

Enthalpy–Entropy Compensation During Sorption of Water in Wood

S. P. S. RAWAT* and D. P. KHALI

Institute of Wood Science and Technology, Bangalore 560003, India

SYNOPSIS

Changes in free energy, enthalpy, and entropy were determined for sorption (desorption and adsorption) of water in wood. Findings were that changes are different for desorption and adsorption, have a strong dependence on moisture content, and have a weak dependence on temperature. Suggestive explanations are given for variation of energy changes during sorption with moisture content and temperature, and the differences in their values for desorption and adsorption are discussed. Studies on enthalpy–entropy compensation effect were made and a linear relationship is found to exist between enthalpy and entropy for both desorption and adsorption of water in wood. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

It has been observed that for a number of physical, chemical, and biological systems, a linear relationship exists between changes in enthalpy and changes in entropy.^{1–5} This relationship is often called enthalpy–entropy compensation or isokinetic effect. Among those who have studied this effect are: Bell,¹ for the solubility of gases; Everett,² for adsorption of vapors on charcoal, glass, and metals; Leffler,³ for organic chemical systems; and Labuza⁴ and Fontan and colleagues,⁵ for food systems.

Recently, Avramidis⁶ has determined energy changes during adsorption of water in wood (which is a complex polymer consisting of cellulose, hemicellulose, and lignin) by applying thermodynamics. He has used these quantities to show the occurrence of enthalpy–entropy compensation for wood and has recommended further investigation of this effect in wood. Since wood is not a perfect elastic material and since the kinetics of desorption and adsorption differ,⁷ there is a need to analyze enthalpy–entropy compensation for both desorption and adsorption. In the present study we determine the various thermodynamic parameters for both desorption and ad-

sorption from sorption isotherms of Klinky Pine⁸ to find out whether enthalpy–entropy compensation is a characteristic of both adsorption and desorption.

THEORY

Changes in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) take place during desorption and adsorption. Sorbed water has different enthalpy, entropy, and free energy than free water, hence we can write

$$\Delta G = \mp(G_s - G_w); \quad \Delta H = \mp(H_s - H_w);$$
$$\text{and} \quad \Delta S = \mp(S_s - S_w);$$

where G_s , H_s , and S_s are free energy, enthalpy, and entropy of the sorbed water, respectively; while G_w , H_w , and S_w are those of free water, respectively. In the above expressions the minus and plus signs denote changes in desorption and adsorption, respectively. For desorption these changes are positive, while they are negative in the case of adsorption.

ΔG as a function of temperature and humidity is given by:

$$\Delta G = \mp RT \ln h \quad (1)$$

* To whom correspondence should be addressed.

Table I Thermodynamic Parameters as a Function of Moisture Content and Temperature for Desorption of Water in Wood

<i>M</i> (%)	ΔG (cal/mol)				ΔH (cal/mol)	ΔS [cal/(mol K)]			
	298	305.2	313	325		298	305.2	313	325
5.0	1345.5	1176.8	1130.4	934.0	3744.88	8.05	8.41	8.35	8.64
7.5	882.6	788.7	699.2	547.9	2933.27	6.88	7.02	7.13	7.33
10.0	589.9	519.0	460.2	345.2	2075.76	4.98	5.10	5.16	5.32
12.5	381.3	345.0	298.0	213.4	1410.95	3.45	3.49	3.55	3.68
15.0	260.3	232.7	190.6	139.7	1018.54	2.54	2.57	2.64	2.70
17.5	172.4	153.5	121.7	88.4	705.40	1.78	1.81	1.85	1.89
20.0	113.5	101.4	77.2	62.4	448.27	1.12	1.13	1.185	1.187

The Gibbs free energy equation is:

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

Combining eqs. (1) and (2), we get

$$\ln h = \mp(\Delta H/RT - \Delta S/R) \quad (3)$$

where h is the relative humidity, T is the temperature in K, and R is the gas constant.

RESULTS AND DISCUSSION

After determining the values of $\ln h$ from the sorption isotherms,⁸ we calculated ΔG values using eq. (1); these are presented in Tables I and II for desorption and adsorption, respectively. Values vary from 1345.5 cal/mol at 5% moisture content (MC) to 62.4 cal/mol at 20% MC for desorption; adsorption values range from -971.6 cal/mol at 5% MC to -34.0 cal/mol at 20% MC.

