

## Wettability and the Hysteresis Effect in the Sorption of Water Vapor by Wood\*

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### Summary

The hysteresis effect in the adsorption and desorption of water vapor by wood has been variously explained as a consequence of differences in (1) the availability of bonding sites for sorption on molecular surfaces, (2) the degree of aggregation of a swelling or shrinking cellulosic gel system, and (3) the wettability of submicroscopic capillaries within the cell wall.

The wettability hysteresis of 28 tropical woods, calculated as the ratio of cosines of advancing and receding contact angles made by water, has been determined by the inclined plate method.

For 13 of these species the availability of complete sorption isotherms permitted analysis by means of the HAILWOOD-HORROBIN model to differentiate between monomolecular and polymolecular sorbed moisture. In the upper range of relative humidities, total sorption hysteresis is primarily the result of hysteresis in polymolecular sorption.

Positive relationships found in this study between polymolecular sorption hysteresis and wettability hysteresis are consistent with the KELVIN equation with respect to the effect of varying contact angle and give at least partial support to ZSIGMONDY'S explanation of hysteresis as a phenomenon of capillary condensation.

Total sorption hysteresis for all 28 species in the upper range of relative humidities was also positively correlated with wettability hysteresis due to the predominant effect of polymolecular sorption hysteresis. It may be concluded that in the range of relative humidity above 60 percent, hysteresis shown by typical sigmoid isotherms is to a considerable degree a phenomenon of capillary condensation explainable by the KELVIN equation in its complete form including cosine of contact angle.

### Zusammenfassung

Die Hysterese bei Adsorption und Desorption von Wasserdampf in Holz wird in der Regel als Folge von Unterschieden bei 1. der Zugänglichkeit von Bindungsstellen für die Sorption an molekulare Schichten, 2. des Aggregatzustandes eines quellenden oder schwindenden Cellulose-Gel-Systems und 3. der Benetzbarkeit der submikroskopischen Kapillaren innerhalb der Zellwand erklärt. Die Benetzbarkeits-Hysterese bei 28 tropischen Holzarten wurde durch das Verfahren mit geneigter Ebene bestimmt durch die Berechnung des Verhältnisses der cos-Werte des vorderen und hinteren Kontaktwinkels von Wasser.

Bei 13 der geprüften Holzarten erlaubte das Vorhandensein der vollständigen Sorptionsisothermen eine Analyse mit Hilfe des Hailwood-Horrobin-Modells zur Unterscheidung zwischen monomolekular und polymolekular sorbierter Feuchtigkeit. In den höheren Bereichen der relativen Feuchtigkeit ist die Gesamtsorptionshysterese vorwiegend das Ergebnis der polymolekularen Sorption.

Die in dieser Untersuchung gefundenen positiven Zusammenhänge zwischen der Hysterese der polymolekularen Sorption und der Benetzungshysterese stehen in Übereinstimmung mit der KELVINschen Gleichung hinsichtlich des Einflusses des variierenden Kontaktwinkels und sie unterstützen, zumindest teilweise, die Theorie von ZSIGMONDY über die Hysterese als einer Erscheinung der Kapillar-Kondensation.

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Im oberen Bereich der relativen Feuchtigkeiten korrelierte die Gesamt-Sorptionshysterese für alle 28 Holzarten ebenfalls positiv mit der Benetzungshysterese infolge des überwiegenden Einflusses der polymolekularen Sorptionshysterese. Hieraus kann geschlossen werden, daß im Bereich der relativen Feuchtigkeit über 60% die Hysterese, die sich in einem typischen S-förmigen Verlauf der Sorptionsisothermen zeigt, zu einem wesentlichen Grade eine Erscheinung der Kapillarkondensation ist und durch die gesamte KELVIN-Gleichung, einschließlich des  $\cos$ -Kontaktwinkels, erklärt werden kann.

### Introduction

Sorption phenomena in wood and other cellulosic materials have been investigated for more than 150 years and concepts of the mechanisms of sorption by wood and cellulose have been developed through numerous studies. These concepts have been reviewed in several reference works [BROWN et al. 1952; BROWNING 1963; KAJITA 1961; KOLLMANN 1951; STAMM 1964] and were briefly summarized in a recent paper by WANGAARD and GRANADOS [1967]. It is well known that the sigmoid isotherms relating equilibrium moisture content of wood to relative vapor pressure differ depending upon whether moisture is being adsorbed or desorbed. This phenomenon known as sorption hysteresis has been widely studied and is commonly attributed to the reduced availability of bonding sites on cellulosic molecular surfaces during adsorption as proposed by URQUHART [1929].

