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SHORT COMMUNICATION

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Stereochemical aspects of micellar properties of esterified glucoside surfactants in water: apparent molar volume, adiabatic compressibility, and aggregation number

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Abstract The apparent molar volume and the apparent molar adiabatic compressibility of the sugar-based surfactants methyl 6-*O*-octanoyl-α-D-glucopyranoside (α-MOnG), methyl 6-*O*-octanoyl-β-D-glucopyranoside (β-MOnG), and octyl β-D-glucoside were measured over a wide concentration range. Also, the aggregation number of their micelles was determined from the Debye plot using static light scattering data. It was found that the micellar aggregation number for α-MOnG is 179 at 35 °C, which is 1.5 times larger than that for β-MOnG, suggesting that the anomerism of the head group influences the packing of the monomers during micelle formation.

Key words Sugar surfactant · Anomerism · Micelle · Compressibility · Static light scattering

Introduction

In recent years, sugar-based surfactants, which can be produced from carbohydrate, have been growing in interest because of their potential use for cosmetic and household products. Alkyl polyglycosides have already been used as low irritant, easily biodegradable, commodity detergents. Also, octyl β-D-glucoside (β-OG) is frequently used in biochemical research as a reagent for nondenaturing extraction and purification of membrane proteins [1, 2]. The properties of sugar surfactants depend considerably on the kind of sugar unit in the head group and its stereochemical nature [3–8]. The present study aims to elucidate the relation between the surfactant properties and the nature of the sugar unit in the head group.

Recently, the process of regioselective esterification of sugars has been developed and new types of sugar-based surfactants having considerable purity have become available in large enough quantities for physicochemical analysis [9, 10]. This allows us to study their basic solution properties in a systematic way. In this study, we measured adiabatic compressibility for aqueous solutions of methyl 6-*O*-octanoyl-D-glucopyranosides to elucidate the hydration behavior and static light scattering to know the aggregation number of the micelles of those surfactants. The data obtained were compared to those of β-OG. We focused our attention on the effect of anomerism at the acetal carbon (C-1) of the glucopyranoside unit. The chemical structures of the surfactants used in this study are illustrated in Fig. 1.

Experimental

Materials

The samples of the α- and β-anomers of methyl 6-*O*-octanoyl-D-glucopyranoside (α-MOnG and β-MOnG, respectively) were synthesized from the corresponding methyl D-glucosides by means of regioselective esterification with lipase [9, 10] and were recrystallized several times from diethyl ether/chloroform (19:1). The purity was above 99% as determined by gas chromatography. The crystal structure of β-MOnG has already been reported [11]. β-OG (purity above 98%) was purchased from Sigma, St. Louis, and was used without further purification. The water used was purified with a Milli-Q Labo. All solutions were made up by weight, and the same solutions were used for density and ultrasound velocity measurements.

Density and ultrasound velocity measurements

For the density measurements, we employed an oscillating tube density meter (Anton Paar DMA 60/602, Graz) in which a glass U-tube cell is set into oscillation by an electronic excitation system. The temperature of the sample was stabilized within ±0.01 °C using a water circulator (Haake DC5-K20). The accuracy of the measurements was $\pm 5 \times 10^{-6}$ g/cm^3.

The ultrasound velocity in the solution was measured by a "sing-around pulse method" using an ultrasound velocimeter (UVM-2, Chou-onpa Kogyo Co., Tokyo) which worked at a frequency 2 MHz. The temperature stability was ±0.002 °C, and the accuracy of the sound velocity measurement was ±0.1 m s^{-1} [12].

The apparent molar volumes, ϕ_V, and apparent molar adiabatic compressibilities, ϕ_K, of solute in water were calculated from the following equations [12]:

$$\phi_V = 1000(\rho_1 - \rho)/(m_2\rho\rho_1) + (M/\rho) \tag{1}$$

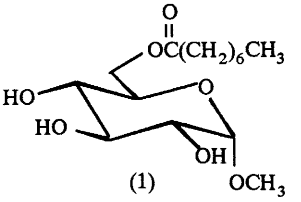
$$\phi_K = 1000(\beta - \beta_1)/(m_2\rho_1) + \beta\phi_V \tag{2}$$

$$\beta = 10^{-3}/(u^2\rho)\ , \tag{3}$$

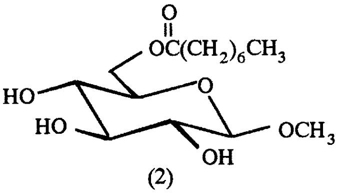
where ρ is the solution density, β the coefficient of adiabatic compressibility of the solution, M the molecular weight of the solute, m_2 the molality, and u the sound velocity in the solution. The subscript 1 refers to solvent, i.e., pure water.