We observed that the magnitude of ΔG decreases with both the moisture content and temperature for both desorption and adsorption (Tables I and II) because at higher moisture contents, the stresses associated with swelling or shrinking are greater. As a result, higher hydrostatic pressure will be exerted on sorbed water and will lead to higher humidity. Hence, ΔG will be small at higher moisture content. Further, at higher temperatures, the kinetic energy of water molecules is greater and therefore more work will be done in the swelling of wood, which will give rise to a higher hydrostatic pressure on sorbed water and a higher humidity. This will result in lower values of ΔG for higher temperatures.

Plots of $\ln h$ against $1/T$ at four different moisture contents were obtained for desorption and adsorption (Figs. 1 and 2), respectively. The relationship was found to be linear. The best fit of eq. (3) provided the values of ΔH which are presented in Tables I and II for desorption and adsorption, respectively. ΔH values range from 3744.9 cal/mol at

Table II Thermodynamic Parameters as a Function of Moisture Content and Temperature for Adsorption of Water in Wood

<i>M</i> (%)	$-\Delta G$ (cal/mol)				$-\Delta H$ (cal/mol)	$-\Delta S$ [cal/(mol K)]			
	298	305.2	313	325		298	305.2	313	325
5.0	971.6	901.2	804.9	755.0	2335.00	4.57	4.69	4.88	4.86
7.5	581.8	548.6	473.5	416.3	1658.22	3.61	3.63	3.78	3.82
10.0	364.7	323.9	279.0	232.0	1158.57	2.66	2.75	2.81	2.85
12.5	220.9	193.9	177.9	135.6	730.09	1.70	1.75	1.76	1.83
15.0	138.5	126.9	114.0	88.4	443.35	1.02	1.03	1.05	1.09
17.5	89.5	80.4	70.1	51.6	321.55	0.77	0.79	0.80	0.83
20.0	60.2	46.9	42.5	34.0	217.31	0.52	0.55	0.558	0.56

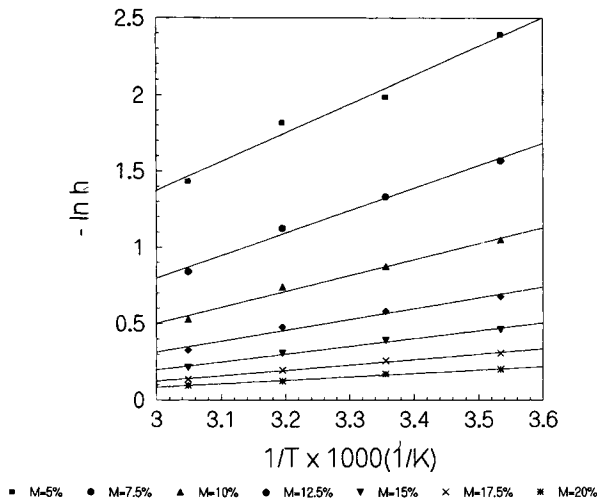


Figure 1 Plot of logarithm of relative humidity as a function of inverse of temperature for different moisture contents for desorption of water in wood.

5% MC to 448.3 cal/mol at 20% MC for desorption; adsorption values range from -2335.0 cal/mol at 5% MC to -217.3 cal/mol at 20% MC. As pointed out by Avramidis,⁶ this procedure assumed the constancy of ΔH with temperature.

Positive values of ΔH for desorption and negative values of ΔH for adsorption for the entire range of moisture content suggest a strong interaction between cellulose and water molecules, since ΔH is a measure of the binding energy of water molecules to the wood substrate. Since ΔH decreases with an increase in moisture content for both desorption and

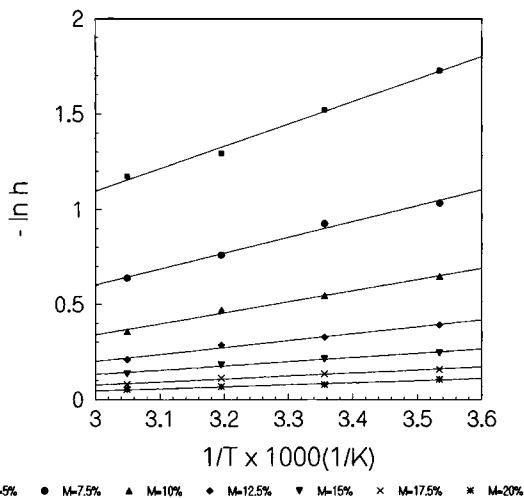


Figure 2 Plot of logarithm of relative humidity as a function of inverse of temperature for different moisture contents for adsorption of water in wood.

