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Enthalpy-entropy compensation in water sorption by various wood species

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Enthalpy and entropy of water sorbed by the sapwood and heartwood of five local softwoods were studied: western hemlock (*Tsuga heterophylla*), Douglas fir (*Pseudotsuga menziesii*), western red cedar (*Thuja plicata*), sitka spruce (*Picea sitchensis*), and lodgepole pine (*Pinus contorta*). Enthalpy and entropy show a strong negative relation to the moisture content, the absolute desorption values always being higher than the adsorption ones, but with no clear trend between and within the species. Furthermore, it is shown that the linear plot of compensation between enthalpy and entropy correlates well for water sorption in wood; that water adsorption or desorption are irreversible, and that both are enthalpy-driven mechanisms.

Enthalpie- und Entropiekompensation bei der Wassersorption verschiedener Holzarten

Enthalpie und Entropie bei der Wassersorption wurden an verschiedenen Holzarten bestimmt: (*Tsuga heterophyll*, *Pseudotsuga menziesi*, *Thuja plicata*, *Picea sitchensis*), und P*inus contorta*. Enthalpie und Entropie steigen mit fallender Feuchte. Die Desorptionswerte sind immer etwas höher als die Adsorptionswerte. Zwischen den Holzarten gab es keine signifikanten Unterschiede. Die lineare Kompensation zwischen Enhalpie und Entropie korrelliert gut mit der Sorption. Absorption und Desorption sind irreversible, Enthalpie-getriebene Prozesse.

1
Introduction

The understanding of how water molecules are sorbed by the hydroxyl sorption sites in wood cell-walls has been the focus of extensive research over the past years. Furthermore, extensive attention has been paid to the thermodynamic properties of wood, namely, enthalpy, entropy and free energy, since they are all important for the design and optimization of unit operations, such as timber kiln drying and conditioning while in service (Skaar, 1988). Changes in thermodynamic properties of wood while losing or gaining water molecules, could provide an indication of the level of wood-water affinity and binding forces, the water molecules, spatial arrangement, and of the spontaneity of the sorption process (Labuza, 1980).

When water sorption by wood takes place, simple patterns of parallel enthalpy and entropy changes which compensate each other to produce minor changes in the free energy of the process, are observed. These patterns result in a linear relationship between enthalpy and entropy that has been debated for many years and which is commonly referred to as the compensation law or the isokinetic relationship. Such compensation is often remarkably precise. Its evidence occurs in phenomena such as chemical reactions, solubility, evaporation of metals, catalytic processes, thermal denaturation of macromolecules, thermal killing of unicellular organisms, semiconduction processes and vapor sorption (Schreiner and Kemball, 1953; Leffler, 1955; Leffler, 1965; Heyrovsky, 1970; Wilson and Galwey, 1973; Labuza, 1980; Krug et al., 1976; Aguerre et al., 1986). The compensation law was implemented in the past by Avramidis (1992), in order to analyze water sorption by western white pine and prove its existence.

The objective of this paper is the further application of the compensation law for water adsorption and desorption in five softwood species and two wood types and the identification of possible thermodynamic differences between them.

2
Experimental procedure

Green wood logs of western hemlock (*Tsuga heterophylla*), WH, Douglas-fir (*Pseudotsuga menziesii*), DF, western red cedar (*Thuja plicata*), RC, sitka spruce (*Picea sitchensis*), SS, and lodgepole pine (*Pinus contorta*), LP, were obtained from the local forests. Specimens, of all-sapwood and all-heartwood, 50 × 50 mm in cross-section and both 5 and 10 mm in thickness, and with no visual defects were cut immediately after delivery of the logs, wrapped with plastic and stored in a freezer until use. The thickness direction of each specimen coincided with the tree's tangential direction.

The specimens were used to generate experimental sorption isotherms at three temperatures (30, 45 and 60 °C). Desorption isotherms were firstly created gravimetrically (to 0.0001 g) with the green specimens that were equilibrated to successively lower relative humidities starting at 95% and ending at 25%. When the last desorption step was completed, the process was reversed and the relative humidity was successively increased up to 95%, thus providing the adsorption isotherm. Equilibra-

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tion took place in conditioning chambers where the temperature could be controlled to ±0.2 °C and the relative humidity to ±0.5 °C. The method is the same as the one described in Avramidis (1992).

A total of five replications were used for each thickness, species and type of wood, thus resulting in a total of three hundred specimens. The six equilibration steps per isotherm resulted in thirty six experimental runs each of which was on the average about 4 to 6 weeks long.

