

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Adsorption-Desorption Hysteresis in Polymers

I. C. Watt<sup>a</sup>

<sup>a</sup> CSIRO Division of Textile Physics Ryde, N. S. W., Australia

**To cite this Article** Watt, I. C.(1980) 'Adsorption-Desorption Hysteresis in Polymers', Journal of Macromolecular Science, Part A, 14: 2, 245 — 255

**To link to this Article: DOI:** 10.1080/00222338008066635

**URL:** <http://dx.doi.org/10.1080/00222338008066635>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Adsorption-Desorption Hysteresis in Polymers

I. C. WATT

CSIRO  
Division of Textile Physics  
Ryde, N. S. W. 2112, Australia

### ABSTRACT

Many polymeric substrates which swell on adsorption exhibit sorption hysteresis; the phenomenon is most striking for water sorption by natural polymers and proteins. Some interpretations of hysteresis for swelling systems have invoked the concept that there are more active sites available for association with sorbate during desorption than for adsorption to the same relative pressure. Chemical modification of hydrophilic groups, which markedly alters the amount of water sorbed by keratin, or the filling of possible voids in the substrate has little effect on keratin-water vapor sorption hysteresis. Sorption in swelling systems occurs by a coupled diffusion-relaxation mechanism. It is demonstrated that the occurrence of hysteresis is associated with the stress relaxation of the cohesive forces opposing swelling. Changes in the structural conformation may be considered as the variable which differs between the adsorption and desorption states. The segmental mobility of the macromolecular chains plays a major role in the irreversibility of the sorption isotherm, leading to wide diversity in hysteresis effects in polymers.

## INTRODUCTION

The amount of sorbate in equilibrium with the external vapor, at a particular relative pressure, is frequently higher following desorption from a higher pressure than for adsorption from a lower pressure. The earliest theories of sorption hysteresis were initially applicable to porous solids. Zsigmondy [1] postulated that hysteresis arises from the difference in the contact angle between a liquid and the wall as pores fill or empty. McBain [2] modified this theory by proposing that the pores could be considered as "ink bottles" with narrow necks. For increasing pressure, condensation occurs at a pressure determined by the radius of the pore. However, desorption is controlled by the dimensions of the neck, evaporation is delayed until a lower vapor pressure is reached and hysteresis occurs. The capillary condensation theories are applications of the Kelvin equation for capillary condensation and their application is restricted to high relative pressures.

Everett and Whitton [3] proposed an independent domain model in which hysteresis is attributed to metastable domains which can exist in two different states, depending upon the direction from which the metastable range is approached. This mechanism may apply to nonporous systems where the observed hysteresis could arise as a direct result of changes accompanying swelling. Barkas [4] has suggested that sorption hysteresis is associated with mechanical hysteresis and must occur in any swelling gel which is a plastic material that undergoes permanent distortion on swelling.

The magnitude and mechanism of hysteresis remain the source of considerable disagreement, and the phenomenon is the outstanding problem requiring elucidation in sorption systems. The size and shape of the hysteresis loop vary greatly from substrate to substrate. More importantly, in some systems the nature of the hysteresis loop depends upon the number of sorption cycles and the time allowed for equilibrium to be established. In general, greater hysteresis effects are observed with native substrates, such as cellulose or proteins, with the small polar water molecule as sorbate. Nonpolar gases show no hysteresis or irreversible binding on sorption by proteins [5].

Interpretations of hysteresis in systems where swelling occurs on sorption of water have frequently been based on the assumption that there are more sites available for association with water after desorption has occurred than for adsorption to the same relative humidity. White and Eyring [6] have postulated that the strongly bound water molecules force the molecular chains of polymers apart and the contractive forces are not sufficient to detach water molecules from the swollen structure as the water vapor pressure decreases. Recent studies [7] of the keratin-water vapor sorption system have shown that the extent of hysteresis is dependent on the experimental procedures followed. In this paper a set of experimental conditions

which give rise to hysteresis effects in keratin is employed. The influence on hysteresis of the geometrical form and chemical modifications of the keratin are considered. Comparisons are drawn with other polymer-penetrant systems, and a model for the origin of sorption hysteresis with general applicability to swelling systems is proposed.

## EXPERIMENTAL

Keratin, in the form of Merino wool fibers and horsehair was degreased with cold petroleum ether and washed with distilled water. Chemical modifications and analyses of wool from this source were carried out as outlined in a previous publication [8] which fully references the original studies. Nylon 66 (MW = 35,000) in the form of undrawn fibers, rhinoceros horn shavings, cotton, and jute fibers were thoroughly washed in distilled water. The collagen sample was a tendon removed from a rat tail and stored in Ringer's solution prior to the sorption studies.