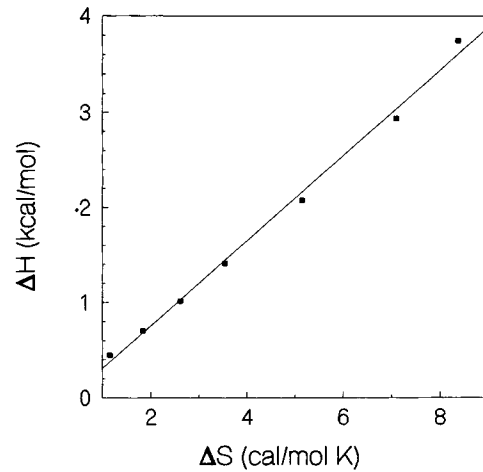


Figure 3 Enthalpy changes as a function of entropy changes for desorption of water in wood.

adsorption (Tables I and II), it suggests that at higher moisture content water molecules are loosely bound to the sorption sites.⁷

Entropy changes were calculated from eq. (2); these values are also given in Tables I and II for desorption and adsorption, respectively. ΔS values range from 8.64 cal/mol K at 5% MC to 1.12 cal/mol K at 20% MC for desorption, while adsorption values range from -4.86 cal/mol K at 5% MC to -0.52 cal/mol K at 20% MC.

We observed that ΔS is greater at lower moisture contents, which shows that the sorbed water molecules are more ordered at lower moisture contents compared to at higher moisture contents.⁹ Tables I and II show that ΔS increases slightly with an increase in the temperature.

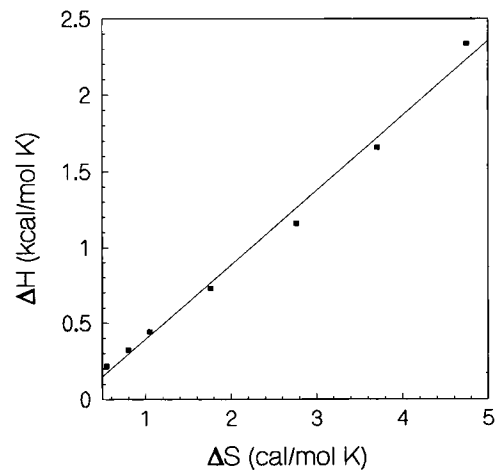


Figure 4 Enthalpy changes as a function of entropy changes for adsorption of water in wood.

Examination of Tables I and II shows that magnitudes of ΔH , ΔG , and ΔS are different for desorption and adsorption. This may be attributed to the fact that during swelling or shrinking, stresses will be generated which may lead to some irreversible changes in wood cell-wall structure.

Plots for the changes in enthalpies and entropies were obtained for desorption and adsorption, respectively. Values of entropies considered were averaged over temperature due to their small variation with temperature. These are straight lines (Figs. 3 and 4) of the following form:

$$\Delta H = T_b \Delta S + A \quad (4)$$

where T_b is the isokinetic temperature³ and A is a constant. T_b and A were found to be 447.3 K and -137.79 for desorption and 488.9 K and -93.62 for adsorption, respectively. It seems that the enthalpy–entropy compensation relationship will have some dependence on temperature. However an investigation of this dependence is beyond the scope of the present paper.

It should be noted here that A has dimensions of energy. Also, the linear enthalpy–entropy relationship [eq. (4)] must be consistent with the Gibbs free energy relation [eq. (2)].¹⁰ This consistency requires the nature of A to be similar to that of changes in free energy, which is the energy required to do the work in swelling the wood. Thus A is related to the degree of swelling which, in turn, is related to the porosity and density of the wood.

Figures 3 and 4 suggest a good degree of correlation between enthalpy and entropy and hence demonstrate the existence of enthalpy–entropy compensation for the wood–water system investigated in the present study. The value of harmonic mean temperature, $T_{hm} (=n / \sum_{i=1}^n 1/T)$ corresponding to the data used here, is 309.9 K—which is signifi-

cantly different from the isokinetic temperatures for desorption and adsorption. It is concordant with the fact that, for the occurrence of enthalpy–entropy compensation, T_{hm} should differ significantly from the isokinetic temperature.¹⁰

CONCLUSIONS

A linear relationship is found to exist between enthalpy (ΔH) and entropy (ΔS) of sorption (desorption and adsorption), hence enthalpy–entropy compensation operates for a wood–water system. We believe that enthalpy–entropy compensation is a manifestation of sorption phenomena because during sorption, the enthalpy of water molecules changes significantly. This would also be reflected in a change in entropy due to restructuring of water molecules. Studies of this effect are important for the characterization and understanding of sorption phenomena.

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