SPALT [1958] has noted, however, that total hysteresis over the range from 0 . . . 100 percent relative humidity is predominantly influenced by the hysteresis shown in polymolecular rather than surface layer sorption. His explanation, basically similar to that of BARKAS [1942], attributes hysteresis to the aggregation of the cellulosic gel upon the removal of water and to the retention of a part of this aggregated condition on subsequent readsorption leading to equilibrium at a lower level of moisture content than was the case during desorption from a relatively dispersed state.

A still different explanation of hysteresis has been offered by ZSIGMONDY et al. [1912] based on the behavior of silica gel during desorption and adsorption of water vapor. He explained the hysteresis loop that he observed in terms of the difference in the amount of water that condenses in the fine capillary structure of a porous material undergoing desorption or adsorption. In desorption the capillary wall is already wet and the contact angle made by the receding meniscus at the water surface is smaller than that of a meniscus advancing on a drier capillary wall in adsorption. The radius of curvature of the receding meniscus is consequently smaller than that of the advancing meniscus in a capillary of the same size, and the vapor pressure over the meniscus will be reduced more in desorption than in adsorption. As a result of this difference in vapor pressure, condensation will occur and the capillary will be filled with water at a lower relative humidity in desorption than in adsorption.

ZSIGMONDY's explanation of hysteresis is thus dependent on a difference in wettability under desorption and adsorption conditions. When a liquid drop attaches to a solid surface, as shown in Fig. 1, the angle  $\theta$  is called contact angle. This angle is an indicator of the affinity of liquid for the solid. The angle  $\theta$  is known as advancing or receding contact angle dependent on whether the liquid is advancing over a dry surface or receding from a wetted surface. This contact angle hysteresis has long been recognized and is explained in terms of the difference between the surface of a dry solid and a surface partially covered with an adhering

film of the wetting liquid. The smaller receding angle of contact is attributed to improved contact between the liquid and the solid with an accompanying increase in the work of adhesion and may reflect nothing more than the removal of an air film from the solid surface [ADAM 1938].

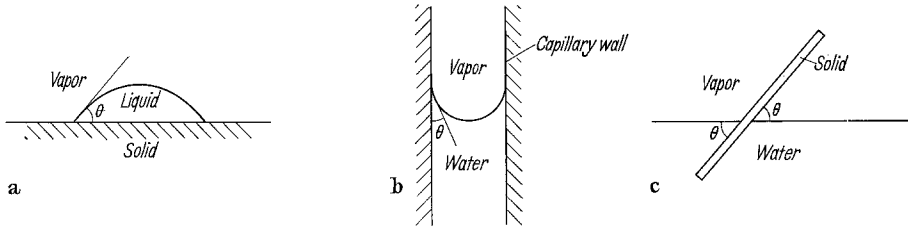


Fig. 1. Contact angle  $\theta$  of liquid on solid: a measure of wettability. a) Angle formed by a liquid drop on a solid surface. b) Angle formed by a meniscus in a capillary. c) Measurement of contact angle by the inclined plate method.

STAMM [1964] has rejected this explanation for the sorption hysteresis of swelling gels such as cellulose and wood on the ground that wetting angle is meaningless due to the lack of solid-vapor interfaces in a capillary system consisting almost completely of solid-solid and solid-liquid-solid interfaces. As noted previously by WANGAARD and GRANADOS [1967] other evidence [WEICHERT 1963] suggests, however, the presence at high relative humidities of a substantial volume of voids to support the concept of capillary condensation.

Both the adsorption and desorption isotherms of wood exhibit slopes of increasing steepness in the range between a relative vapor pressure of 0.60 and the saturation pressure. The equilibrium moisture content of wood increases at a faster rate with an increase in relative vapor pressure. In the upper range of relative humidities, the water adsorbed in wood is basically different than that in the lower range of relative humidities. At lower humidities moisture in wood exists predominantly in a monomolecular layer on the internal surfaces of the cell wall whereas at higher humidities water is adsorbed as polymolecular water and, at least in part, by a process of capillary condensation.