Static light scattering measurements

Static light scattering measurements were carried out with an apparatus described previously [13] using a He-Ne laser (NEC, GLG 5601, 15 mW) as a light source. The scattering angle was fixed to 90°. The solutions were filtered twice through Milex VV25 (0.1-μm pore size, Millipore) and were introduced into a clean cell made of quartz (12 × 16 × 16 mm). The refractive index increments (d*n*/d*c*) were determined with a differential refractometer (Otsuka Electronics, RM102) at 632.8 nm. The apparatus was calibrated with aqueous solutions of potassium chloride [14].



(1)



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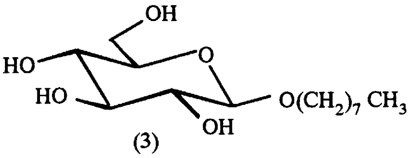

(3)

Fig. 1 The chemical structures of three surfactants used. **1** Methyl 6-*O*-octanoyl-α-D-glucopyranoside (*α-MOnG*). **2** Methyl 6-*O*-octanoyl-β-D-glucopyranoside (*β-MOnG*). **3** Octyl β-D-glucopyranoside (*β-OG*)

Results and discussion

Partial molar volume and partial molar compressibility

The concentration dependence of the density and ultrasound velocity for aqueous solutions of β-MOnG, β-OG (at 25 and 35 °C), and α-MOnG (at 35 °C) are shown in Fig. 2. (The measurements were not made for concentrations of β-MOnG solutions higher than 1 wt% due to precipitation at 25 °C.) The plots in Fig. 2 may be fitted well with two straight lines having different slopes to give a break at the critical micelle concentration (cmc). The cmc values thus estimated are listed in Table 1. ϕ_V and ϕ_K were calculated from Eqs. (1)–(3) and are plotted against molality Fig. 3. The concentration dependences of ϕ_V and ϕ_K are similar to those of other common surfactants [15–17]; they do not change

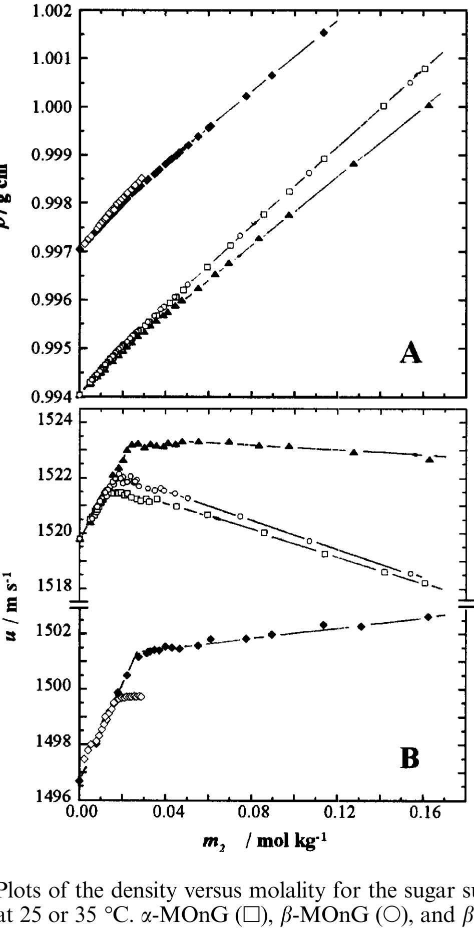

Fig. 2 **A** Plots of the density versus molality for the sugar surfactant solutions at 25 or 35 °C. α-MOnG (□), β-MOnG (○), and β-OG (▲) at 35 °C. β-MOnG (◇) and β-OG (◆) at 25 °C. **B** Plots of the ultrasound velocity versus molality of the surfactants at 25 or 35 °C. *Symbols* are the same as in **A**

Table 1 Physicochemical properties of sugar-based surfactants in water

Surfactant	T/°C	Critical micelle concentration /mol kg^{-1}	V_0/cm^3 mol^{-1}	K_0/10^{-8} cm^3 mol^{-1} Pa^{-1}	V_{mic}/cm^3 mol^{-1}	K_{mic}/10^{-8} cm^3 mol^{-1} Pa^{-1}
β-MOnG	25	0.017	266.3	−1.5	274.5	9.6
	35	0.018	270.0	2.3	279.4	11.8
α-MOnG	35	0.013	269.8	2.5	278.6	11.6
β-OG	25	0.026	244.0	−2.1	254.7	9.3
	25	0.024[a]	246[a], 253[b]	−1.28[b]	254 ± 1.5[a], 261[b]	10[b]
	35	0.024	247.0	0.0	256.6	9.6

