J. Chem. Thermodynamics 81 (2015) 184–226

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

A thermodynamic investigation of the cellulose allomorphs: Cellulose(am), cellulose Iβ(cr), cellulose II(cr), and cellulose III(cr) ☆

Robert N. Goldberg [a,*], Jacob Schliesser [b], Ashutosh Mittal [c], Stephen R. Decker [c], Ana Filipa L.O.M. Santos [d], Vera L.S. Freitas [d], Aaron Urbas [a], Brian E. Lang [a], Christian Heiss [e], Maria D.M.C. Ribeiro da Silva [d], Brian F. Woodfield [b], Rui Katahira [c], Wei Wang [c], David K. Johnson [c]

[a] Biosystems and Biomaterials Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
[b] Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, USA
[c] National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401, USA
[d] Centro de Investigação em Química, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal
[e] Complex Carbohydrate Research Center, 315 Riverbend Road, Athens, GA 30602, USA

ARTICLE INFO

Article history:
Received 29 July 2014
Received in revised form 5 September 2014
Accepted 8 September 2014
Available online 14 October 2014

Keywords:
Cadoxen
Calorimetry
Cellulose amorphous
Cellulose I
Cellulose II
Cellulose III
Enthalpy
Entropy
Gibbs free energy
Heat capacity
NMR

ABSTRACT

The thermochemistry of samples of amorphous cellulose, cellulose I, cellulose II, and cellulose III was studied by using oxygen bomb calorimetry, solution calorimetry in which the solvent was cadoxen (a cadmium ethylenediamine solvent), and with a Physical Property Measurement System (PPMS) in zero magnetic field to measure standard massic heat capacities $C^{\circ}_{p,w}$ over the temperature range $T = (2$ to $302)$ K. The samples used in this study were prepared so as to have different values of crystallinity indexes *CI* and were characterized by X-ray diffraction, by Karl Fischer moisture determination, and by using gel permeation chromatography to determine the weight average degree of polymerization DP_w. NMR measurements on solutions containing the samples dissolved in cadoxen were also performed in an attempt to resolve the issue of the equivalency or non-equivalency of the nuclei in the different forms of cellulose that were dissolved in cadoxen. While large differences in the NMR spectra for the various cellulose samples in cadoxen were not observed, one cannot be absolutely certain that these cellulose samples are chemically equivalent in cadoxen. Equations were derived which allow one to adjust measured property values of cellulose samples having a mass fraction of water w_{H_2O} to a reference value of the mass fraction of water w_{ref}. The measured thermodynamic properties (standard massic enthalpy of combustion $\Delta_c H^{\circ}_w$, standard massic enthalpy of solution $\Delta_{sol} H^{\circ}_w$, and $C^{\circ}_{p,w}$) were used in conjunction with the measured *CI* values to calculate values of the changes in the standard massic enthalpies of reaction$\Delta_r H^{\circ *}_w$, the standard massic entropies of reaction $\Delta_r S^{\circ *}_w$, the standard massic Gibbs free energies of reaction $\Delta_r G^{\circ *}_w$, and the standard massic heat capacity $\Delta_r C^{\circ}_{p,w}$, for the interconversion reactions of the pure $(CI = 100)$ cellulose allomorphs, *i.e.*, cellulose(am), cellulose I(cr), cellulose II(cr), and cellulose II(cr), at the temperature $T = 298.15$ K, the pressure $p^{\circ} = 0.1$ MPa, and $w_{H_2O} = 0.073$. The "*" denotes that the thermodynamic property pertains to pure cellulose allomorphs. Values of standard massic enthalpy differences $\Delta^T_0 H^{\circ}_w$, standard massic entropy differences $\Delta^T_0 S^{\circ}_w$, and the standard massic thermal function $\Phi^{\circ}_w = \Delta^T_0 S^{\circ}_w - \Delta^T_0 H^{\circ}_w / T$ were calculated from the measured heat capacities for the cellulose samples and for the pure cellulose allomorphs. The extensive literature pertinent to the thermodynamic properties of cellulose has been summarized and, in many cases, property values have been calculated or recalculated from previously reported data. The thermodynamic property data show that cellulose(am) is the least stable of the cellulose allomorphs considered in this study. However, due to the uncertainties in the measured property values, it is not possible to use these values to order the relative stabilities of the cellulose (I, II, and III) crystalline allomorphs with a reasonable degree of certainty. Nevertheless,