The Kelvin equation has been widely used to account for capillary condensation through the reduction in vapor pressure that occurs in small capillaries and has been cited extensively as the basis for capillary condensation in cellulosic materials [BROWN et al. 1952; KAJITA 1961; KOLLMANN 1951; STAMM 1964]. As represented by BROWNING [1963] the KELVIN equation describes the reduced vapor pressure in a capillary as a function of capillary size and the relationship is expressed in the following form<sup>1</sup>:

$$\ln (p_0/p) = \frac{2V\gamma \cos \theta}{rRT} \quad (1)$$

where  $p$  is the vapor pressure at any equilibrium moisture content and  $p_0$  is the vapor pressure at saturation;  $V$  is the molar volume of the liquid adsorbate;  $\gamma$  is the surface tension of the normal liquid adsorbate;  $\theta$  is the contact angle;  $r$  is the capillary radius;  $R$  is the gas constant; and  $T$  is the absolute temperature.

<sup>1</sup> Most authors presenting this equation assume a contact angle of 0 degrees and cosine  $\theta = 1$ . Due to typographical error in BROWNING [1963] the left hand side of the equation appears as  $\ln (p/p_0)$ .

At any specified equilibrium moisture content the capillary system in wood may be considered constant. In calculating the relative humidity at which condensation will occur in the capillary system at constant temperature, the terms  $V$ ,  $\gamma$ ,  $R$ , and  $T$  will also be constant so that the KELVIN equation can be simplified to  $\ln(p_0/p) = k \cos \theta$ . In the case of adsorption,  $\theta$  is the advancing contact angle, whereas in desorption it is the receding contact angle. From this it follows that

$$\frac{\text{adsorbing } \ln(p_0/p)}{\text{desorbing } \ln p_0/p} = \frac{\text{advancing } \cos \theta}{\text{receding } \cos \theta} \quad (2)$$

In this study, the wettability hysteresis of a number of tropical woods, determined from advancing and receding contact angles, has been investigated with a view toward establishing a possible relationship between wettability hysteresis and sorption hysteresis in the upper range of relative humidities.

### Experimental Procedure

The 28 species used in this study are listed in Table 1.

Table 1. *Advancing and Receding Contact Angles (shown as  $\cos \theta$ ) and Wettability Hysteresis Ratios for 28 Species*

	Contact angle		Hysteresis ratio in wettability $\frac{\text{Adv. } \cos \theta}{\text{Rec. } \cos \theta}$
	$\cos \theta$ Advancing	$\cos \theta$ Receding	
Cupiuba ( <i>Goupia glabra</i> )	0.5225	0.9250	0.5649
Copaia ( <i>Jacaranda copaia</i> )	0.4720	0.7470	0.6319
Manwood ( <i>Minguartia guianensis</i> )	0.6539	0.9528	0.6862
Tauary ( <i>Couratari pulchra</i> )	0.6841	0.9051	0.7559
Ceiba ( <i>Ceiba pentandra</i> )	0.5015	0.6494	0.7722
Santa Maria ( <i>Calophyllum brasiliensis</i> )	0.7392	0.9216	0.8021
Mora Amarilla ( <i>Chlorophora tinctoria</i> )	0.7951	0.9868	0.8058
Kaneelhart ( <i>Licaria cayennensis</i> )	0.4669	0.5736	0.8140
Angeliqne ( <i>Dicorynia paraensis</i> )	0.7509	0.9126	0.8230
Primavera ( <i>Tabebuia Donnell-Smithii</i> )	0.6406	0.7660	0.8362
Sangre ( <i>Pterocarpus vernalis</i> )	0.8166	0.9596	0.8510
Mahogany ( <i>Swietenia macrophylla</i> )	0.6713	0.7880	0.8519
Teak ( <i>Tectona grandis</i> )	0.3611	0.4014	0.8995
Cedro Granadino ( <i>Cedrela Tonduzii</i> )	0.6604	0.8975	0.7358
Manbarklak ( <i>Eschweilera subglandulosa</i> )	0.3773	0.5053	0.7471
Quillo Sisa ( <i>Vochysia lanceolata</i> )	0.6428	0.8339	0.7708
Bannia ( <i>Swartzia bannia</i> )	0.6450	0.8307	0.7765
Angelim ( <i>Hymenolobium excelsum</i> )	0.5175	0.6614	0.7824
Gronfoeloe ( <i>Qualea albiflora</i> )	0.7274	0.9205	0.7902
Almendo ( <i>Coumarouna oleifera</i> )	0.3201	0.4041	0.7921
Mora ( <i>Mora excelsa</i> )	0.5125	0.6406	0.8001
Black Kakeralli ( <i>Eschweilera Sagotiana</i> )	0.6777	0.8371	0.8096
Banak ( <i>Virola surinamensis</i> )	0.7431	0.9075	0.8189
Guayabo Amarilla ( <i>Terminalia guyanensis</i> )	0.7092	0.8488	0.8355
Acapu ( <i>Vouacarpoua americana</i> )	0.1750	0.2051	0.8509
Purpleheart ( <i>Peltogyne venosa</i> )	0.6018	0.6799	0.8852
Parinari ( <i>Parinari Rodolphi</i> )	0.7698	0.8602	0.8949
Quaruba ( <i>Vochysia hondurensis</i> )	0.8732	0.9387	0.9302

