# Sorption of Liquids by Wool. Part II. Determination of Partial Specific Volumes of Wool

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## INTRODUCTION

Sorption of a liquid by wool is usually accompanied by a reduction in the total volume of the system, due to interaction between the two components. In 1926 King[1] suggested two possible methods by which such a volume contraction could occur. Firstly, he postulated compression of the liquid as a result of swelling forces. Although this explanation is incorrect, nevertheless there is a volume contraction due to electrostriction of sorbate molecules around charged groups in the wool[2-6] and possibly for other reasons (see Part III[7]). The second type of interaction simply consists in the filling of empty space or pores in the wool fiber by the sorbate. (The word "pore" is applied to all sorts of porous solids[8,9] and is therefore used here in preference to such terms as empty space, empty volume, and dead space in order to integrate the specialist fields of fibers and proteins with the general field.) It is postulated[10] that these pores are of various sizes and are distributed throughout the fiber as a result of the impossibility of obtaining 100% close packing of polypeptide chains in the protein structure.

The best evidence for the occurrence of pores in dry wool is obtained by measuring its specific volume in a nonpenetrating solvent such as n-hexane or benzene and comparing this value with the theoretical value, calculated by summation of the volume contributions of the amino acid residues.[7] In this way it is found that the pore volume is 0.055 cm.³/g. wool. A related method is to compare the specific volume obtained by measurement in benzene with that found by the use of helium gas. The latter fills only part of the total pore volume, viz. 0.013 cm.³/g. wool.[7,11] Another method is to measure the amount of polymer which can be deposited inside the fiber without causing any swelling.[12] This amounted to about 0.2 g./g. Lincoln wool and <0.07 g./g. Merino wool. However, not much reliance should be placed on these figures because of the inaccurate method of measurement of swelling (as stated by the author[12]) and the very high value obtained for Lincoln wool. Finally, it has been found with soluble pro-

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teins that there are pores which are inaccessible to the sorbate, the volume of which is called the excluded volume.[6,13-15]

In previous work on wool and other fibers it has been customary to express the results in terms of density[16] or apparent density when dealing with a swelling solvent,[1,17] whereas with soluble proteins the results are recorded in terms of partial and apparent specific volume.[4,18] This paper records the partial specific volume of wool and the volume contraction which occurs on sorption of water and various organic liquids by wool. The detailed behavior at saturation is considered in Part III.[7]

## EXPERIMENTAL

### Materials

Merino 64's virgin root wool and various organic liquids were purified as described in Part I.[10] n-Hexane (B.D.H. lab. reagent) was refluxed over sodium and then fractionally distilled. Denatured wool was produced by treatment for 1 hr. at 100°C. in 8$M$ LiBr.

### Specific Volume of Dry Wool

A pycnometer was used which consisted of a test tube with a B24 cone stopper which was fitted with a short, marked capillary tube and small, metal stopper. The volume of the pycnometer (about 50 cm.[3]) was determined by weighing the amount of distilled water it contained at 25°C.

About 1.5 g. of wool, previously immersed in distilled water for 16 hr.[19] and centrifuged to remove excess water, was placed in the pycnometer of weight $w_1$ g. The pycnometer and wool were heated for 1.5 hr. at 100°C. and 10$^{-4}$ mm. Hg pressure and weighed ($w_2$). The bottle was then filled with n-hexane and any air bubbles left in the wool removed with a syringe. Removal of air bubbles by evacuation of the pycnometer prior to filling with n-hexane gave the same results. The pycnometer was placed in a thermostat bath at 25 ± 0.01°C. for 15 min., and then the liquid level was adjusted to the mark in the capillary tube with a syringe. The pycnometer was then removed from the bath, dried with filter paper and weighed ($w_3$). A small correction was necessary at this stage due to diffusion of n-hexane through the B24 joint. Since the penetration of the wool by n-hexane was negligibly small,[10] the specific volume $v_D$ of the dry wool in n-hexane was then calculated by the equation

$$v_D = \frac{(w_4 - w_1) - (w_3 - w_2)}{d_h(w_2 - w_1)},\tag{1}$$

where $w_4$ is the weight of the pycnometer filled with n-hexane and $d_h$ is the density of n-hexane.