3
Results and discussion

When the experiments were completed, the Hailwood-Horrobin (1946) model

$$m = \frac{18}{w}\left(\frac{k_1k_2h}{1+k_1k_2h} + \frac{k_2h}{1-k_2h}\right) \qquad (1)$$

where m is the fractional moisture content, h is the fractional relative humidity, k_1 and k_2 are equilibrium constants, and w is the molecular weight of the dry cell-wall per sorption site (Skaar, 1988), was fitted to the sorption data using a nonlinear regression technique for the calculation of its parameters. A list of these parameters for all five species and both adsorption and desorption at three temperatures is given in Table 1.

The model was then used to create plots of the logarithm of fractional relative humidity against the inverse of temperature so that the relationship (Avramidis, 1992),

$$-\ln(h) = \mathrm{d}H/RT - \mathrm{d}S/\mathrm{R} \qquad (2)$$

where dH is the enthalpy change, (cal/mol), dS is the entropy change, (cal/mol K), T is the temperature, (K), and R is the universal gas constant (2 cal/mol), could be linearly fitted to the data, thus allowing the estimation of dH and dS. This equation assumes that dH and dS do not vary with temperature or that they are constant in the temperature range under consideration. The validity of this assumption was proven by Avramidis (1992). A typical [$-\ln(h)$ vs. $1/T$] plot for Douglas-fir heartwood (adsorption and desorption) for the 7 to 13% moisture content range is shown in Fig. 1

The calculated regression values of dH and dS from Eq. (2) are listed in Table 2. It can be seen that all dH values were negative within the entire moisture content and temperature range covered for all five wood species, the two wood types, i.e., sapwood and heartwood, and sorption mode, i.e., adsorption and desorption, thus verifying the strong attractive forces between water molecules and cell-wall sorption sites. Also, the absolute values of dH

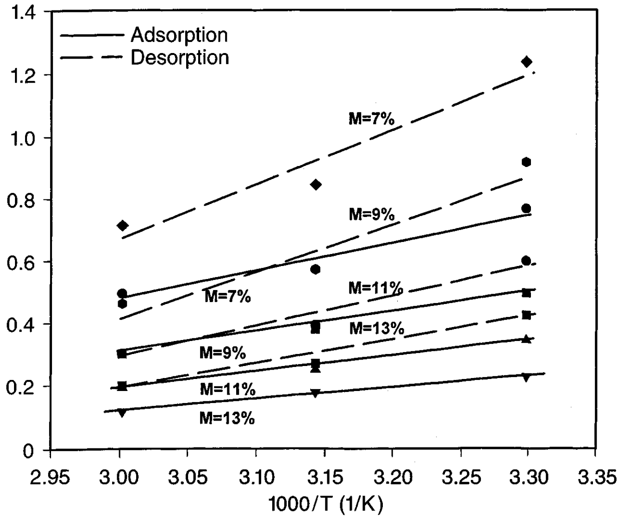

Fig. 1. Water sorption isostere für Douglas-fir heartwood in adsorption and desorption
Bild 1. Sorptions-Isostere für Douglasienkernholz bei Adsorption und Desorption

Table 1. Fitting parameters using the Hailwood-Horrobin model for water adsorption and desorption by five species at three temperatures

T (°C)	w_p	k_1	k_2	w_p	k_1	k_2	w_p	k_1	k_2	w_p	k_1	k_2	w_p	k_1	k_2
	Western Hemlock sapwood adsorption			Douglas-fir sapwood adsorption			Western Red Cedar sapwood adsorption			Sitka Spruce sapwood adsorption			Lodgepole Pine sapwood adsorption		
30	248.6	4.704	0.7266	271.1	4.881	0.7349	382.6	3.085	0.7585	269.9	5.635	0.7405	295.7	7.148	0.7656
45	337.8	5.570	0.7776	362.6	5.583	0.7891	494.0	5.032	0.8018	354.0	5.637	0.7887	360.7	5.613	0.7916
60	327.6	4.299	0.7296	422.5	6.148	0.8016	414.1	2.846	0.7069	389.0	5.669	0.7482	402.1	7.194	0.7908
	Western Hemlock sapwood desorption			Douglas-fir sapwood desorption			Western Red Cedar sapwood desorption			Sitta Spruce sapwood desorption			Lodgepole Pine sapwood desorption		
30	202.8	9.318	0.6976	220.9	11.19	0.7265	308.9	56.180	0.6904	217.9	10.510	0.7296	228.0	11.120	0.7304
45	214.1	3.738	0.6908	241.7	4.099	0.7295	416.0	15.770	0.7649	239.2	4.292	0.7261	237.9	3.968	0.7148
60	218.1	4.168	0.6469	300.0	6.189	0.7612	438.7	12.110	0.7388	243.3	4.614	0.6693	254.3	4.705	0.6770
	Western Hemlock heartwood adsorption			Douglas-fir heartwood adsorption			Western Red Cedar heartwood adsorption			Sitta Spruce heartwood adsorption			Lodgepole Pine heartwood adsorption		
30	274.2	4.988	0.7448	310.3	5.031	0.7531	396.9	3.761	0.7670	273.0	5.868	0.7518	294.5	5.508	0.7682
45	363.4	6.145	0.7947	400.6	5.950	0.8018	452.9	4.453	0.7735	358.0	5.709	0.7915	373.7	5.861	0.8000
60	394.4	5.749	0.7902	439.8	7.612	0.7826	466.9	4.858	0.7237	351.5	4.181	0.7315	421.0	7.332	0.7965
	Western Hemlock heartwood desorption			Douglas-fir heartwood desorption			Western Red Cedar heartwood desorption			Sitta Spruce heartwood desorption			Lodgepole Pine heartwood desorption		
30	209.1	9.951	0.6943	251.7	14.670	0.7330	279.5	29.730	0.6619	226.3	12.290	0.7447	242.9	13.640	0.7450
45	230.7	4.259	0.6991	276.3	5.066	0.7319	373.6	10.850	0.7257	250.8	4.866	0.7390	267.7	5.318	0.7430
60	227.6	4.616	0.6298	324.0	6.219	0.7392	420.8	11.180	0.7221	244.3	4.685	0.6703	247.4	4.486	0.6502