### Wettability Measurement

Wettability was expressed as cosine of the contact angle of water on wood. All materials used in this study were sawn from a stock of air-dry lumber. Tangen-

tial specimens  $\frac{1}{2} \times 2$  in. in cross section and 6 in. long were used for the measurement of advancing and receding contact angles by means of the inclined plate method [ADAM 1938; ADAM et al. 1925]. All test specimens were heartwood free from defect.

An apparatus designed to meet all requirements of contact angle measurement [FOWKES et al. 1940] is shown in Fig. 2 and represents a refinement of that used previously in this laboratory by FREEMAN [1959]. It is composed of a supporting stand on a level base with a clamp holding the test specimen that can be easily rotated and set at any angle with a liquid surface; the specimen can also be raised or lowered by rack and pinion. A pointer fixed to the shaft of the specimen clamp permits the angle of the specimen to be read from a protractor scale. Distilled water, conditioned to room temperature, is contained in a glass vessel coated with a paraffin on its inside surface and on the brim. Before each test this vessel was filled to the brim with water and overflowed to assure a water surface free from contamination.

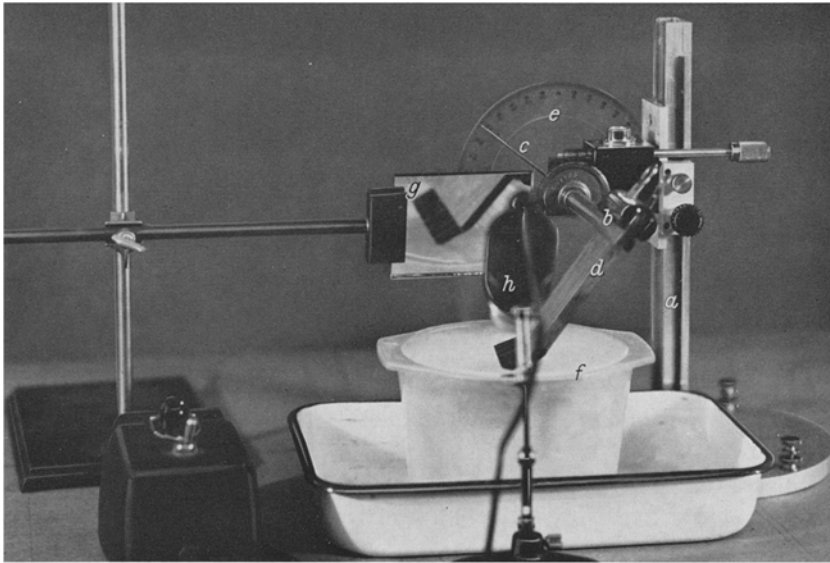


Fig. 2. Apparatus for measurement of contact angle. *a* Supporting stand *b* Specimen clamp *c* Pointer *d* Specimen *e* Protractor *f* Glass vessel *g* Mirror *h* Slit light.

Initially, flat-grain sticks 30 in. in length were conditioned to equilibrium moisture content in a constant humidity room maintained at 73° F. and 50 percent relative humidity. The surface of each stick was smoothly machine-planed one hour before measurement of contact angle to avoid surface contamination. Immediately following machining, the 6-in. test specimen was cut from the stick and end-coated with a thin layer of paraffin.

The specimen was lowered at an angle into the distilled water until immersed about 1 in. at the lower end. The beam from a slit light source was directed at the wood-water contact surface and its reflection observed in a mirror. Bending of the reflected slit indicated that the water surface was not plane where it made contact with the wood and the specimen was then rotated and lowered slightly deeper into

the water. This adjustment was repeated until the reflection of the slit of light was straight indicating that the water surface was plane at the point where it met the dry wood surface. Advancing contact angle was then read from the protractor.

Advancing contact angle was measured five times for each specimen, each time at a previously unwetted surface. Following this the specimen was lowered until it was almost completely immersed in water. It was then successively raised and measured five times to obtain receding contact angle by the same technique. One measurement of contact angle required approximately one minute.

