisture sorption) of the specimen45). $W(a)$ (cal per unit mass of dry material), as a function of moisture regain $a$ at 30.0°C. The differential heat of moisture sorption, $Q_L$, which is defined as the heat evolved when one gram of liquid water is sorbed by infinite mass of material possessing moisture regain $a$, is also a function of moisture regain and can be derived from the heat of wetting $W(a)$ as follows47):

$$Q_L(a) = -\frac{dW(a)}{da}$$

In order to obtain $Q_L(a)$ by differentiating $W(a)$ numerically, as given by Eq. (4), and, subsequently, as a function of relative humidity, curve fitting of $W(a)$ to an empirical formula was performed by nonlinear regression assuming the formula to be given by46)

$$W(a) = a + b \exp \left( -ca \right)$$

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Analysis of Moisture Sorption Isotherm in Terms of the B. E. T.’s Multilayer Adsorption Model

Thick solid lines with open circles in Figs. 4 through 6 show the moisture sorption isotherms observed at 30°C for three kinds of representative specimen of sheep, goat and camel families, respectively.

All isotherms display typical sigmoids and resemble each other. Generally, this type of sorption isotherm has been observed for hydrophilic textile fibers, such as cellulosic fibers48,49), and analyzed in terms of the B. E. T.'s multilayer adsorption model22).

The B. E. T.'s multilayer adsorption model is written for unrestricted adsorption of infinite number of adsorption layer as:

$$v = \frac{v_n C x}{\left( 1 - x \right) \left( 1 + \left( C - 1 \right) x \right)}$$

(6)

and for restricted adsorption of finite number of adsorption layers $n$ as:

$$v = \frac{v_n C x \left[ \left( 1 - \left( n + 1 \right) x \right)^n + x^n \left( n x^n + 1 \right) \right]}{\left( 1 - x \right) \left[ 1 + \left( C - 1 \right) x - C x^n + 1 \right]}$$

(7)

where $x$ is the relative humidity defined by the ratio of vapour pressure $p$ to maximum vapour pressure $p_s$ at a given temperature, $v$ and $v_n$ are the total volume of adsorbed moisture in multilayer fashion and the maximum volume of adsorbed moisture in monolayer (Langmuir) fashion, respectively, both per unit mass of dry material, and $C$ is the adsorptive energy factor.

Eq. (6) can be rewritten as a linear relation of $x/v(1-x)$ to $x$, and the values of $v_n$ and $C$ can be determined from the slope and the intercept of the linear relation. This linear relationship (B. E. T.’s linear plots) has been usually found for the moisture sorption isotherm data of hydrophilic polymers in a range of relative humidity less than ca. 50%. Fig. 7 demonstrates this situation for the data of sorption isotherms of the four kinds of represent-
Fig. 4 Comparison of moisture sorption isotherm of Australian Merino 60's wool observed at 30°C with those calculated from B.E.T.'s multilayer adsorption model.

Fig. 5 Comparison of moisture sorption isotherm of Cashmere wool (white) observed at 30°C with those calculated from B.E.T.'s multilayer adsorption model.

Fig. 6 Comparison of moisture sorption isotherm of Alpaca hair observed at 30°C with those calculated from B.E.T.'s multilayer adsorption model.

Fig. 7 B.E.T.'s linear plots for Australian Merino 60's wool, Cashmere wool (white), Alpaca hair, and Angora rabbit, all at 30°C.
tative specimen including an additional specimen of Angora Rabbit. As can be seen in the figure, the linear relationship is well satisfied in a relative humidity range less than ca. 50% with exception near dryness at which the plots deviate slightly downward from the linear relation.

The deviation from the B. E. T.'s linear plots near dryness, though being slight, has been already pointed out in a previous paper\(^{49}\). Strictly speaking, the B. E. T.'s multilayer adsorption model was formulated for the system having a single kind of adsorption site. To the system of multiple kinds of adsorption site, such as natural polypeptides including wool keratin, an extended B. E. T.'s model with multicomponent surfaces by Walker and Zettlemoyer\(^{50}\) and by Takizawa\(^{51}\) or a composite adsorption model by D'Arcy and Watt\(^{32}\) must be applied.

Nevertheless, let us analyze the sorption isotherms of the test specimens in terms of the B. E. T.'s model on assuming the parameters, \(C\) and \(v_m\), to be a sort of averaged adsorptive energy factor and a summation of maximum volumes of adsorbed moisture in monolayer fashion, respectively, for the multiple kinds of adsorption site. This is simply because of the fact that the B. E. T.'s model can describe the isotherm fairly well, at least phenomenologically, with a relatively few number of adjustable parameters with exception of some discrepancy at high relative humidities near saturation.