☆ This is an official contribution of the National Institute of Standards and Technology and is not subject to copyright in the United States. Certain commercial equipment, instruments, or materials are identified in this paper to specify the experimental procedures adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology (NIST), nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

* Corresponding author. Tel.: +1 3019752584; fax: +1 3013305449.
E-mail addresses: robert.goldberg@nist.gov (R.N. Goldberg), jacob_schliesser@me.com (J. Schliesser), ashutosh.mittal@nrel.gov (A. Mittal), steve.decker@nrel.gov (S.R. Decker), ana.santos@fc.up.pt (A.F.L.O.M. Santos), vera.freitas@fc.up.pt (V.L.S. Freitas), aaron.urbas@nist.gov (A. Urbas), brian.lang@nist.gov (B.E. Lang), cheiss@ccrc.uga.edu (C. Heiss), mdsilva@fc.up.pt (M.D.M.C. Ribeiro da Silva), brian_woodfield@byu.edu (B.F. Woodfield), rui.katahira@nist.gov (R. Katahira), wei.wang@nrel.gov (W. Wang), david.johnson@nrel.gov (D.K. Johnson).

http://dx.doi.org/10.1016/j.jct.2014.09.006
0021-9614/

based on chemical reactivity information, the qualitative order of stability for these three allomorphs is cellulose III(cr) > cellulose II(cr) > cellulose Iβ(cr) at $T = 298.15$ K. However, as evidenced by the fact that cellulose I(cr) can be reformed by the application of heat and water to a sample of cellulose III(cr), the differences in the stabilities of these three allomorphs appear to be small and may be temperature dependent. Standard thermodynamic formation properties as well as property values for the conversion reactions of the cellulose allomorphs to α-D-glucose(cr) have been calculated on the assumption that $S^{\circ}_{w} \rightarrow 0$ as $T \rightarrow 0$. The values for the standard massic Gibbs free energy of reaction $\Delta_r G^{\circ}_{w}$ for the conversion of the cellulose allomorphs to α-D-glucose(cr), with the exception of anhydrous cellulose(am), all have positive values and thus are thermodynamically not favored for mass fractions of water $w_{H_2O} < 0.073$.

1. Introduction

Cellulose, as the most abundant biological substance on Earth, has been the subject of much study [1]. Four distinct crystalline forms of cellulose are known to exist [2]. Cellulose I exists as an α or a β form [3,4]. These two forms have essentially the same backbone but differ in their hydrogen bonding patterns and in the conformations of the anhydroglucose residues and the β-1,4 linkages [5]. Cellulose II can be prepared from cellulose I either by treatment with NaOH or by solubilization followed by recrystallization. Cellulose III is obtained by treatment of either cellulose I or cellulose II with liquid ammonia. Samples of cellulose III prepared from cellulose I are often referred to as cellulose III_I in order to distinguish them from the allomorph cellulose III_{II} prepared from cellulose II. The detailed structural differences between cellulose III_I and cellulose III_{II} have not been established. Cellulose IV is obtained by heating cellulose III. In recent years, X-ray and neutron diffraction studies [5–9] have much improved our understanding of the unit cell structure and hydrogen bonding arrangements in the cellulose allomorphs. Additional information on the cellulose allomorphs can be found in the literature [2,10–12]. Actual samples of cellulose (I, II, and III) share two common features. Specifically, each contains some amorphous cellulose, often at a high mass fraction, and, unless dried thoroughly and handled with extreme care, water is present.

The aim of this study is an improved knowledge of the thermodynamic properties of the following cellulose allomorphs: cellulose(am), cellulose Iβ(cr), cellulose II(cr), and cellulose III(cr). To accomplish this, we prepared samples of the aforementioned allomorphs having various values of crystallinity indexes. We then measured values of these crystallinity indexes *CI*, of the weight average degree of polymerization DP_w, and of the mass fraction of water w_{H_2O} in each of these samples. An early decision was made to work with cellulose samples that contained water. The principal reason for this decision was the fact that naturally occurring celluloses, in fact, contain water. Also, when one is working with anhydrous cellulose, the establishment that all water has been removed without changing the character of the cellulose sample [13] is a matter of concern. Additionally, the handling of anhydrous samples of cellulose requires extreme care.