Advancing and receding contact angles for a species were measured from one specimen. All measurements were done in the same room in which the specimens had been conditioned. Equilibrium moisture content was determined from a small specimen cut from the same stick.

The average value obtained from five measurements was recorded as advancing or receding contact angle, and the hysteresis ratio in wettability was calculated for each species as shown in Table 1.

#### Determination of Hysteresis in Water-Vapor Sorption

Sorption isotherms for the first 13 species listed in Table 1, determined by means of a vacuum-sorption apparatus at 90° F., were available from previous work in this laboratory [SPALT 1958; WANGAARD et al. 1967] in the form of constants derived from the HAILWOOD and HORROBIN model [1946].

This model yields the following equation for the water-vapor sorption isotherm:

$$\frac{Mu}{1800} = \frac{\alpha h}{1 - \alpha h} + \frac{\alpha \beta h}{1 + \alpha \beta h} \quad (3)$$

where  $M$  is molecular weight of the polymer substance associated with one molecular weight of water as hydrate;  $\alpha$  is equilibrium constant of the solid solution;  $\beta$  is equilibrium constant of monohydrate, and  $u$  is the equilibrium moisture content at relative humidity  $h$ . The model partitions the total sorbed water  $u$  into two forms, hydrate water and free dissolved water. The former is sorbed in a layer one molecule thick and is referred to as monomolecular sorbed water and the latter is referred to as polymolecular sorbed water. These two types of sorbed water can be calculated from the equilibrium constants of the theoretical model since from Eq. (3):

$$u = u_m + u_p \quad (4)$$

$$u_m = \left( \frac{\alpha \beta h}{1 + \alpha \beta h} \right) \frac{1800}{M} \quad (5)$$

$$u_p = \left( \frac{\alpha h}{1 - \alpha h} \right) \frac{1800}{M} \quad (6)$$

where  $u_m$  is monomolecular sorbed water and  $u_p$  is polymolecular sorbed water, both at relative humidity  $h$ .

Through use of these constants and Eqs. (4), (5), and (6), complete isotherms in desorption and adsorption, as illustrated for Copaia in Fig. 3, can be constructed for total, polymolecular, and monomolecular sorption. From ratios of adsorbed to desorbed moisture shown by these isotherms, hysteresis values in sorption were calculated at 10 percentile intervals over the range from 60 ... 90 percent relative humidity and averaged as shown in Table 2.

Table 2. Sorption Hysteresis Ratios in the Upper Range of Relative Humidities for 13 Species

	Sorbed water hysteresis			Humidity hysteresis
	Total	Monomolecular layer	Polymolecular	$\left[ \frac{\text{Adsorbing } \ln(p_0/p)}{\text{Desorbing } \ln(p_0/p)} \right]$
Cupiuba	0.743	0.823	0.698	0.397-
Copaia	0.793	0.803	0.788	0.575
Manwood	0.754	0.886	0.688	0.387
Tauary	0.790	0.757	0.800	0.602
Ceiba	0.848	0.787	0.871	0.763
Santa Maria	0.779	0.742	0.796	0.566
Mora Amarilla	0.755	0.754	0.757	0.439
Kancelhart	0.795	0.677	0.862	0.777
Angelique	0.798	0.785	0.802	0.588
Primavera	0.804	0.741	0.831	0.655
Sangre	0.810	0.728	0.844	0.731
Mahogany	0.836	0.725	0.899	0.880
Teak	0.844	0.742	0.894	0.800

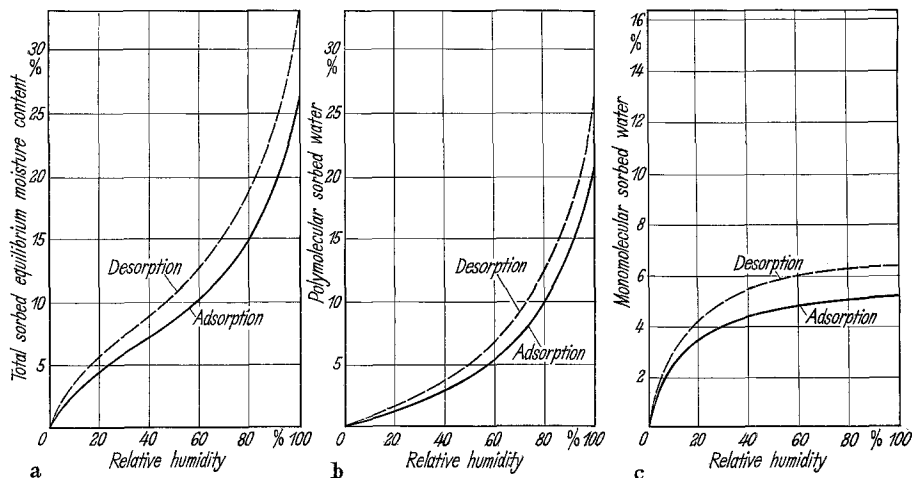


Fig. 3. Sorption isotherms for Copaia. a) Total sorbed water, b) Polymolecular sorbed water, c) Monomolecular sorbed water