### Specific Volume of Wool Containing Sorbate and Volume Contraction on Sorption

**1. Nonpenetrating Liquid such as n-Hexane.** Samples of wool containing known amounts of various organic liquids were obtained after the sorp-

tion experiments,[10] and samples containing water were produced by sorption of water vapor by dry wool. The specific volume of the sorbed samples $v$ was then determined pycnometrically with the use of $n$-hexane as already described for the case of dry wool. The $n$-hexane on the surface of the wool, together with some sorbate, was then removed *in vacuo* and a further determination of $v$ made at a lower value of the per cent sorption. This process was repeated, and a series of values of $v$ obtained over the sorption range. In some cases volume measurements were made on the sample, before removal of surface sorbate by the washing technique,[10] by filling the pycnometer with the sorbate instead of $n$-hexane.

The contraction of volume $v_C$ which accompanies sorption is given by the equation

$v_C$ (cm.$^3$/g. dry wool) = vol. of sorbate (cm.$^3$/g. dry wool) − vol. swelling (cm.$^3$/g. dry wool)

$$= \frac{\text{wt. sorbed wool − wt. dry wool}}{\text{wt. dry wool} \times d_s} - (\text{vol. of wool}$$

containing sorbate/g. dry wool $-v_D$)

where $d_s$ is the density of sorbate at 25°C.

**2. Penetrating (Swelling) Liquid such as Water.** The principle of this method is the same as that used for the determination of the apparent density of fibers in swelling solvents[1,20,21] and partial specific volumes of soluble proteins in aqueous solution.[6,15] The technique is the same as that used in the measurement of the specific volume of dry wool in $n$-hexane, except for the replacement of the latter with a swelling liquid. It can be readily shown from first principles that

$$v_C = v_D - \frac{(w_4 - w_1) - (w_3 - w_2)}{(w_2 - w_1)d_s}, \tag{3}$$

where the $w$ symbols have their previous significance except for the replacement of $n$-hexane by a swelling liquid. When water is used sorption occurs so rapidly that saturation is reached during the time of the experiment. With other liquids, such as ethanol, where sorption is much slower, the value of $v_C$ calculated by eq. (3) agrees closely (as expected) with the figure calculated by eq. (2). In view of the experimental error of about $\pm 0.001$ in the determination of $v$ leading to about $\pm 0.002$ in $v_C$ it was not necessary to make buoyancy corrections.[22]

### Partial Specific Volume

The partial specific volume was determined by the method of intercepts,[23] in which the specific volume of the wool plus sorbate was plotted against the weight fraction of wool present. Figure 1 gives such a graph for the case of water. The partial specific volume $\bar{v}$ of wool at a particular weight fraction is given by the intercept on the left hand ordinate of the tangent
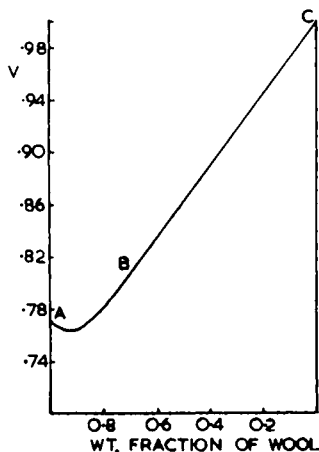
Fig. 1. The specific volume of (wool + water) as a function of weight fraction of wool
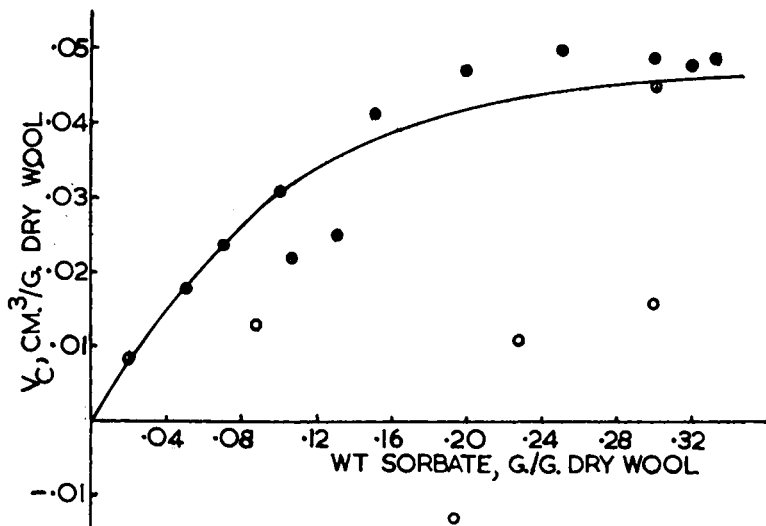