The thin solid lines in Figs. 4 through 6 are calculated results from Eqs. (6) and (7) for the infinite and finite numbers of adsorbed layers. The calculated one with \(n = 1\) (Langmuir’s monolayer adsorption) fits with the observed result of thick solid line only in the near dry state, whereas the calculated result with \(n = \infty\) fits with the observed result in a humidity range up to about 50% beyond which it increases much more rapidly than the observed result. Between the two extremes with number of layers \(n = 1\) and \(\infty\), there is a calculated result with a maximum number of \(n_{\text{max}}\) with which the calculated result is closest but never exceeds the observed result. The

Table IV Moisture Sorption Characteristics of Wool and Hair Fibers in Terms of the B. E. T.'s Multilayer Adsorption Parameters at 30°C.

<table>
<thead>
<tr>
<th>Specification</th>
<th>B. E. T.'s parameters</th>
<th>Moisture regain at 95% r. h.</th>
<th>Moisture regain at 65% r. h.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(v_m)</td>
<td>(C)</td>
<td>(n_{\text{max}})</td>
</tr>
<tr>
<td>(sheep family)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Australian Merino 66's wool</td>
<td>0.0652</td>
<td>10.28</td>
<td>6</td>
</tr>
<tr>
<td>Australian Merino 64's (descaled)</td>
<td>0.0574</td>
<td>11.72</td>
<td>6</td>
</tr>
<tr>
<td>Australian Merino 60's wool</td>
<td>0.0658</td>
<td>10.36</td>
<td>6</td>
</tr>
<tr>
<td>Argentine X-Bred 56's wool</td>
<td>0.0659</td>
<td>10.27</td>
<td>6</td>
</tr>
<tr>
<td>Argentine Luster wool</td>
<td>0.0676</td>
<td>10.08</td>
<td>6</td>
</tr>
<tr>
<td>New Zealand Luster 48's wool</td>
<td>0.0673</td>
<td>9.66</td>
<td>5</td>
</tr>
<tr>
<td>New Zealand Luster 48's (descaled)</td>
<td>0.0648</td>
<td>9.40</td>
<td>5</td>
</tr>
<tr>
<td>Lincoln wool</td>
<td>0.0650</td>
<td>10.62</td>
<td>6</td>
</tr>
<tr>
<td>(goat family)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cashmere wool (white)</td>
<td>0.0630</td>
<td>11.04</td>
<td>6</td>
</tr>
<tr>
<td>Cashmere wool (brown)</td>
<td>0.0640</td>
<td>11.32</td>
<td>6</td>
</tr>
<tr>
<td>South Africa Adult Mohair</td>
<td>0.0718</td>
<td>9.34</td>
<td>5~6</td>
</tr>
<tr>
<td>(camel family)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Camel hair</td>
<td>0.0708</td>
<td>10.53</td>
<td>5~6</td>
</tr>
<tr>
<td>Alpaca hair</td>
<td>0.0680</td>
<td>10.28</td>
<td>6</td>
</tr>
<tr>
<td>Llama hair</td>
<td>0.0684</td>
<td>10.14</td>
<td>6</td>
</tr>
<tr>
<td>(rabbit)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Angora Rabbit</td>
<td>0.0702</td>
<td>10.18</td>
<td>6</td>
</tr>
</tbody>
</table>

* Maximum number of adsorbed layers below which the calculated isotherm by B. E. T.'s model is closest but never exceeds the observed isotherm.
calculated results of $n_{\text{max}}$ were found to be 6 for the Merino 60's wool, Cashmere wool (white), and Alpaca hair. We can define three kinds of moisture regain at a given relative humidity; with $n = 1$ due to Langmuir’s monolayer adsorption, with $n_{\text{max}} \geq n > 1$ due to the B.E.T.'s multilayer adsorption, and with $n > n_{\text{max}}$ due to other kind of sorption mechanisms, such as water clustering.