The terminology, symbols, and conventions used in this study are basic to the thermodynamic discussion and treatment of results. The reader is referred to the "Glossary and conventions" (see section 4).

NMR measurements on solutions containing the samples dissolved in cadoxen, a cadmium ethylenediamine solvent, were also performed. This was followed by measurements of standard massic enthalpies of combustion $\Delta_c H^{\circ}_{w}$ of the samples in an oxygen bomb calorimeter, of standard massic heat capacities $C^{\circ}_{p,w}$ over the temperature range $T = (2$ to $302)$ K, and of standard massic enthalpies of solution $\Delta_{sol} H^{\circ}_{w}$ of the cellulose samples in cadoxen. Equations were derived which allow one to adjust measured property values of cellulose samples having a mass fraction of water w_{H_2O} to a reference value of the mass fraction of water w_{ref}. Thus, the aforementioned measurements led to values of the standard massic enthalpies of reaction $\Delta_r H^{\circ *}_{w}$, the standard massic entropies of reaction $\Delta_r S^{\circ *}_{w}$, and the standard massic Gibbs free energies of reaction $\Delta_r G^{\circ *}_{w}$ for the interconversion reactions of the pure ($CI = 100$) cellulose allomorphs at the temperature $T = 298.15$ K, the pressure $p^{\circ} = 0.1$ MPa, and $w_{H_2O} = 0.073$. The "*" denotes that the thermodynamic property pertains to pure cellulose allomorphs. Values of standard massic enthalpy differences $\Delta^{T}_{0} H^{\circ}_{w}$, standard massic entropy differences $\Delta^{T}_{0} S^{\circ}_{w}$, and the standard massic thermal function $\Phi^{\circ}_{w} = \Delta^{T}_{0} S^{\circ}_{w} - \Delta^{T}_{0} H^{\circ}_{w}/T$ were calculated from the measured heat capacities for the cellulose samples and for the pure allomorphs. The extensive literature pertinent to the thermodynamic properties of cellulose has been summarized and, in many cases, property values have been calculated or recalculated from previously reported data. The comparison of results at different values of w_{H_2O} required values of the standard massic enthalpies of hydration $\Delta_{hyd} H^{\circ *}_{w}$ of the cellulose allomorphs. These values were calculated from results reported in the studies of Nelson [14] and Rees [15]. In addition to having these thermodynamic property values available for practical engineering calculations, a quantitative understanding of the energy relationships amongst the aforementioned allomorphs is important in understanding the biomass recalcitrance problem [16], *i.e.*, the extreme difficulty of converting cellulose to glucose. Standard thermodynamic formation properties as well as property values for the conversion reactions of the cellulose allomorphs to α-D-glucose(cr) have been calculated on the assumption that $S^{\circ}_{w} \rightarrow 0$ as $T \rightarrow 0$.

2. Experimental

2.1. Preparation of cellulose samples

A sample of cellulose Iβ (cotton linters, CAS Number 9004-34-6; catalog number 22183, lot number BCBB5964V) was obtained from Sigma-Aldrich. Amorphous cellulose samples were prepared from the cellulose Iβ sample by using a planetary ball mill (Retsh model PM100, Haan, Germany). In order to evaluate the effect of ball milling on the de-crystallization of cellulose, a sample of the cellulose Iβ was subjected to ball milling for three different time periods, *i.e.* 24 h, 30 h, and 36 h at 25 °C and at 600 rpm using ZrO_2 bowls (volume = 50 mL) and nine ZrO_2 balls. In order to avoid excessive heating of the cellulose sample during ball milling, a 5 min on and 55 min off cycle was employed. Therefore, for 24 h, 30 h, and 36 h periods the effective milling times were 120, 150, and 180 min, respectively. From X-ray diffraction, it was found that each ball milling period (24 to 36) h produced essentially amorphous cellulose with no differences in the crystallinity of the three samples. The ball milled samples are designated respectively as amorphous cellulose (24 h), amorphous cellulose (30 h), and amorphous cellulose (36 h).