Fig. 2. Volume contraction on absorption (and desorption) of water by (———) virgin wool (full line) with the 35 experimental points omitted for the sake of clarity; (●) virgin wool with the values calculated from Warburton;[24] (⊙) wool supercontracted by LiBr, absorption; (O) wool supercontracted by LiBr, desorption; (◐) wool with an increased equilibrium weight *in vacuo* of 1.95%.[19]

to the curve at that point. The partial specific volume of water is obtained by the intercept on the right hand ordinate of the same tangent. Thus in moving from point $A$ to point $B$ on the graph, $\bar{v}$ for wool decreases from 0.770 to 0.724 and $\bar{v}$ of water increases from 0.62 to 1.0. At $B$ the wool is
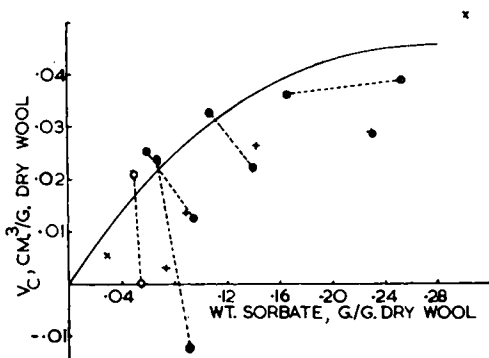
Fig. 3. Volume contraction(———) on absorption (and desorption) of ethanol by virgin wool, with most of the experimental points omitted for the sake of clarity. Results are also given for sorption of ethanol by dry virgin wool for (O) 0.5, (●) 0.75, (◑) 1, and (◐) 2 hr. at 25°C., followed by (- -) rearrangement to a stable state; also for (×) sorption of ethanol by supercontracted wool at 25°C. and (+) desorption of ethanol after sorption at 80°C. for 6 weeks.
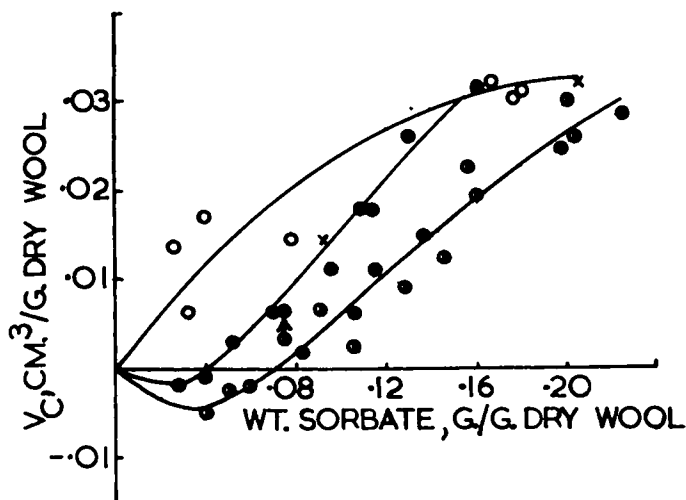


Fig. 4. Volume contraction of wool + n-butanol on (O) absorption of n-butanol at 25°C.; (●) desorption of n-butanol after absorption at 25°C.; (◑) desorption of n-butanol after absorption at 80°C.; (×) desorption of n-butanol after successive absorptions first at 80°C. and then at 25°C.

saturated with water and further addition of water (in moving to point C) occurs without any further interaction between the components, as shown by the constancy of their partial specific volumes and the fact that the value for water is 1.0. Measurements of partial specific volume and apparent

specific volume $\phi$ with soluble proteins are always made in the region $BC$. in which these two quantities are equal.[18]   By definition,

$\phi$ = volume of wool + sorbate/g. dry wool − volume of sorbate/g. dry wool

= $v_D$ + volume of sorbate/g. dry wool − $v_C$ − volume of sorbate/g. dry wool

= $v_D − v_C$.