Table IV lists the values of the B.E.T.’s parameters, $C$, $v_m$, and $n_{\text{max}}$ thus determined, which characterize the moisture sorption properties of all of the test specimens at 30°C, together with the three values of moisture regain at 95% relative humidity as well as the bulk regain at 65% relative humidity. It must be first pointed out that the values of $v_m$ and $C$ somewhat vary with the specimens, but are rather close to each other within ranges of $0.0574 \pm 0.0718$ and $9.40 \pm 11.72$, respectively, when the wide variety of animal families is taken into account. This must be attributed to the simple fact that the wool and hair fibers are composed of a common protein molecule of keratin with similar supermolecular structures to build up the fiber structure. Second, the $n_{\text{max}}$ is found to be six for almost every specimen with a few exceptions of New Zealand Luster 48’s wool, South Africa Adult Mohair and Camel hair. Irrespective of the wide variety of animal families, the constancy in the number of multilayers with a value as large as six is also surprising, and is difficult to understand without accounting any long-range order between the adsorbent and adsorbate; i.e., some ordered structure for the adsorbed water molecules with $n_{\text{max}} \geq n > 1$, as will be studied in terms of thermodynamics in the following section.

Fig. 8 shows the plots of the value of $v_m$ against the degree of noncrystallinity, $(1-X_s)$, which was estimated from the X-ray crystallinity in Table 1, for the respective specimens at 30°C. Although the plots scatter considerably in expanded scales of the coordinates, the plots given by open circles for the sheep family can be represented roughly by a straight line relation, as drawn by a solid line. That is, the value of $v_m$ is proportional to the degree of noncrystallinity of the specimen, validating a concept that the initial moisture sorption is primarily affected by the chemical and physical properties of the noncrystalline region of the material. As demonstrated in a whole range of the degree of noncrystallinity in Fig. 9, the linear relation passes through the origin of the coordinates with a given slope of $9.27 \times 10^{-2}$, which corresponds to a maximum volume of adsorbed water in monolayer fashion (Langmuir’s adsorption) per one gram of dried noncrystalline material for the sheep family.
The values of $v_m$ for some specific specimens of the camel family, as denoted by dots, and of Angora rabbit and Argentine Luster wool, are plotted in the up-side to the straight line, possibly due to the existence of medulla texture consisting of amino acid residues with much more chemical affinity but less cystine content than the other residues. Large deviations in the value of $v_m$ for South Africa Adult Mohair and Cashmere wool, both of goat family denoted by open square, from the straight line can not be explained in terms of any structural parameter listed in Table I. The values of $C$, a sort of averaged adsorptive energy factor, also fluctuate within a small range of ca. 10.6 ± 1.2 in consistence with the value in literature. It is, however, difficult to find any systematic change in the value of $C$ with the animal's families or with the structural parameters listed in Table I.

As has been compared in Table IV for two sets of non-treated and biochemically descaled wool specimens; Australian Merino fine wools and New Zealand Luster 48's wools, the descaling does not necessarily affect the moisture sorption properties in equilibrium.

Table V  Moisture Sorption Characteristics of New Zealand Luster 48's Wool in Terms of the B. E. T.'s parameters at Three Different Temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Density in bulk (g/cc)</th>
<th>Degree of crystallinity (%)</th>
<th>B. E. T.'s parameters</th>
<th>Moisture regain at 95% r.h. (%)</th>
<th>Moisture regain at 65% r.h. (%) in bulk (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.0730</td>
<td>9.62</td>
<td>$v_m$</td>
<td>6</td>
<td>6.6</td>
</tr>
<tr>
<td>30</td>
<td>1.3062</td>
<td>25.9</td>
<td>$v_m$</td>
<td>5</td>
<td>6.0</td>
</tr>
<tr>
<td>45</td>
<td>0.0575</td>
<td>9.84</td>
<td>$v_m$</td>
<td>5</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Fig. 10 Moisture sorption isotherms of New Zealand Luster 48's wool at three different temperatures, 15, 30, and 45°C.

Fig. 11 Moisture sorption isotherms of New Zealand Luster 48's wool at low relative humidities at three different temperatures of 15, 30, and 45°C.
3.2 Isosteric and Calorimetric Measurements of the Heat of Moisture Sorption; Thermodynamic Investigation of Sorption Process

Figures 10 and 11 show the temperature dependence of the moisture sorption isotherms of New Zealand Luster 48's wool over a whole range of relative humidity and a low relative humidity range in detail, respectively. The higher the temperature, the less the amount of sorbed water in equilibrium at any relative humidity. This is because the wool specimen in taking up moisture releases heat; i.e., displaying an exothermic process, as is demonstrated later in the calorimetric measurement.

Table V lists the results of analyzing the isotherm at three different temperatures in terms of the B. E. T.'s multilayer adsorption model. The temperature dependence of the less hygroscopicity with increasing temperature is well represented by the change in the B. E. T.'s parameters and in the three kinds of moisture regain at relative humidity of 95%, though C remaining almost unchanged with temperature.

