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Anomeric proportions of D-glucopyranose at the equilibrium determined from ^{1}H NMR spectra II. Effects of alkali metal chlorides, $CaCl_2$ and $BaCl_2$ on the anomeric equilibrium at 25.0 °C

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ABSTRACT

The isomeric proportions of saccharides are important information to discuss the properties of the saccharides such as the solvation states, structures, functions and so on in aqueous solutions. However, the isomeric composition, which is one of the fundamental properties of saccharides in the aqueous solution, has not been fully explored experimentally. Successively to our previous study on the anomeric proportion of D-glucopyranose in the aqueous solution [J. Mol. Liq., 232 (2017) 408–415.], the salt effect on these anomeric proportions at 25.0 °C were investigated by ^{1}H NMR measurement for the cases of all alkali metal chlorides, $CaCl_2$ and $BaCl_2$. The experimental conditions were; the glucose concentration was from 0.1 wt% to 1.0 wt% and the salt molality was from 0.1 mol kg^{-1} to 0.5 mol kg^{-1}. At first, the optimal experimental conditions were confirmed in terms of the irradiation power and the target frequency of the presaturation pulse in ^{1}H NMR measurement. The ^{1}H NMR spectra measured under the optimal conditions with adequate accumulation number allowed us to determine the anomeric proportions within the error of 0.0004. The anomeric proportions of α-glucopyranose in the presence of each salts were determined from peak areas corresponding to the anomeric hydrogens of α- and β- D-glucopyranoses. For all kinds of the salts, the anomeric proportion increased consistently and the slope of the proportion decreased gradually with increasing glucose concentration at a given molality of the salts. The anomeric proportions at the infinite dilution of glucose were determined from these concentration dependences of glucose, and then the Gibbs energies of reaction for the anomerization $\Delta_r G°$ were estimated from these results. The effects of the salts on $\Delta_r G°$ were divided into two groups: (1) $\Delta_r G°$ increased when LiCl, NaCl and $CaCl_2$ were added, and (2) $\Delta_r G°$ decreased when KCl, RbCl, CsCl and $BaCl_2$ were added. The plots of $\Delta_r G°$ against the ionic radius of the cations clearly illustrated this result, that is, $\Delta_r G°$ for these two groups fell on the quite different cation radius dependences. $\Delta_r G°$ of the first group of the salts were greater than that of the salt free system. $\Delta_r G°$ for each molality of the salts linearly decreased with the cation radius, and became $\Delta_r G°$ of the salt free glucose aqueous solution around 0.17 nm irrespectively to the salt molality. On the other hand, $\Delta_r G°$ of the second group of the salts were less than that of the salt free system. $\Delta_r G°$ for each molality of the salts linearly decreased with the cation radius, and became $\Delta_r G°$ of the salt free solution around 0.08 nm irrespectively to the salt molality.

1. Introduction

Saccharides play many important biological and physiological roles such as energy storage, structural units of glycoproteins, cell walls and membranes. For aqueous solution of saccharides, the thermodynamic quantities including partial molar volume, partial molar adiabatic compression, partial molar heat capacity have been measured to investigate behaviors of the saccharides, e.g. solvation states, conformational change and so on [1–15]. Among these investigations, several research groups have studied effects of the other chemical species, such as aqueous electrolytes and aqueous non-electrolytes, on thermodynamic quantities for the saccharide aqueous solutions [9–15]. Although, in aqueous solutions, a number of the saccharides form six structures, that is anomers of pyranose, those of furanose, acyclic aldehyde form and its hydrate [16,17], precise compositions of the isomers for these saccharides have not been comprehensively investigated [16–24]. To achieve those investigations of the behaviors of the saccharides in aqueous solutions, it is necessary to measure sophisticatedly not only thermodynamic quantities but also the isomeric composition of saccharides with adequate accuracies. Probably due to difficulties in accurate determination of the composition, most of the thermodynamic quantities yet reported have been the average values of the quantities for isomers under a given condition. Thus, there is no report about the

