

THE EFFECT OF TEMPERATURE ON THE SURFACE TENSION OF SAP OF *THUJA PLICATA* HEARTWOOD

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ABSTRACT

Capillary rise and drop volume methods were applied to the measurement of heartwood sap surface tension. Increase in sap temperature appeared to cause a substantial decrease in surface tension as measured by the former method. Since with the latter method surface tension values only decreased from 58.1 to 56.8 dyne/cm over the temperature range 25 to 80 C, it was concluded that changes in the contact angle of sap on glass were likely to have affected the results obtained by the capillary rise method. The absence of a substantial decrease in sap surface tension with increasing temperature is of considerable relevance to lumber drying.

Keywords: Sap, surface tension, temperature, contact angle, *Thuja plicata*.

INTRODUCTION

It is generally acknowledged that interfacial forces are partly responsible for many phenomena in timber drying. Such phenomena include the aspiration of bordered pits in coniferous species, the collapse of wood in lumber drying, the reduction of mass (liquid) flow through intercellular passageways due to the blockage of pores by gas embolisms. Stamm and Arganbright (1970) have reported measurements of sap surface tension for a number of species at ambient temperature. Since lumber drying is carried out at elevated temperatures, it is surprising that the literature appears to contain no reference to the effect of temperature on sap surface tension. Some relevant results were obtained in the course of a study of collapse in lumber drying (Koutsianitis 1978).

MATERIALS AND METHODS

Five 5-cm-thick discs were cut from a 40-year-old *Thuja plicata* tree from a local plantation; the first was taken at a point 50 cm above the ground, and the others at intervals of about 29 cm above this. One disc containing a node was excluded from the study. Only material lying outside the juvenile core (assumed to be confined to 15 annual rings from the pith) but inside the fourth ring within the sapwood-heartwood boundary was sampled. This area was subdivided into two concentric zones of similar width. From each zone and disc, enough 4-cm cubes were cut to produce at least 100 cm³ of sap by the compression technique used by Stamm and Arganbright (1970). The sap produced was filtered three times through Whatman No. 1 filter paper. Evaporation of a quantity of sap over a steam bath indicated that its nonvolatile content was of the order of 0.46 g/100 cm³. This is within the range reported for redwood by Stamm and Arganbright (1970).

Two methods of surface measurement were used. The first was a capillary rise

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method involving the use of two capillaries of different radius, in order to overcome the difficulties of obtaining a flat liquid reference surface. In such a system surface tension, γ_c is given by:

$$\gamma_c = (\Delta h \rho g) / (2 \cos \theta [1/r_1 - 1/r_2]) \quad (1)$$

where Δh is the difference in rise heights in capillaries of radius r_1 and r_2 , ρ is the fluid density, θ its contact angle with glass, and g the acceleration due to gravity (Glasstone 1946). In the present study, precision pyrex glass capillaries of internal radius 0.075 cm and 0.125 cm were used. The sap reservoir and capillary tubes were placed in a viscometer bath temperature controlled to ± 0.1 C. Δh values were measured with a travelling microscope accurate to ± 0.001 cm from both advancing and retreating interfaces. The capillary tubes were cleaned with a 10% potash solution before each use (Partington 1951).

The difficulty with the double capillary method is the uncertainty in the magnitude of the contact angle of sap on glass. The contact angle of water on glass is usually assumed to be zero when the glass is very clean. However, an angle of 10° – 12° of water on pyrex glass was reported by Moser (1956, cited by Holland 1964). If sap contains some surface active substances, as indicated by the low value of surface tension observed at ambient temperatures by Stamm and Arganbright (1970), then the contact angle of sap is likely to differ from that of water on glass (Harkis and Alexander 1959). For this reason a drop-volume method surface tension determination was also used. In this case, the surface tension, γ_d is given by

$$\gamma_d = (\rho v g F) / r \quad (2)$$

where ρ and g are as before, v is the volume of one drop formed on a tip of radius r , and F a correction factor dependent on $r/v^{1/3}$ which is obtained from Tables (Harkis and Alexander 1959). It should be noted that contact angle does not appear in this equation. The tip used was a fine hypodermic needle, with its end ground normal to its long axis. This needle was attached to a syringe of 0.5 cm³ capacity, the plunger of which was depressed with a micrometer screw to ensure even and slow formation of drops. The drops were formed in an environment of saturated sap vapor. As above, the equipment was placed in a viscometer bath for temperature control. However, measurements at 100 C were not possible with this method, because the formation of drops was poorly controlled because of the boiling of sap. The number of drops formed from 0.4 cm³ of sap, as indicated by the scale on the syringe, was recorded and the average drop volume calculated.

RESULTS AND DISCUSSION

Mean sap surface tensions obtained by both methods, together with the standard deviations about these means, are presented in Table 1. The standard deviations at each temperature were higher with the double capillary method, despite the fact that the number of replications was higher with this method than with the drop volume method. The latter method therefore appears to be the more reliable. This was confirmed by the results of control measurements performed on distilled water. (See Table 1.)

The mean sap surface tensions obtained by both methods at 25 C are reasonably

TABLE 1. Effect of temperature on surface tension of sap and distilled water, and on the calculated contact angle of sap on glass.