The differential heat of moisture sorption, $Q_L$, can be readily obtained from the temperature dependence of the sorption isotherm data by the following isosteric equation:

$$Q_L (\alpha) = -\frac{R}{M} \frac{d(\varphi n p/p_c)}{d(1/T)} |_{\alpha}$$  \hspace{1cm} (9)

where $R$ is the gas constant, and $M$ is the molecular weight of water. Such an analysis of the sorption data for wool specimens at various temperatures was first provided by Speakman and Cooper [18] and recently by Miyagawa et al. [19].

The application of Eq. (9) to the sorption data measured at different temperatures contains some problems because of the non-reversibility shown by hysteresis between sorption and desorption process. However, Eq. (9) has been applied widely to calculate the value of $Q_L$ from the sorption data [17, 53, 54]. The isosteric $Q_L$ thus calculated from the data in Fig. 10 and 11 for the New Zealand Luster 48's wool is shown later in comparison with directly observed $Q_L$ by calorimetry.

Fig. 12 shows the plots of heat of wetting $W$ against moisture regain $\alpha$ for the New Zealand Luster wool, observed at 30°C by the heat transfer type calorimeter. The wetting process was found to be exothermic over whole range of moisture regain from dryness up to saturation. The heat of wetting is the largest at dryness and decreases rapidly down to almost zero with increasing moisture regain up to saturation. The heat of wetting, $W(\alpha)$ in calorie per gram of dry material, is a sort of integral heat of moisture sorption over a range of moisture regain from $\alpha$ up to $\alpha_s$ (saturation regain), so that it is too complicated to characterize the nature of the sorbed water as a function of moisture regain of the material. Instead, the differential heat of moisture sorption, $Q_L (\alpha)$ in calorie per gram of liquid water, is more straightforward quantity than $W (\alpha)$ for characterizing the sorbed water in terms of thermodynamic parameters.

The solid line in Fig. 12 is the result drawn by an empirical formula best-fitted by nonlinear regression assuming the formula to be given by Eq. (5) with the values of $a=0.160$, $b=22.1$, and $c=0.123$. The heat of wetting at dryness, $W (\alpha=0)$, and at saturation, $W (\alpha=\alpha_s)$, are found to be $22.3 \pm 0.2$ and $0.3 \pm 0.05$ cal/gram of dry wool, respectively.

The differential heat of moisture sorption, $Q_L$, derived by differentiating Eq. (5) with respect to $\alpha$, as shown by
Eq. (4), is plotted in Fig. 13 by open squares to be compared with the results of the isosteric $Q_L$ presented by open circles for this work for the New Zealand Luster 48's wool and by dots for a previous work for the Australian Merino 60's wool. It is at first pointed out that the calorimetric $Q_L (a = 0)$ is found to be $273 \pm 9$ cal/gram of liquid water with a fairly good agreement with literature values and that $Q_L (a = a_s)$ to have a finite non-zero value of several cal/gram of liquid water. The results of calorimetric $Q_L$ deviate considerably from those of isosteric $Q_L$, i.e., the calorimetric $Q_L$ being greater at low humidity region, but smaller at high humidity region than the isosteric $Q_L$. The same tendency has been found not only viscose rayon and nylon 6 fiber, but also for wool specimens when compared with the isosteric $Q_L$ derived by Miyagawa et al. from the isotherm data by Speakman and Cooper with the calorimetric $Q_L$ by Headge. Nevertheless, general tendency in $Q_L$ decreasing rapidly with increasing relative humidity is fairly similar to each other.

It is interesting from the theoretical viewpoint to compare the heat and the free energy of sorption of moisture by the system, in general. In this connection, the Gibbs-Helmholtz equation may be applied to relate the changes in the total (or internal) energy, in the work content (or free energy) and in the unavailable energy (or entropy) of the system. For the moisture sorption process, we have the Gibbs-Helmholtz equation

$$\Delta G = Q_L - T \Delta S \tag{10}$$

where $\Delta G$ is the decrease in free energy, $Q_L$ is the heat of moisture sorption lost by the system (exothermic), and $\Delta S$ is the change in entropy, when one gram of liquid water is sorbed by an infinite mass of the specimen having a moisture regain of $a$ at the absolute temperature $T$. The decrease in the free energy per gram of liquid water is given by