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thermodynamic quantities for each isomer and these quantities under coexistence with other solutes. Some of rare results are the apparent molar volume and the apparent molar heat capacity for each anomer of D-glucopyranose estimated by Bernal et al. [7] and Kishore et al. [8]. However, these quantities for the anomers of D-glucopyranose were the "apparent" molar quantities determined by the extrapolation of the density or the heat capacity measured as a function of the elapsed time from dissolution of glucose into water at some finite concentrations of glucose. The deficiencies of accurate isomeric composition and thermodynamic quantities for each of isomers are now leading to prevent understanding rigorously the solvation state and behavior of the saccharides in aqueous solutions.

In recent years, the experimental equipment and techniques for analysis have been continually improved and thereby the accuracy of quantities obtained as results has been enhanced remarkably. Previously, we obtained accurate anomeric proportions of the D-glucopyranoses in the aqueous solutions at 25.0 °C from the ^{1}H NMR spectra measured under the optimal experimental conditions, and then determined the equilibrium constant and the Gibbs energy of reaction for the anomerization of D-glucopyranoses [25]. The proportion of α-D-glucopyranose increased with concentration of glucose from 0 to 10 wt%: the proportion increased steeply under 1 wt%, that was almost constant between 1 and 3 wt% and that increased again over 3 wt%. The isomeric proportions of saccharides are a considerable information to obtain the thermodynamic quantities for each of the isomers from the averaged thermodynamic quantity, and the proportions themselves are critical characteristics corresponding to hydration of the isomers. For the effects of aqueous electrolytes on the isomeric equilibria in aqueous solutions, there is no report with the exception of the experimental results reported in refs. [26,27]. However, the anomeric proportion obtained by them was roughly estimated at certain finite concentrations of glucose and the electrolytes. The comprehensive and accurate investigations for the effects of the electrolytes on the isomeric equilibria have not been conducted yet even in the aqueous solutions of glucose.

Successively to our previous study [25], we have investigated the effects of the alkali metal chlorides, $CaCl_2$ and $BaCl_2$ on the anomeric equilibrium of D-glucopyranose. At first, the optimal experimental conditions investigated in the previous study were confirmed to obtain ^{1}H NMR spectra adequate for the determination of the anomeric proportions in terms of the irradiation power and the target frequency of the presaturation pulse in ^{1}H NMR measurement. Then, we determined anomeric proportions in the glucose concentration range between 0.1 wt% and 1.0 wt% from ^{1}H NMR spectra measured at the optimal conditions for the glucose aqueous solutions including each of the alkali metal chlorides, $CaCl_2$ and $BaCl_2$ in its molality range from 0.1 mol kg^{-1} to 0.5 mol kg^{-1}. From these results, the anomeric proportion at the infinite dilution of glucose and the Gibbs energy of reaction for the anomerization were determined.

2. Experiments

2.1. Sample preparations

Glucose used as a solute was D(+)-Glucose anhydrous for biochemistry (Merck KGaA), which was crystalline of α-D(+)-glucopyranose. D_2O used as a solvent was Deuterium Oxide for NMR 99.8 atom%D (ACROS Organics). LiCl was an anhydrous chemical whose purity was 99.998% on trace metals basis (Sigma-Aldrich Co. LLC). NaCl and KCl were special grade chemicals whose purities were 99.5% (Wako Co., Ltd.). RbCl, CsCl and $CaCl_2$ were anhydrous chemicals whose purities were 99.99% on trace metals basis (Sigma-Aldrich Co. LLC). $BaCl_2$ was barium chloride dihydrate whose purity was 99.999% on trace metals bases (Sigma-Aldrich Co. LLC). These chemicals were used without further purification.