Sorption isotherms were determined by a gravimetric technique in which 10 mg samples were suspended from a calibrated quartz helical spring balance mounted in an evacuable sorption chamber. The chamber was connected to a wide-bore differential mercury manometer and a reservoir in which water vapor from previously degassed liquid water was stored. Water vapor was admitted to, or evacuated from, the chamber as required. The entire system was located in an air thermostat and the temperature controlled to  $\pm 0.01^\circ\text{C}$ . The spring sensitivity was 500 cm/g, and the extension was read to 0.01 mm from a cathetometer, enabling changes of 0.02% water content to be monitored.

## RESULTS AND DISCUSSION

### Validity of Hysteresis Values

The size and shape of the sorption hysteresis loop for a particular substrate are determined by the experimental procedure adopted. For wool keratin [9] and cellulose [10] the width of the hysteresis loop can be increased by drying the material from a water content below saturation. This operation decreases the affinity for water with increasing temperature of drying and lowers the adsorption limb of an isotherm measured subsequently. The normal affinity of the substrate for water is restored by saturation and the desorption limb determined after saturation is not lowered correspondingly. On the other hand, if the same materials are allowed to condition for long periods at intermediate humidities, subsequent determinations

of water content are higher and the position of the adsorption limb is raised [ 11].

A possible source of the considerable variation in the position of the water vapor desorption isotherm for wool fibers has recently been demonstrated [ 7]. Desorption values of water content are strongly dependent upon the packing density of the wool samples and smaller hysteresis values are achieved by desorption from saturation by large steps. The initial rate of desorption becomes greater as the packing density decreases and is further increased for the larger desorption steps. It was concluded that the rapidity with which the water content changes is important, and for a large desorption step sorption hysteresis can be eliminated. Under these conditions desorption from an intermediate humidity yields a higher value of water content than desorption from saturation. Hence, both the shape and the magnitude of the hysteresis loop may be quite diverse for a particular sorption system.

There are additional reasons, related to the preparation of the sample, for the discrepancies between literature values of the hysteresis effect. One problem has been the most suitable value to adopt as the sample weight at zero humidity, as the "dry weight" of many polymers changes with temperature. Bull [ 12] found that the loss of water from proteins as the temperature increased graded directly into protein decomposition and chose drying at 105°C as a compromise. Since the equilibrium weight of wool at zero humidity decreases by 0.4% over the temperature range of 20-105°C [ 13], the initial weight of a wool sample determined at an elevated temperature is lower than the weight reached on desorption at a lower temperature; i. e., there is not a closed loop to the adsorption-desorption cycle and the apparent hysteresis values are correspondingly enhanced.

If we accept that measured isotherms are a function of the experimental conditions employed, observed hysteresis is a permanent effect for a particular set of conditions. Careful experimental determinations [ 14] have shown that after many months the adsorption and desorption curves asymptotically approach quite different values which constitute the boundary lines of the permanent hysteresis effect. Consequently, it appears that the external independent variables are insufficient to define the state of the system uniquely and there is at least one additional variable which has to be defined in order to fully characterize or predict the future behavior of the material.

### Origin of Sorption Hysteresis

The sorption of water by wool exhibits non-Fickian kinetics; it is characterized by an inflection in the uptake curve as a function of  $(\text{time})^{1/2}$ , and the initial rate of desorption is faster than the initial rate of adsorption. However, after equilibration at an intermediate