A second phase of his study was concerned with determining sorption hysteresis for the remaining 15 species. Cross-sectional wafers,  $\frac{1}{16}$ -inch thick and weighing one to two grams each, were used to obtain values for equilibrium moisture content under adsorption and desorption conditions at two levels in the upper range of relative humidity.

For adsorption measurements, air-dry wood wafers were placed in a desiccator over anhydrous  $P_2O_5$  to be dried, and for desorption measurement, a matched set of wafers was placed in a sealed vessel over water to obtain a high moisture content close to saturation. After this preliminary treatment, all wafers were placed in a sealed chamber at approximately 76 percent relative humidity provided by a saturated solution of  $NaCl$  at  $77^\circ F.$  and conditioned to constant weight. The determination was repeated employing a saturated solution of  $K_2SO_4$  which gives a relative humidity of approximately 95 percent at the same temperature. Moisture content was calculated on the basis of oven-dry weight determined after equi-

librium weights had been established. A Sartorius direct-reading analytical balance was used to weigh all wafers. Hysteresis ratios at these two relative humidities were calculated and average values were used to describe total sorbed water hysteresis for these species as shown in Table 3.

Table 3. Total Sorbed Water Hysteresis in the Upper Range of Relative Humidities for 15 Species

Species	Sorbed water hysteresis	Species	Sorbed water hysteresis
Cedro Granadino	0.753	Black Kakeralli	0.836
Manbarklark	0.803	Banak	0.793
Quillo Sisa	0.814	Guyabo	0.829
Bannia	0.790	Acapu	0.828
Angelim	0.845	Purpleheart	0.880
Gronfoeloe	0.757	Parinari	0.827
Almendro	0.815	Quaruba	0.836
Mora	0.824		

### Discussion of Results

Polymolecular sorbed water hysteresis, represented by the ratio of adsorbed to desorbed polymolecular moisture content, averaged over the range of relative humidity from 60...90 percent as given in Table 2 for 13 species was plotted against wettability hysteresis for the same species as given in Table 1. The relationship is shown in Fig. 4. It is evident that polymolecular sorbed water hysteresis

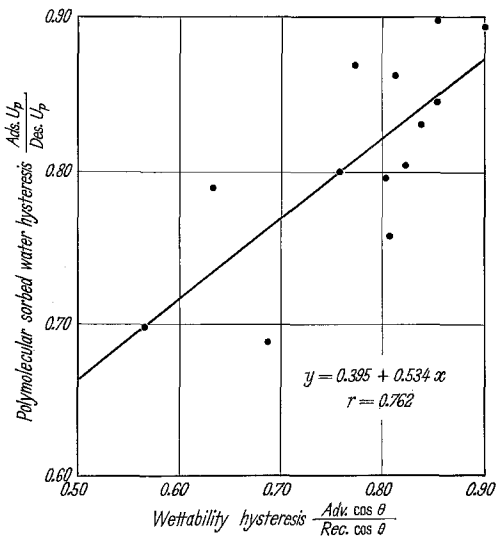


Fig. 4. Relationship between polymolecular sorbed water hysteresis and wettability hysteresis.

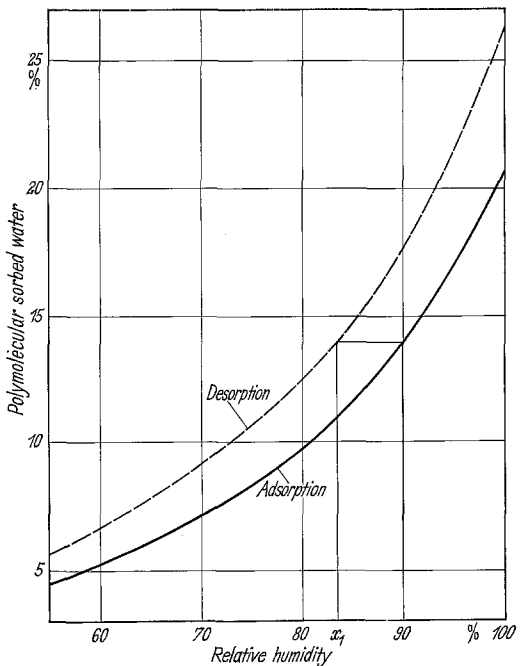


Fig. 5. Measurement of relative humidity hysteresis  $\ln(100/90)/\ln(100/X_1)$  from adsorption-desorption isotherms. Data for Copala.