Temperature	25.0 C	40.0 C	60.0 C	80.0 C	100.0 C
<i>Sap Surface Tension: Double Capillary Method¹</i>					
Number of measurements	34	60	44	78	41
Sap density (g/cm ³)	1.0137	1.0087	0.9998	0.9927	0.9827
γ_c (dyne/cm)	54.8	53.6	46.2	39.6	28.3
Standard deviation of γ_c	6.1	7.4	8.7	9.4	8.2
<i>Sap Surface Tension: Drop Volume Method^{2,3}</i>					
Number of measurements	10	10	10	10	
γ_d (dyne/cm)	58.1	57.8	57.3	56.8	
Standard deviation of γ_d	0.5	0.5	0.5	0.5	
<i>Distilled Water Surface Tension: Double Capillary Method^{1,4}</i>					
Number of measurements	6	6	6	6	
Water density (g/cm ³) ⁵	0.9971	0.9922	0.9832	0.9718	
γ_c (dyne/cm)	69.6	68.4	65.3	61.1	
Standard deviation of γ_c	3.1	3.3	2.6	4.1	
<i>Distilled Water Surface Tension: Drop Volume Method^{2,6}</i>					
Number of measurements	3	3	3	3	
γ_d (dyne/cm)	71.3	69.3	65.7	62.3	
Standard deviation of γ_d	0.0	0.0	0.0	0.0	
<i>Distilled Water Surface Tension: From Tables⁵</i>					
γ (dyne/cm)	72.0	69.6	66.2	62.6	
<i>Calculated Contact Angles of Sap on Glass</i>					
$\cos \theta = \gamma_c/\gamma_d$	0.9440	0.9317	0.8105	0.6987	
θ (degrees)	19.3	21.9	36.3	45.8	

¹ Contact angle, θ , is assumed to be zero, so that $\cos \theta = 1$.

² Tip radius, r , was 0.025 cm at 25 C; thermal expansion effects are negligible.

³ Sap density as above; tabular F value = 0.197.

⁴ Capillary radii $r_1 = 0.042$ cm, $r_2 = 0.058$ cm, and not as stated in the text.

⁵ Kaye and Laby (1973).

⁶ Water density as above; tabular F value = 0.196.

similar (54.8 and 58.1 dyne/cm) and are of the same order as values reported by Stamm and Arganbright (1970) for other softwood species (45.5 to 56.9 dyne/cm).

Although the general trend for surface tension to decrease with increasing temperature is apparent from the results of both methods, the rate of decrease is far greater with the double capillary method. Yet both methods gave similar results with distilled water. One possible explanation for the lower double capillary values with sap is that the contact angle of sap on glass may not be zero. If sap surface tension values obtained by the drop volume method are assumed correct, and the difference in the results obtained by the two methods is attributed wholly to positive contact angles, then values for the sap/glass contact angle may tentatively be calculated. (See Table 1.) Experiments with carbon tetrachloride and oleic acid, which have contact angles of 0° and 27° respectively with pyrex glass (Bartell and Merrill 1932), suggest that contact angles of this order would not lead to change of meniscus shape readily detectable with the capillary radii and travelling microscope used.

The increase of the calculated contact angles of sap on glass with temperature

is substantial and apparently at variance with the general tendency of contact angles of pure liquids on solids to decrease with increasing temperature. Yet since sap contains surfactants, it is unlikely to behave as a pure liquid in this respect: it is well known that surfactants can influence the contact angle of aqueous solutions on glass (Harkis and Alexander 1959). Further, the extraneous substances in sap, some of which give it its special physical properties, may well be chemically changed at the higher temperatures used in the present work. It therefore seems possible that an increase of sap contact angle with increasing temperature could be attributed to temperature-dependent changes in the nature of substances in the sap, and/or changes in their influences on the behavior of the interface. Irrespective of whether this explanation is correct, it is certainly the view of Harkis and Alexander (1959) that capillary height methods should not be trusted for surface tension determination of aqueous surfactants, because contact angles will be in doubt.

If the drop volume sap surface tension values are therefore taken as the more reliable, it is noteworthy that the change in surface tension with increasing temperature is very small, and that the difference in the surface tension of sap and water decreases with increasing temperature. It therefore appears that the surfactants in sap are chemically modified, and/or lose some activity, at higher temperatures.

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REFERENCES

- BARTELL, F. E., AND E. J. MERRILL. 1932. Determination of adhesion tension of liquids against solids: A microscopic method for the measurement of interfacial contact angles. *J. Phys. Chem.* 36(4):1178-1198.
- GLASSTONE, S. 1946. *Textbook of physical chemistry*. 2nd ed. MacMillan, London.
- KAYE, G. W. C., AND T. H. LABY. 1973. *Tables of physical and chemical constants and some mathematical functions*. 14th ed. Longmans, London.
- KOUTSIANITIS, G. 1978. *A study of collapse in timber drying*. M.Sc. Thesis, University of Wales.
- HARKIS, W. D., AND A. E. ALEXANDER. 1959. Surface and interfacial tension. *In* A. Weissberger., ed. *Technique of organic chemistry*. 3rd ed. Interscience, New York.
- HOLLAND, L. A. 1964. *The properties of glass surfaces*. Chapman and Hall, London.
- MOSER, F. 1956. *The glass industry*. April Issue. Cited by Holland (1964).
- PARTINGTON, J. R. 1951. *An advanced treatise on physical chemistry: Vol. 2 The properties of liquids*. Longmans, Green and Co., London.
- STAMM, A. J., AND D. G. ARGANBRIGHT. 1970. Surface tension of the sap of several species of wood. *Wood Fiber* 2(1):65-66.