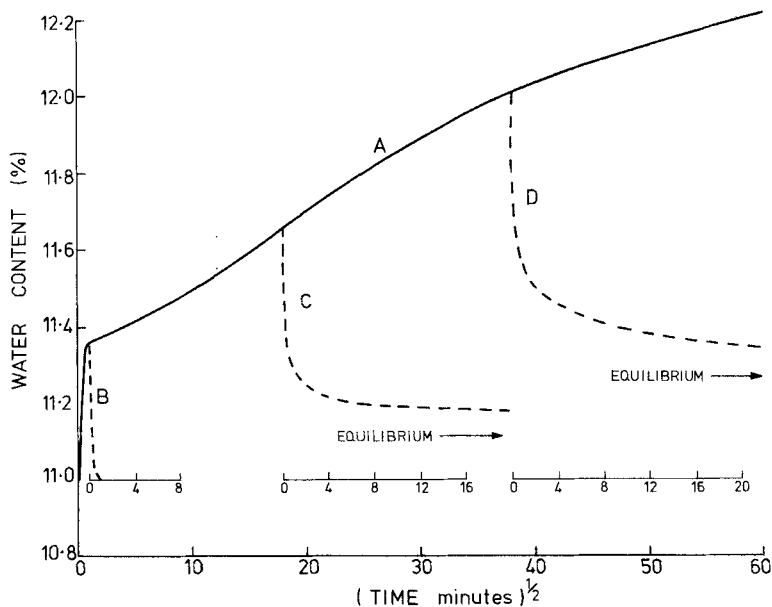


FIG. 1. Interval adsorption and desorption for Merino wool-water vapor at 35°C: (A) two-stage adsorption following a vapor pressure increment from 48.3% RH to 55.4% RH; (B) desorption from the quasi-equilibrium following a return to the initial vapor pressure; (C) desorption after time  $t^{1/2} = 18 \text{ min}^{1/2}$ ; (D) desorption after time  $t^{1/2} = 38 \text{ min}^{1/2}$ .

humidity and a small increase in the concentration of water vapor, adsorption occurs in two distinct stages. The initial uptake to a quasi-equilibrium is quite rapid, and is characteristic of Fickian diffusion with a concentration-dependent diffusion coefficient. Further adsorption proceeds by a much slower second stage of uptake which cannot be characterized by any generalized form of Fick's equation. This second-stage sorption results from a slow rearrangement of interchain bonds, brought about by the swelling of the substrate during the first-stage uptake, and is most marked around 50% RH.

Adsorption-desorption kinetics obtained for the wool used in this study are illustrated by Fig. 1. Curve A represents a typical adsorption step after equilibration at an intermediate humidity. If the adsorption is interrupted and the concentration of water vapor reduced to the initial value just as the quasi-equilibrium is reached, desorption occurs at the same rate as adsorption and the water content returns to the original value (curve B of Fig. 1). On the other hand, if final equilibrium has been established or some second-stage uptake has

occurred before returning the water vapor concentration to its initial value, desorption is initially faster than the initial rate of first-stage adsorption, but becomes progressively slower. The change of water content with time becomes negligible without returning to its initial value (curves C and D of Fig. 1). That is, desorption from the quasi-equilibrium shows no hysteresis, but desorption after some second-stage uptake has occurred displays a "permanent" change of water content which is greater the longer the length of second-stage adsorption.

The second stage of two-stage adsorption is considered to occur as a result of the breakdown of interchain bonds in glassy-type polymers, allowing additional swelling of the structure and entry of penetrant to maintain thermodynamic equilibrium with the environment [16]. The rate of uptake is increased as a result of greater uptake in the first stage and for humidity steps in excess of 15% RH the two stages are indistinguishable. Adsorption is described by a single uptake curve which appears to result from a coupled diffusion-relaxation mechanism in which the stress relaxation occurs concurrently with diffusion. Hence, stress relaxation is an integral part of adsorption in swelling conditions, but the special case of small step adsorption allows a more detailed study of this parameter.

### Effect of Chemical Modifications

The hysteresis effects for chemically modified wools were compared to that observed for Merino wool from the same source for identical adsorption-desorption cycles at 35°C. The magnitude of the hysteresis effect was determined at 50% RH. Adsorption to 50% RH was achieved in less than a day and desorption from saturation was carried out in a single step. The water content values, together with the saturation water content, which gives a quantitative measure of the swelling attained, are tabulated in Table 1.

The deamination and methylation treatments remove or modify the most strongly hydrophilic groups in wool, and the reduction of water content is indicative of this effect. The high saturation water content following methylation is an indication that considerable peptide hydrolysis has occurred in addition to the specific modification of the carboxylic groups. The effect of rupturing covalent bonds in this manner is illustrated by the sample modified by controlled peptide hydrolysis. Deposition of polyacrylonitrile (PAN) and addition of ninhydrin reduce the saturation water content and increase the internal viscosity of wool and would be expected to fill any voids. The striking feature of the results is that the hysteresis effect is unaltered by any of these modifications—decrease in water content, greater maximum swelling, or internal deposition of additives—suggesting that the effect is related to the properties of the main chains of the substrate.