Table 2. Thermodynamic parameters for water adsorption and desorption by five species as a function of moisture content

M %	−d*H* cal/mol	−d*S* cal/mol K	*M* %	−d*H* cal/mol	−d*S* cal/mol K	*M* %	−d*H* cal/mol	−d*S* cal/mol K	*M* %	−d*H* cal/mol	−d*S* cal/mol K	*M* %	−d*H* cal/mol	−d*S* cal/mol K
Western Hemlock sapwood adsorption			Douglas-fir sapwood adsorption			Western Red Cedar sapwood adsorption			Sitka Spruce sapwood adsorption			Lodgepole Pine sapwood adsorption		
5	1088	2.80	7	598	1.54	4	525	1.19	5	1042	2.70	5	1091	2.83
8	516	1.32	9	408	1.06	6	307	0.71	8	588	1.57	8	488	1.25
11	357	0.95	11	309	0.82	8	256	0.65	11	410	1.13	11	327	0.87
14	261	0.72	13	222	0.59	10	185	0.50	13	328	0.93	14	204	0.55
Western Hemlock sapwood desorption			Douglas-fir sapwood desorption			Western Red Cedar sapwood desorption			Sitka Spruce sapwood desorption			Lodgepole Pine sapwood desorption		
5	1300	3.28	7	1102	2.92	4	1503	3.90	5	998	2.37	5	1307	3.34
8	917	2.39	9	808	2.17	6	1081	2.95	8	757	1.93	8	758	1.95
11	548	1.44	11	553	1.47	8	955	2.72	11	572	1.53	11	487	1.28
14	377	1.01	13	438	1.19	10	466	1.30	13	445	1.21	14	374	1.03
Western Hemlock heartwood adsorption			Douglas-fir heartwood adsorption			Western Red Cedar heartwood adsorption			Sitka Spruce heartwood adsorption			Lodgepole Pine heartwood adsorption		
5	1050	2.71	7	460	1.14	4	603	1.42	5	1103	2.88	5	940	2.39
8	449	1.13	9	328	0.84	6	316	0.74	8	565	1.49	8	444	1.13
11	295	0.77	11	254	0.67	8	250	0.63	11	373	1.01	11	297	0.78
14	185	0.49	13	185	0.50	10	207	0.56	13	300	0.83	14	203	0.55
Western Hemlock heartwood desorption			Douglas-fir heartwood desorption			Western Red Cedar heartwood desorption			Sitka Spruce heartwood desorption			Lodgepole Pine heartwood desorption		
5	1545	4.03	7	889	2.33	4	1656	4.38	5	1281	3.23	5	1467	3.83
8	979	2.61	9	770	2.10	6	1498	4.21	8	757	1.93	8	761	1.97
11	566	1.51	11	502	1.37	8	955	2.72	11	560	1.49	11	492	1.31
14	405	1.12	13	380	1.05	10	599	1.73	13	444	1.21	14	373	1.03

decreased as the moisture content of wood increased in all species and types. This trend supported the fact that as moisture content increases, the forces of water molecules attraction by wood decrease (Skaar, 1988).

The d*S* values also showed a strong dependence on moisture content and furthermore, their absolute values decreased as moisture content increased. This entropy decrease during sorption could be attributed to an increase in order of sorbed water molecules, particularly at low moisture contents. Furthermore, according to the second law of thermodynamics, the process of water desorption or adsorption is irreversible (hysteresis effect) because entropy is produced during the process.