Prior to the preparation of aqueous solutions, glucose and the salts were dried for more than 9 h by using a drying oven (FS-42D, Toyo Seisakusho Co., Ltd.). The drying temperature for glucose and salts except for LiCl and $CaCl_2$ was 80 °C, and that for LiCl and $CaCl_2$ which were deliquescent chemicals was 170 °C. Then, those dried chemicals were cooled down to room temperature in a desiccator containing silica gels. At more than 16 h before the measurement of ^{1}H NMR spectra, D-glucose and a salt were dissolved in D_2O by stirring for an hour. Any reference compound was not used in our NMR measurements. The molalities of the salts in the aqueous solutions m_s were 0.1, 0.2, 0.3, 0.4 and 0.5 mol kg^{-1}, and the concentrations of D-glucose C_{glu} were 0.1, 0.3, 0.5, 0.7 and 1. Here, m_s and C_{glu} are defined respectively as following Eqs. (1) and (2),

$$m_s = \frac{w_s}{M_s\, w_{D_2O}} \tag{1}$$

$$C_{glu} = \frac{w_{glu}}{w_{glu} + w_{D_2O}} \cdot 10^2 \tag{2}$$

In these equations, w and M represent the mass and the molar mass, respectively. The subscripts s, glu and D_2O refer to the salt, glucose and D_2O, respectively.

The sample solution prepared along the above procedure was loaded into a 5 mm thin-wall NMR tube with a tube cap (Wilmad LabGlass 528-PP-8, SP scienceware Ind.), and then these were sealed with Parafilm (Bemis Co., Inc.). The solution within the NMR tube was stored in an incubator (IJ201, Yamato Scientific Co., Ltd.) at 25.0 °C for more than 15 h to equilibrate the anomerization of glucose. This minimum storing time for the equilibration has been determined from the result of an optical rotation measurement described in our previous paper [25].

2.2. ^{1}H NMR spectrum measurements

^{1}H NMR spectrum was measured by a pulse FT-NMR equipment (JNM-ECA-500, JEOL Ltd.) with an auto-tunable probe for solutions (TH5ATFG2, JEOL Ltd.). The intensity of the magnetic field and the center frequency of the RF pulse irradiated for ^{1}H nucleus were 11.629 T and 495.13 MHz, respectively. The spectral width was 9.3 kHz and a number of the time domain acquisition points was 16,384. The spinning frequency of the sample within the NMR tube in the probe was 12 Hz. Shim for the magnetic field was adjusted by an auto-gradient shim adjustment function. Free induction decay (FID) signals were acquired by using a single π/4-pulse sequence whose pulse length and pulse repetition period were 6.1 μs and 6.76 s, respectively. The resonant peak of HDO in spectra was suppressed by a standard presaturation function of the ECA-500 spectrometer in which a 71 W transmitter for presaturation was incorporated as a standard equipment. The attenuation rate and the target frequency of the presaturation pulse were 80 dB and $\delta_{HDO} + 0.0005$ ppm, respectively. Here, δ_{HDO} represents the peak chemical shift of the signal of HDO measured without the presaturation. The attenuation rate and the target frequency of the presaturation pulse were determined in our previous work [25] to obtain spectra in which resonant peaks of protons bonding to the anomeric carbons in α- and β- D-glucopyranoses were symmetric and a baseline drew a flat line without any remarkable phase distortion. The accumulation numbers n_{acc} employed in this study were listed in Table 1 with maximum deviation $D_{max}(P_{a\text{-}gp})$ from averaged value for the anomeric proportion of α-D-glucopyranose $P_{a\text{-}gp}$ obtained by analyzing spectrum of a glucose-salt aqueous solution at each glucose concentration. The definition of the anomeric proportion in this study can be found in the latter section. The temperature in the probe involving the NMR tube was maintained at 25.0 ± 0.1 °C. All spectra were analyzed by using Delta NMR software produced by JEOL Ltd. On the fast Fourier transform, the accumulated FID signals were apodized by a multiplication with an exponential decay whose width was 0.2 Hz, and were processed using the zero-filling factor of 1.