At saturation $\phi = \bar{v}$, hence $\bar{v} = v_D − v_C$.                           (4)
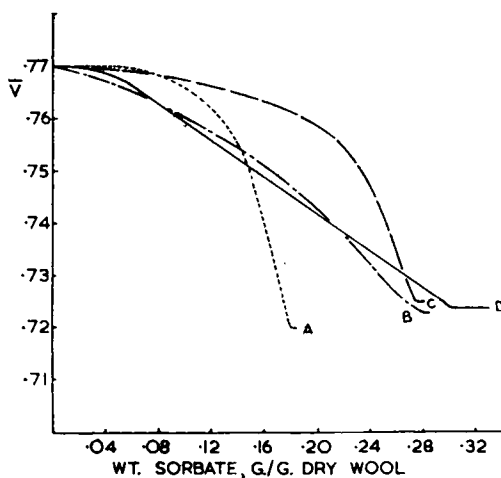


Fig. 5. Partial specific volume of wool $\bar{v}$ on sorption of $(A)$ acetone, (B) ethanol, $(C)$ $n$-propanol, and $(D)$ water.
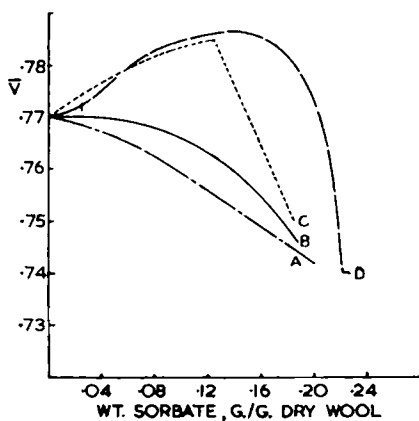


Fig. 6. Partial specific volume of wool $\bar{v}$ on $(A)$ absorption of $n$-butanol at 25°C.; $(B)$ absorption of isopropanol at 25°C.; $(C)$ desorption of $n$-butanol after absorption at 25°C.; and $(D)$ desorption of $n$-butanol after saturation sorption at 80°C.

## RESULTS

Because of the usefulness of both the concepts of volume contraction on sorption and partial specific volume of wool the results are given in terms of either one or both of these forms.   The graph in Figure 2 is constructed from 35 experimental points (which are omitted for the sake of clarity) obtained on absorption and desorption of water by virgin wool.   The results lie very close to the line, irrespective of whether water has been absorbed or desorbed prior to the measurement.   However, with wool supercontracted in LiBr, there is a large difference between the results obtained after absorption and those measured after desorption of water.   This behavior still persists when measurements are made on denatured wool three weeks after desorption has occurred.   The graph is in good agreement with the values calculated from the results of Warburton[24] up to 10% sorption, but deviations are noted above this figure.

In Figure 3 the volume contraction accompanying absorption and desorption of ethanol by virgin wool is given by the full line, most of the individual experimental results being omitted for the sake of clarity.   In this case it was possible to measure $v_C$ during the sorption experiments described in Part I,[10] i.e., 0.5–2 hr. after mixing the dry wool and ethanol.   It is seen from the dotted lines in the figure that the initial values of $v_C$ are in all cases much lower than the values obtained two to four days later, thus indicating that a rearrangement must occur inside the fiber.   Two sorption experiments with supercontracted wool fit the curve with similar precision to the results obtained with virgin wool.   Also included are four points obtained from a sample of wool which was yellowed by immersion in ethanol at 80°C. for 6 weeks, after which values of $v_C$ were obtained by the desorption technique.