increases with increasing wettability hysteresis. The regression has a correlation coefficient of .762 and is significant at the 1 percent level of probability. This



result is consistent with the KELVIN equation and carries the implication that polymolecular sorption hysteresis is at least in part a consequence of the difference in wettability shown by cell-wall capillaries when undergoing adsorption or desorption.

When the KELVIN-equation is rearranged in the form  $r = \frac{2V\gamma\cos\theta}{\ln(p_0/p)RT}$ , it is evident that a reduced value for advancing  $\cos\theta$  (holding all other terms in the right side of the equation constant) will permit condensation to occur only in the capillaries having a small radius  $r$ . This is the situation when wood is undergoing adsorption. With the larger  $\cos\theta$  (receding contact angle) applicable when wood is undergoing desorption, moisture will condense in capillaries having a larger radius  $r$ , as well as in the smaller capillaries, and consequently will come to equilibrium at a higher moisture content. Without specific information as to the distribution of capillary sizes in the cell wall, it is not possible to test the relationship quantitatively. Nevertheless, this evidence gives support to ZSIGMONDY's explanation of hysteresis as a phenomenon of capillary condensation [ZSIGMONDY et al. 1912].

A more rigorous test of the applicability of the KELVIN equation to polymolecular hysteresis was also attempted as suggested by Eq. (2). Taking the value for polymolecular sorbed moisture in adsorption at 90 percent relative humidity, the relative humidity  $x_1$  in equilibrium with the same moisture content in desorption was calculated as illustrated for Copaia in Fig. 5. At constant moisture content, the ratios  $\frac{\text{adsorbing } \ln(p_0/p)}{\text{desorbing } \ln(p_0/p)}$  and  $\frac{\text{advancing } \cos\theta}{\text{receding } \cos\theta}$  should theoretically be equal. Values for relative humidity hysteresis  $\frac{\text{adsorbing } \ln(p_0/p)}{\text{desorbing } \ln(p_0/p)}$  were calculated for each species as shown in Table 2.

In Fig. 6 relative humidity hysteresis is plotted against wettability hysteresis for 13 species. A significant correlation between these variables ( $F$  ratio significant at 1 percent) is shown, indicative of a positive relationship between humidity hysteresis and wettability hysteresis. The correlation coefficient is .702. The regression line, however, lies considerably below the broken line drawn on the graph to represent theoretical equality of these two variables. This may be interpreted as evidence that sorption hysteresis is not fully explained by wettability hysteresis and that polymolecular sorption at this level is only in part the result of capillary condensation. A likely possibility is that advancing and receding contact angles as determined in this study only approximate the actual contact angles found in the capillaries of the cell wall. Other sources of experimental error are also involved. In any event, the significant correlations shown in Figs. 4 and 6 are positive evidence of a substantial influence of wettability on polymolecular sorption hysteresis and hence of the occurrence of capillary condensation in the range of relative humidity from 60 ... 90 percent.

Hysteresis in total sorption, taken for the first 13 species from Table 2, and for the remaining species from Table 3, has been plotted against wettability hysteresis in Fig. 7. Data from these two series are identified on the graph. By combining both series of data a significant correlation between total sorption hysteresis and wettability hysteresis was obtained. The regression is positive and significant at the