The presence of pores within a substrate is sufficient to cause

TABLE 1. Adsorption and Desorption Water Contents of Wool

Substrate	Equilibrium water content (%)		
	50% RH adsorption	50% RH desorption	100% RH
Unmodified Merino Wool	11.3	12.3	34.2
Deaminated wool (88%)	8.7	9.7	28.4
Methylated wool (79%)	9.0	10.0	46.0
Peptide hydrolysis	11.2	12.2	45.0
Wool + 54.2% PAN	11.6	12.5	29.0
Wool + 14.3% ninhydrin	11.1	12.1	29.2

hysteresis but, in general, the phenomenon is limited to humidities higher than 50% RH. Hysteresis will not occur in pores of diameter less than four molecular diameters of the adsorbate, and, below 50% RH, any pores being filled would fall into this category. A stoichiometric analysis of protein-water isotherms reveals that at least up to 50% RH the water uptake can be fully accounted for by association of water with specific sites in the proteins [ 16 ].

Modification of wool by the internal deposition of polymer or the inclusion of an additive such as ninhydrin might be expected to change the nature of voids existing in the wool structure. Neither of these treatments has any effect on the hysteresis loop of the modified wool. Also, the greater uptake of water at saturation following the rupture of covalent bonds, which could create larger pores, does not affect the hysteresis loop. Consequently, in the absence of direct evidence for the presence of voids in wool, or any effects due to voids, there appears to be no support for the concept of hysteresis depending on capillary condensation. There is no direct evidence to support the suggestion that hysteresis arises because some sites become available for adsorption only in the highly swollen state and that these sites continue to bind water molecules as the water vapor pressure is lowered. Failure of deamination and methylation of wool to change the observed hysteresis shows that the most strongly hydrophilic groups in wool do not participate in such a mechanism. Peptide hydrolysis lowers the constraints to swelling and allows greater water uptake at high humidities, without any change in the sorptivity of the sample at intermediate humidities. The unchanged hysteresis following this treatment indicates that covalent bonding plays no part in determining hysteresis.



TABLE 2. Sorption Hysteresis in Polymers

Substrate	Equilibrium water content (%)		
	50% RH adsorption	50% RH desorption	100% RH
Horsehair	10.9	12.3	32.8
Rhinoceros horn	11.4	13.3	49.0
Rat tail tendon	16.3	17.2	> 150
Cotton	6.3	7.1	22.9
Jute	9.2	9.9	38.8
Nylon 66	3.4	3.4	11.5

### Hysteresis Effects in Different Polymers

The hysteresis effects associated with the adsorption-desorption isotherms were determined for a range of substrates under the same experimental conditions as applied to the Merino wool. The results are summarized in Table 2 for the keratins horsehair and rhinoceros horn, the fibrous protein collagen, the celluloses cotton and jute, and the polyamide nylon 66.

The substitution of a horsehair fiber of diameter 170  $\mu\text{m}$  increases the magnitude of the hysteresis effect compared to that for Merino wool fibers of diameter 20  $\mu\text{m}$ . Desorption from the horsehair occurs more slowly than from the wool because of the greater fiber diameter. The rat tail tendon, with a diameter of 210  $\mu\text{m}$  but composed of collagen, displays a reduced hysteresis. This emphasizes that not only the geometry of the sample and the conditions of desorption but the rate at which sorption stresses relax in a particular substrate need to be known in order to predict the magnitude of sorption hysteresis. The rhinoceros horn sample exhibits a greater hysteresis effect; with this keratin the rate of desorption is slowed because the shavings cannot be widely separated on the supporting pan. The hysteresis value is of the same order as values frequently reported for keratin.

The rate of desorption from a bundle of fibers is not directly related to the individual fiber diameter because of a temperature interaction between the fibers; the rate of desorption from the cotton, jute, and nylon samples does not vary greatly. The difference in the adsorption and desorption water contents is a property of the polymer for the particular sorption conditions. It is notable that nylon does not exhibit a hysteresis effect.

Hysteresis Related to Stress Relaxation

Barkas [4] has proposed that swelling gels exhibit hysteresis because the swelling pressure of the gel resists adsorption. He suggests that if the material is plastic and desorption is started from a stage on the adsorption route where the swelling is sufficient to break interchain bonds, hysteresis will result. The level of swelling at saturation where the structure is strongly disrupted does not determine the amount of hysteresis. The present data demonstrate that breaking of interchain bonds at saturation does not give rise to hysteresis, without stress relaxation at intermediate humidities. The breaking and re-formation of interchain bonds leading to a different structural conformation requires a level of swelling greater than that given by adsorption at the humidity of measurement. There is not a sufficient impetus to regain the original conformation until the swelling stress is further reduced below the level represented by the initial adsorption value. Thus, changes in the structural conformation may be considered as an independent variable giving rise to the metastability of the sorption system as represented by the Everett and Whitton [8], independent domain theory. However, the concept of domains is difficult to test experimentally.