In Figure 4 the detailed experimental results are given for $n$-butanol. The deviations of the experimental points from the curves is much greater than that obtained with water.   There appears to be a definite hysteresis between the curves obtained for measurements made after absorption at 25°C. and those made after desorption of $n$-butanol from wool which had previously absorbed $n$-butanol at 25°C.   As with ethanol (Fig. 3), the curve obtained on desorption of $n$-butanol from wool, which had previously absorbed $n$-butanol at 80°C., is displaced laterally from the other desorption curve.   The dotted line with arrow shows the change in $v_C$ when the sample of wool plus $n$-butanol is allowed to stand in dry air for 30 weeks.   It appears that partial rearrangement occurs towards the 25°C. desorption curve.   Complete rearrangement was effected by removing the $n$-butanol (previously absorbed at 80°C.) by immersion in water, drying *in vacuo*, and allowing absorption of $n$-butanol at 25°.   Thus, although absorption of ethanol or $n$-butanol at 80°C. produces irreversible yellowing of the wool, yet the change in sorption characteristics (as shown in Figs. 3 and 4) is reversible.   Figures 5 and 6 show the change in the partial specific volume of wool which accompanies absorption and desorption of various liquids.

## DISCUSSION

In the sorption of 0–2.5% of water by wool it is found that the process is simply one of diffusion involving no appreciable amount of breakdown or rearrangement of the wool structure.[25–27] The activation energy of the so-called first-stage diffusion process decreases from 11 kcal./mole at zero sorption to about 5 kcal./mole at 10% sorption,[26] and that associated with desorption increases from 5 kcal./mole at 5% sorption to 15 kcal./mole at zero sorption.[28] The increased energies of activation at 0–2.5% sorption and the fact that the water sorbed in this region produces no increase in the conductivity of the wool, indicates that the water is bound tightly at specific sites in the wool. Watt et al.[28] have stressed binding to $NH_3^+$ groups.

The initially linear section of Figure 2, up to about 2.5% sorption, shows that the volume contraction accompanying sorption amounts to a constant fraction (36%) of the total sorption. Thus additional dry wool could be added to a sample of wool in this range without any volume contraction. The same conclusion is reached from a consideration of the constancy of $\bar{v}$ in this sorption range (see Fig. 5). It is therefore concluded that in the range of sorption 0–2.5% there are unoccupied sites available, each of which will give the same volume contraction on bonding. In addition, wool which has an increased equilibrium weight *in vacuo*, due to sorption of water which cannot be removed by heating at 100°C. *in vacuo*,[19] also fits the curve in Figure 2. Hence volume measurements cannot distinguish between water bound (in the sorption range 0–2.5%) with various energies of activation or even between this and water which is bound so tightly that it cannot be removed at 100°C. *in vacuo.*

The volume contraction, which amounts to 36% of the total sorption in the region 0–2.5% sorption, is due to electrostriction and/or filling of pores, assuming that volume contraction of sorbate in the neighborhood of non-polar groups is zero.[7] Since the evidence of Watt et al.[25–28] points to attachment at charged sites, it is probable that electrostriction is the major contributor to volume contraction in this range. A simple calculation shows that there are sufficient positively and negatively charged groups on neutral wool to accommodate all the water, viz., 1.1 groups per water molecule at 2.5% sorption. One would expect sorption at these sites to occur with different energies of activation (as observed[26,28]) and with slightly different amounts of electrostriction.[2] However, the latter was not detected, perhaps because of the large experimental errors involved in volume measurements in this sorption range.

In the sorption of ethanol by wool there is an initial small amount of volume contraction during the sorption period (0.5–2 hr.) followed by a subsequent rearrangement of ethanol within the fiber (during the next 48 hr.) leading to an increase in $v_C$. This behavior, shown in Figure 3, has also been observed with *n*-propanol and may occur with water, although the experimental conditions are such that it could not be observed in this case.

This indicates that the charged group on the wool (about which electrostriction of ethanol occurs) and the pores are not immediately accessible to the sorbate.