By considering the trend of the calculated d*H* values within each species as listed in Table 2 it can be seen that for the same wood type, i.e. sapwood, the desorption absolute values are always higher than the adsorption ones. The same trend can be observed for the calculated d*S* values for the same wood type, namely, the desorption absolute d*S* values are always higher than the adsorption ones.

No clear trend could be identified for both d*H* and d*S* values in a similar comparison between sapwood and heartwood within the same species. For example, the sapwood dH and d*S* values in western hemlock, lodgepole pine and western red cedar are higher than the heartwood ones in adsorption, but the reverse is true in desorption. In the other two species, the trend is more ambiguous.

Between the different species for adsorption and both wood types, the absolute values of d*H* and d*S* have the same order, namely, SS > WH ≥ LP > DF > RC where ≥ indicates very small differences, and depending on the moisture content, either the one or the other has slightly larger values. The order was the same for the absolute values of d*H* for desorption of both sapwood and heartwood (WH > RC > SS > DF > LP). Furthermore, the general order of the absolute values of d*S* in desorption for both sapwood and heartwood was RC > WH > SS > DF > LP.

The enthalpy-entropy compensation was calculated from the plots of d*H* against d*S* for the various species, wood types and sorption modes. The plot produced a straight line and an equation of the form:

$$\mathrm{d}H = T_b \mathrm{d}S + A \qquad (3)$$

where T_b is the isokinetic temperature (K) and *A* is a constant, was fitted to the data. A typical example of such plot along with the regression equations for adsorption and desorption of Douglas-fir heartwood are shown in Fig. 2. The parameters were calculated by linear regression from the data in Table 2 and the isokinetic temperatures are listed in Table 3. The very high degrees of correlation (over 0.997) obtained suggested that compensation existed. However, no distinct differences and trends are apparent from Table 3 for the calculated T_b values within and between species, wood types and sorption modes.

To strengthen the fact that compensation took place, the isokinetic temperatures were compared to the mean harmonic temperature $T_{\mathrm{hm}} = n/\sum(1/T)$ where n is the total number of isotherms used. Compensation exists only when $T_b \neq 1\ T_{\mathrm{hm}}$ (Krug et al., 1976a, 1976b). In our experiments, the harmonic mean temperature was found to be 317.7 K which significantly differs from the isokinetic temperatures listed in Table 3.

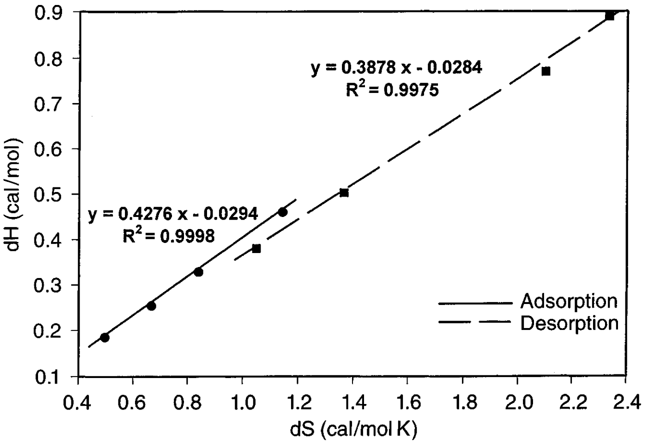

Fig. 2. Enthalpie (d*H*) against entropy change (d*S*) for Douglas-fir heartwood in adsorption and desorption

Bild 2. Enthalpieänderung (d*H*) in Abhängigkeit von der Entropieänderung (d*S*) für Douglasienkernholz bei Adsorption und Desorption

Table 3. Calculated isokinetic temperatures

Type/mode	Species				
	WH	DF	RC	SS	LP
Sapwood/adsorption	396	398	493	404	389
Sapwood/desorption	405	380	397	477	402
Heartwood/adsorption	389	428	450	391	400
Heartwood/desorption	391	388	386	414	389

According to Leffler (1955), if $T_b > T_{\mathrm{hm}}$, the process is enthalpy-driven and if the contrary condition exists, the process is entropy-controlled. As can be seen in Table 3, the T_b values were always larger that the T_{hm} ones, thus strongly supporting the fact that water sorption in wood within the moisture ranges examined is an enthalpy-driven process.

4
Conclusions

From this study it can be concluded that enthalpy and entropy of water sorbed by the sapwood and heartwood of five local softwoods show a strong negative relation to the moisture content with the absolute desorption values always being higher than the adsorption ones but with no clear trend between and within species.

Furthermore, it was shown that the linear plot of compensation between enthalpy and entropy correlates well for water sorption in wood, that water adsorption or desorption are irreversible, and that both are enthalpy driven mechanisms.

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