The contrast in hysteresis behavior between the natural polypeptides keratin and collagen and the polyamide nylon is striking. A parallel contrast exists between the strong sorption hysteresis exhibited by the native celluloses and the lack of hysteresis with the linear hydroxylic polymer, poly(vinyl alcohol) [17]. It appears that the segmental mobility of the molecular chains is greater for the chemical polymers than for the natural polymers. Considerable swelling of the chemical polymers occurs on adsorption and, in fact, poly(vinyl alcohol) is soluble unless crosslinks are introduced into the structure. However, changes in conformation may take place sufficiently rapidly to ensure that the dynamic equilibrium of disruption and re-formation of interchain bonds depends only on the amount of sorbate present and is independent of the previous sorption history. On the other hand, polyester fibers, which sorb less water vapor than either nylon or poly(vinyl alcohol), exhibit a permanent hysteresis [18].

At intermediate humidities, where the degree of hysteresis in the keratin-water vapor system is greatest, the sorbed water is predominantly associated with peptide groups. It is reasonable to suppose that hysteresis water is associated with specific sites, as the heat of wetting of keratin is a function of its water content, irrespective of the sorption path. However, it is unlikely that additional groups are exposed by the swelling but, at a particular instant, more sites are occupied to maintain thermodynamic equilibrium between the vapor and the changed conformation of the substrate. This conclusion is supported by the fact that similar chemical groupings exist in nylon and do not lead to hysteresis.

As the structure of the substrate is a determinant factor in sorption hysteresis, similar hysteresis effects are observed with other sorbates which can swell keratin, e. g., ethyl alcohol. However, for a molecule of this size, sorption rates are reduced and the time to approach equilibrium may become inordinately long. At low relative pressures it becomes necessary to swell the keratin with water vapor or to raise the temperature in order to allow ethyl alcohol to diffuse out of the structure. Consequently, the observed hysteresis effects with large sorbate molecules in the low relative pressure region may be attributable to a slow approach to equilibrium.

In most polymer systems which exhibit hysteresis, the amount of hysteresis decreases markedly with an increase in temperature. The changes are too large to be attributed to the lower uptakes at the higher temperatures. Undoubtedly, part of the decrease in hysteresis is due to the more rapid sorption of vapor with increasing temperature, but it is probable that the major cause is the increased mobility of the molecular chains. From the nature of the hysteresis effects in swelling polymers, it can be concluded that the cohesive interchain forces are controlling factors in determining the ability of polymers to follow environmental changes.

#### REFERENCES

- [1] A. Zsigmondy, Allgem. Anorg. Chem., **71**, 356 (1911).
- [2] J. W. McBain, J. Am. Chem. Soc., **57**, 699 (1935).
- [3] D. H. Everett and W. I. Whitton, Trans. Faraday Soc., **48**, 749 (1952).
- [4] W. W. Barkas, Trans. Faraday Soc., **38**, 194 (1942).
- [5] S. W. Benson and J. M. Seehof, J. Am. Chem. Soc., **73**, 5053 (1951).
- [6] H. J. White and H. Eyring, Text. Res. J., **17**, 523 (1947).
- [7] I. C. Watt and R. L. D'Arcy, J. Polym. Sci. Polym. Symp. Ed., **55**, 155 (1976).
- [8] I. C. Watt and J. D. Leeder, Trans. Faraday Soc., **60**, 1335 (1964).
- [9] J. B. Speakman and J. Stott, J. Text. Inst., **27**, T186 (1936).
- [10] E. Hubert, A. Matthew, and K. Weisbred, Kolloid-Z., **98**, 173 (1942).
- [11] A. G. Scroggie, H. A. Mereness, W. P. Cooper, and J. S. Crary, Text. Res. J., **32**, 923 (1962).
- [12] H. B. Bull, J. Am. Chem. Soc., **66**, 1499 (1944).
- [13] I. C. Watt, R. H. Kennett, and J. F. P. James, Text. Res. J., **29**, 975 (1959).
- [14] J. Chabert, Bull. Inst. Text. France, **20**, 553 (1966).
- [15] I. C. Watt, Text. Res. J., **30**, 443 (1960).
- [16] J. D. Leeder and I. C. Watt, J. Colloid Interface Sci., **48**, 339 (1974).

- [ 17 ] J. B. Taylor, J. Text. Inst., 43, T489 (1952).
- [ 18 ] J. Chabert, J. Diemunsch, A. Banderet, and J. Meybeck, J. Text. Inst., 57, T158 (1966).