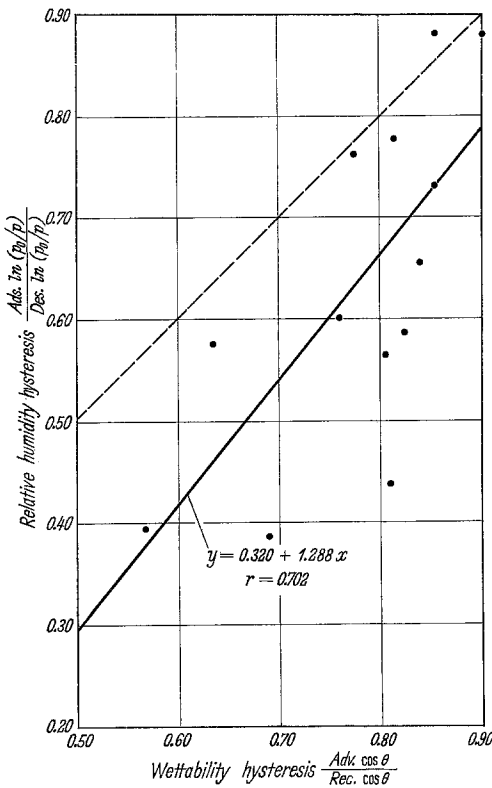


Fig. 6. Relationship between relative humidity hysteresis and wettability hysteresis.

1 percent level of probability with a correlation coefficient of .647. The significance of this relationship substantiates the conclusions drawn from the relationship in Fig. 4 and furthermore indicates that hysteresis in poly-molecular sorption is a predominant factor influencing total sorption hysteresis. It is now evident that in the upper range of relative humidities above 60 percent the hysteresis shown by typical sigmoid isotherms in desorption and adsorption as represented by the curve for Copaia shown in Fig. 3a is at least to a considerable degree a capillary condensation phenomenon explainable by the KELVIN-equation in its complete form including cosine  $\theta$ . Predicated on this evidence the sigmoid hysteresis loop probably remains open at its upper limit in equilibrium with relative humidity until closure is attained very close to saturation vapor pressure through the condensation of liquid water in

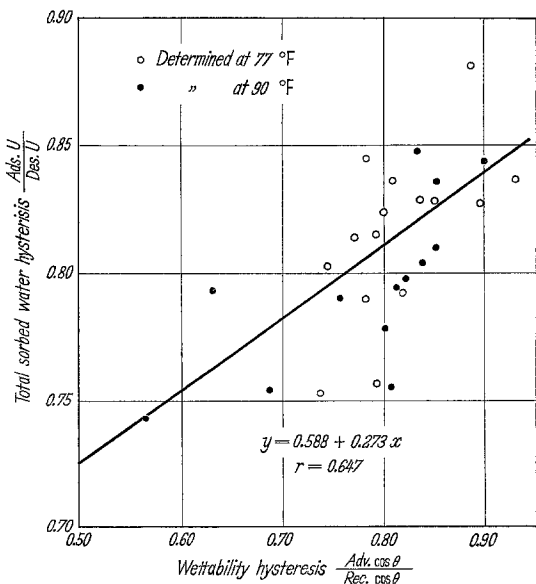


Fig. 7. Relationship between total sorbed water hysteresis and wettability hysteresis.

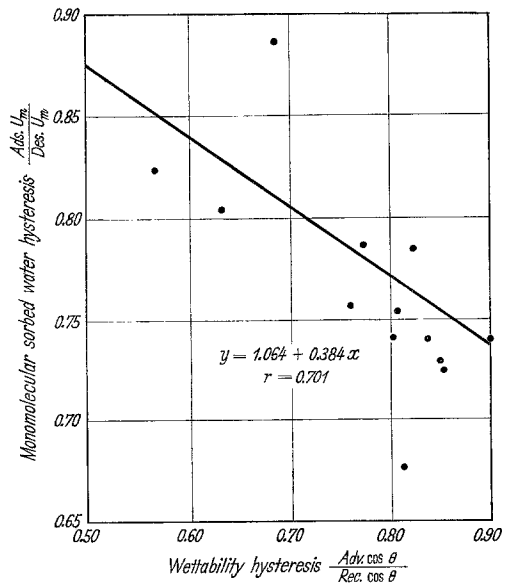


Fig. 8. Relationship between monomolecular sorbed water hysteresis and wettability hysteresis.

the largest capillaries in the cell wall undergoing adsorption. This explains the open hysteresis loops determined from the extrapolation of isotherms to 100 percent relative humidity [SPALT 1958; WANGAARD et al. 1967].

On the basis of this reasoning there was no expectation that monomolecular sorption hysteresis would be related in any way to wettability hysteresis. Monomolecular sorption hysteresis values from Table 2 are plotted against wettability hysteresis in Fig. 8. Surprisingly, the relationship was found to be significant. However, the slope of the regression line was negative, sorption hysteresis decreasing as wettability hysteresis increases. No explanation of this relationship appears reasonable but it should be noted that hysteresis in monomolecular sorbed moisture is an extremely small contributor to total hysteresis in the range of relative humidities from 60 percent upward.

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