$$\Delta G = \frac{RT}{M} \ln (\frac{p}{\rho}) \tag{11}$$

The value of $\Delta G$ calculated from the above equation, is plotted against relative humidity ($p/\rho$) also in Fig. 13 at $30^\circ C$ in comparison with the plots of the isosteric and calorimetric $Q_L$. As can be seen in the figure, either isosteric or calorimetric $Q_L$ of the wool-water system is
greater than the $\Delta G$ over the whole range of relative humidity, resulting in a significant conclusion that the term of $T\Delta S$ in Eq. (10), the so-called excess energy, is always negative also over the whole range of relative humidity. The excess energy means the energy necessary to arrange the sorbed water molecules in more ordered state than in liquid state. The excess energy thus evaluated and, consequently, the decrease in entropy $\Delta S$ are plotted against relative humidity on the left- and right-hand side ordinates, respectively, in Fig. 14. The results derived from the isosteric $Q_i$ and the calorimetric $Q_L$ differ considerably, reflecting the difference in the values of $Q_i$ in Fig. 13. However, we prefer the result from the calorimetric $Q_L$, rather than that from the isosteric $Q_i$, because of difficulty of determining $Q_i$ with high accuracy by the isosteric method, especially near dryness and saturation, as fully discussed by Rees for cellulosic materials.

As demonstrated in Fig. 14, the excess energy is largest at near dryness, attaining a value of about 100 cal/gram of liquid water for the result derived from the calorimetric $Q_L$, and decreases at first rather rapidly and then gradually down to a finite value of several cal/gram of liquid water, but not to zero, at saturation. The value of excess energy of about 100 cal/g at near dryness, which is somewhat smaller than for regenerate cellulose and is almost the same as that for nylon 6, is still comparable to the latent heat of fusion of ice and, consequently, to the entropy of fusion of ice. This is simply because at the transition from solid to liquid state, $\Delta G = 0$ and $\Delta H_m = T_m \Delta S_m$.

These facts result in the following conclusions: i) the sorbed water at near dryness is in a very ordered state similar to the crystal lattice of ice; ii) the sorbed water at near saturation is still in a more ordered state than in the liquid state; and iii) the application of B. E. T.'s multilayer adsorption model, based on a long range interaction between adsorbate and adsorbent to the analysis of sorption isotherm of water-wool system, is valid, at least phenomenologically.

ACKNOWLEDGEMENTS

The authors are deeply indebted to Dr. Takashi Kondo, former professor of Gifu University, for his discussion and comments through the course of this study. Test specimens of wool and hair fibers were provided from the Japan Technical Center, International Wool Secretariat. Density measurements and scanning electron microscopy were carried out at the Research Center, Toyo-bo Co. Optical microscopy for evaluating the ortho/para/medulla ratio was performed at the Department of Applied Chemistry, Fukui University and at the Department of Polymer Engineering, Kyoto Institute of Technology. To all of these institutions, the authors are also deeply indebted.

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被服材料と水との相互作用に関する基礎的研究：
第X報、羊毛および軟毛繊維の吸湿性

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高岡 昭、河合弘雄

シープ、ゴート、キャメル、およびラビットに分類される15種の纖維繊維の等温水分収着曲線を、主として秤量職を用いて、30℃において観測した。得られた結果を、Brunauer、Emmett、Teller (B. E. T.) の多分子層吸着式によって解析し、そのパラメータ C (吸着エネルギー値)、v_m (最大単分子層吸着水分率) および n_max (最大多分子層吸着層数) と構造との関連を論じた。

多種にわたる繊維にかかわらず、パラメータの値は相互に類似しており、C は 9.40 ～ 11.7、v_m は 5.74 ～ 7.18%、さらに n_max は 5 ～ 6 の範囲にあった。X 線回折強度分布より Ruland 法によって決定された結晶化度 x_e を用いて、v_m を非晶度 (1 - x_e) の関数としてプロットすると、羊毛繊には原点を通る直線関係が認められ、その完全非晶物での v_m は 9.27%、顕微構造をもつ羊毛類はこの直線より上にプロットされ、さらにスケールの等温収着への影響はほとんどないことが判明した。

特定の羊毛について、その水分収着熱を乾燥状態から飽和水分収着の範囲にわたり、収着水分率の関数として測定し、収着過程の熱力学的考察を行った。羊毛の吸湿性は発熱過程であり、微分収着熱 Q_e (収着水の液相水に比較したエンタルピー差) および過剰エネルギー T&S (収着水の液相水に比較したエントロピー差) を収着水分率の関数として決定し、収着された水分が乾燥状態近傍では極めて高い秩序状態にあり、飽和収着でも液相水に比較してなお高い秩序状態にあることを論じた。