It is found that the graph of $v_C$ versus weight of sorbate is the same whether the determination of $v_C$ is made after an absorption or desorption step for water, ethanol, n-propanol, isopropanol, and acetone on virgin wool. However, such reversible behavior does not occur for water on wool supercontracted with LiBr (Fig. 2) or for n-butanol on virgin wool. (Fig. 4). Such irreversibility or hysteresis is unlikely to be a rate effect, because there is no appreciable change in density after standing 3 weeks in the case of water or 6 weeks in the case of n butanol. The value of $v_C$ is lower during desorption than absorption and even reaches a negative value, giving rise to a maximum in the curve of $\bar{v}$ versus weight of sorption. It is probable that sorbate is removed without an equivalent contraction of the fibers, until a stage is reached where the swelling is in excess of the volume of sorbate. At this point $v_C$ becomes negative. Removal of the remaining sorbate results in considerable contraction of the fibers.

Sorption of ethanol or n-butanol by virgin wool at 80°C. for 4 weeks or longer produces slight yellowing and leads to desorption curves shown in Figures 3 and 4, displaced to the right from those with virgin wool. However, the unusual volume behavior is partially removed on prolonged standing and completely removed on desorption of the alcohol by immersion in water, after which the sample again behaves like virgin wool (Fig. 4). This is a case of reversible alteration of structure as regards volume behavior, although the yellowing process shows that irreversible chemical changes have occurred. That the latter is a more sensitive measure of change than are volume measurements is not surprising in view of the relatively small decrease of specific volume in n-hexane brought about by irreversible supercontraction in LiBr, viz., 0.770 to 0.766.

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## Synopsis

The partial specific volume of wool in water and various organic liquids is determined pyconometrically over the whole range of concentrations during absorption and desorption. Sorption of water in the range 0–2.5% by weight occurs with a constant volume contraction amounting to 36% of the volume of the liquid sorbed. This is due largely to electrostriction of water molecules sorbed on charged groups in the wool. Ethanol sorbed by wool undergoes a rearrangement within the fiber which increases considerably the volume contraction. Volume measurements performed during absorption and desorption indicate reversible behavior with water, *n*-propanol, isopropanol, and acetone on virgin wool and irreversibility (hysteresis) with *n*-butanol on virgin wool and with water on supercontracted wool.

## Résumé

On détermine par pyconométrie le volume spécifique partiel de la laine dans l'eau et dans différents liquides organiques pour toute la gamme de concentrations pendant l'adsorption et la désorption. L'adsorption de l'eau dans le domaine de 0 à 2,5% en poids se produit avec une contraction constante du volume, s'élevant à 36% du volume du liquide adsorbé. Ceci est en grande partie dû à l'électrostriction des molécules d'eau adsorbées sur les groupes chargés de la laine. L'éthanol adsorbé sur la laine subit un réarrangement dans la fibre qui accroit considérablement la contraction du volume. Les mesures de volume effectuées pendant l'adsorption et la désorption indiquent un comportement réversible avec l'eau, le *n*-propanol, l'isopropanol et l'acétone pour la laine vierge; par contre on constate une irréversibilité (hystérésis) avec le *n*-butanol sur la laine vierge et avec l'eau sur la laine supercontractée.

## Zusammenfassung

Das partielle spezifische Volumen von Wolle in Wasser und verschiedenen organischen Flüssigkeiten wird über den gesamten Konzentrationsbereich während Absorption und Desorption pyknometrisch bestimmt. Sorption von Wasser im Bereich von 0 bis 2,5 Gewichtsprozenten verläuft unter einer konstanten Volumkontraktion von 36% des sorbierten Flüssigkeitsvolumens. Dies ist hauptsächlich auf Elektrostriktion der an

geladene Gruppen der in Wolle sorbierten Wassermoleküle zurückzuführen.    Von Wolle sorbiertes Äthanol erleidet innerhalb der Faser eine Umlagerung, die die Volumskontraktion wesentlich vergrössert.    Während der Adsorption und Desorption durchgeführte Volumsmessungen zeigen bei Wasser, $n$-Propanol, Isopropanol und Azeton auf unbehaldelter Wolle ein reversibles Verhalten, bei $n$-Butanol auf unbehandelter Wolle und bei Wasser auf superkontrahierter Wolle ein irreversibles Verhalten (Hysteresis).