Chemistry of Natural Compounds, Vol. 40, No. 5, 2004

THERMODYNAMIC ANALYSIS OF THE STATE OF WATER IN VARIOUS CELLULOSES

Kh. I. Akbarov

UDC 541:64:536:634.0813.13

Several monographs [1-4] and articles [5-13] address the interaction of water with cellulose. We compared the thermodynamics of the state of water in various celluloses based on existing theories and sorption models. At present, no theory completely characterizes the sorption of water by cellulose as a function of vapor activity over a wide range of relative pressures. However, a combination of the generally accepted theory of polymer solutions with those of clusters (Zimm—Lundberg [4]), BET, and de Boer—Zwicker [11-13] enables the results of investigations on the sorption of water in polar polymers to be interpreted.

Table 1 lists calculated properties of the capillary-porous structure, monolayer volume, molecular packing, and thermodynamic parameters for the interaction of various celluloses with water. It can be seen that native cellulose (NC) and then wood cellulose (WC), for which the monolayer volume is also high, have the most developed surfaces. The Gibbs energy is also most negative for these samples.

It should be noted that the enthalpy factor dominates for highly crystalline samples for which the coefficient of molecular packing is also high. For NC and cotton cellulose (CC), the entropic component of the Gibbs energy contributes most to the energy.

The calculated thermodynamic parameters of mixing agree in general with the calculated Flory—Higgins parameter and the Zimm—Lundberg cluster-formation function (Table 2), i.e., the most extensive cluster formation is observed for flax, WC, and microcrystalline cellulose (MCC), for which χ_{Is} has the highest values.

It seemed interesting to explain the results obtained from the BET theory with those from pulsed NMR [8-10]. The calculations showed (Table 2) that samples of flax, WC, and MCC have high values for the energy consants and the most extensive cluster formation. The thermodynamic parameters for the interaction agree with the calculated cluster formation.

Therefore, the energy constants from the BET theory can predict cluster formation, like NMR. This is confirmed by Zimm—Lundberg calculation of the cluster number. An analysis of the results using the de Boer—Zwicker theory, which was developed to describe the interaction of polar sorbates with polar sorbents, showed that linearization of the sorption isotherms for water vapor can determine the value of the "true" sorption that is not complicated by capillary condensation and water cluster formation. The values of the equilibrium water sorption **a** given in Table 2 refer to the linear part of the sorption isotherm.

Thus, the combination of various theoretical models for describing the sorption of water vapor by cellulose is fruitful and facilitates a better understanding of the mechanism of interaction in the cellulose—water system and the mechanism of cluster formation.

The sorption investigations were carried out in a high-vacuum apparatus with a McBain balance of sensitivity $3 \cdot 10^{-3}$ g/mm with a residual pressure of 10^{-3}-10^{-4} Pa and 298 K. The spring expansion was monitored using a Km-8 cathetometer. The enthalpy of mixing was determined using an Calvet DAK-1-1 isothermal microcalorimeter; the density and molecular packing of samples, by pycnometry in heptane as a standard and water.

Mirzo Ulugbek National University of Uzbekistan, 700174, Tashkent, NUUz, fax (99871) 144 77 28, e-mail: akbarov_Kh@rambler.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 425-426, September-October, 2004. Original article submitted June 21, 2004.

0009-3130/04/4005-0518

TABLE 1. Properties of the "Aqueous Surface" and Thermodynamics of Mixing of Various Celluloses with Water

Sample	X_m	r_{av}, cm^2/g	W_O, cm^3/g	S_{sp}, m^2/g	-ΔH, J/g	TΔS, J/deg·g	$-\Delta g_{max}^m$	$-\Delta G_i$
							J/g	
NC	0.0509	26.44	0.24	178.9	8.76	15.57	21.5	24.30
CC	0.0348	21.86	0.13	116.0	7.12	11.53	16.2	18.65
WC	0.0415	30.70	0.22	145.9	18.00	3.30	18.1	21.30
Flax	0.0376	25.73	0.17	132.2	20.30	-8.40	10.5	11.90
MCC	0.0309	17.20	0.12	113.7	15.00	1.20	14.0	16.20

TABLE 2. Analysis of the State of Water in Cellulose Based on Various Theoretical Sorption Models

Sample	$K_{st.por}$	C	a (mmol/g), at $a_i = 0.80$	$\Delta G_{11}/V_1$, at $a_i = 0.20$	χ_{ls}, at $a_i = 0.05$	Nc
NC	0.7672	6.24	6.4	7.72	1.29	1-2
CC	0.6924	7.05	4.4	10.90	1.38	1-3
WC	0.7067	7.34	4.2	16.20	1.86	1-5
Flax	0.7018	7.50	3.7	18.30	1.55	1-5
MCC	0.7776	7.30	2.7	10.59	1.67	1-4

REFERENCES

1. E. E. Fainberg and S. P. Papkov, *Interaction of Cellulose and Cellulosic Materials with Water* [in Russian], Khimiya, Moscow (1976).
2. I. A. Tarchevskii and G. N. Marchenko, *Biosynthesis and Structure of Cellulose* [in Russian], Nauka, Moscow (1985).
3. B. S. Chudinov, *Water in Wood* [in Russian], Nauka, Novosibirsk (1984).
4. S. P. Rowland (ed.), Am. Chem. Soc. Symp. Ser. No. 127: *Water in Polymers*, Am. Chem. Soc., Washington, D. C. (1980).
5. I. D. Zenkov, V. Yu. Men′ko, M. V. Frolov, V. I. Slovetskii, and S. P. Papkov, *Vysokomol. Soedin., Ser. B*, **27**, No. 6, 407 (1985).
6. S. Sh. Rashidova, V. L. Voropaeva, Yu. V. Pakharukov, and I. N. Ruban, in: Abstracts of Papers of the International Conference *"Synergy of Macromolecular Hierarchical Structures,"* Tashkent (2000), 19.
7. Kh. I. Akbarov, R. S. Tillaev, B. U. Umarov, B. S. Sagdullaev, and A. S. Sidikov, *Khim. Prir. Soedin.*, Spec. Issue, 39 (2002).
8. N. Sh. Ashurov, M. A. Karabaeva, and T. I. Usmanov, in: Abstracts of Papers of the International Symposium *"Science of Polymers on the Threshold of the XXIst Century,"* Tashkent (1999), 108.
9. T. I. Usmanov, N. Sh. Ashurov, and S. Sh. Rashidova, Collection of Works of The Institute of Polymer Chemistry and Physics, Academy of Sciences of the Republic of Uzbekistan, Tashkent (2001), 179.
10. T. I. Usmanov, N. Sh. Ashurov, and S. Sh. Rashidova, *Vysokomol. Soedin., Ser. B*, **43**, No. 9, 1570 (2001).
11. Kh. I. Akbarov and R. S. Tillaev, in: Abstracts of Papers of the Conference *"Chemistry and Reactivity of Cellulose and Its Derivatives,"* Cholpon-Ata (1991), 25.
12. Kh. I. Akbarov and R. S. Tillaev, *Khim. Prir. Soedin.*, Spec. Issue, 58 (1999).
13. I. S. Tyukova, A. I. Suvorova, A. P. Petrova, and G. A. Vikhoreva, *Vysokomol. Soedin., Ser. A*, **45**, No. 5, 791 (2003).