[a] Ref. [19]
[b] Ref. [20]

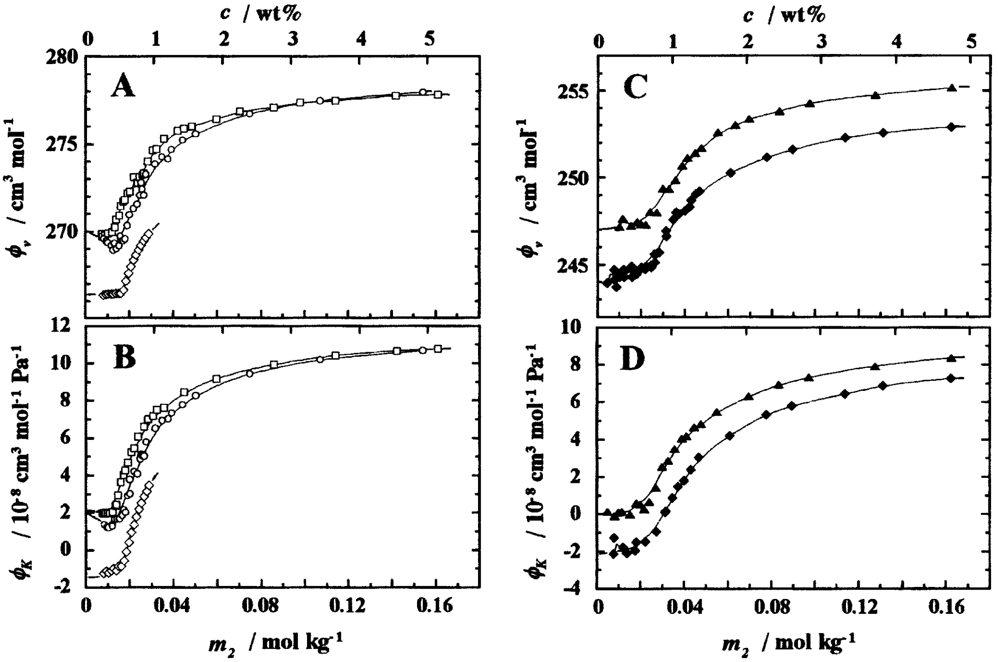

Fig. 3 Concentration dependence of the apparent molar volume (**A, C**) and of the apparent molar compressibility (**B, D**) at 25 or 35 °C. **A, B** Data for α-MOnG and β-MOnG. **C, D** Data for β-OG. *Symbols* are the same as in Fig. 2

much in the premicelle region, increase sharply around the cmc, and level off gradually at higher concentration. The values of the partial molar quantities at infinite dilution, V_0 and K_0, were estimated by extrapolation of the curve to zero concentration. Also, the partial molar quantities in the micellar state, V_{mic} and K_{mic}, were derived from the following equations using the data from above the cmc.

$$\begin{aligned} V_{\mathrm{mic}} &= \phi_{\mathrm{v}} + m_2\left(\frac{\partial\phi_{\mathrm{v}}}{\partial m_2}\right)_{T,P} = \left(\frac{\partial(m_2\phi_{\mathrm{v}})}{\partial m_2}\right)_{T,P}, \\ K_{\mathrm{mic}} &= \phi_{\mathrm{K}} + m_2\left(\frac{\partial\phi_{\mathrm{K}}}{\partial m_2}\right)_{T,P} = \left(\frac{\partial(m_2\phi_{\mathrm{K}})}{\partial m_2}\right)_{T,P}. \end{aligned} \tag{4}$$

When the concentration was well above the cmc, the values obtained from Eq. (4) were independent of the concentration. These quantities are summarized in Table 1.

One can see from Table 1 that

1. The cmc is in the following order: β-OG > β-MOnG > α-MOnG.
2. The partial molar quantities of β-MOnG and α-MOnG are almost the same.
3. V_{mic} and K_{mic} in the micellar state are 8.2–10.7 cm^3 mol^{-1} and (9.1–11.4) × 10^{-8} cm^3 mol^{-1} Pa^{-1} larger than V_0 and K_0, respectively.

The volume data usually give us poor information on the hydration layer around the surfactant molecules since the largest part of V_0 and V_{mic} may be caused by the intrinsic volume of the surfactant in water and in the micellar aggregates, respectively. In contrast, the compressibility data provide insight into the compressibility of the hydration layer around the surfactant molecules. Usually those solutes with more negative the partial molar compressibility, the occurrence of strong hydra-

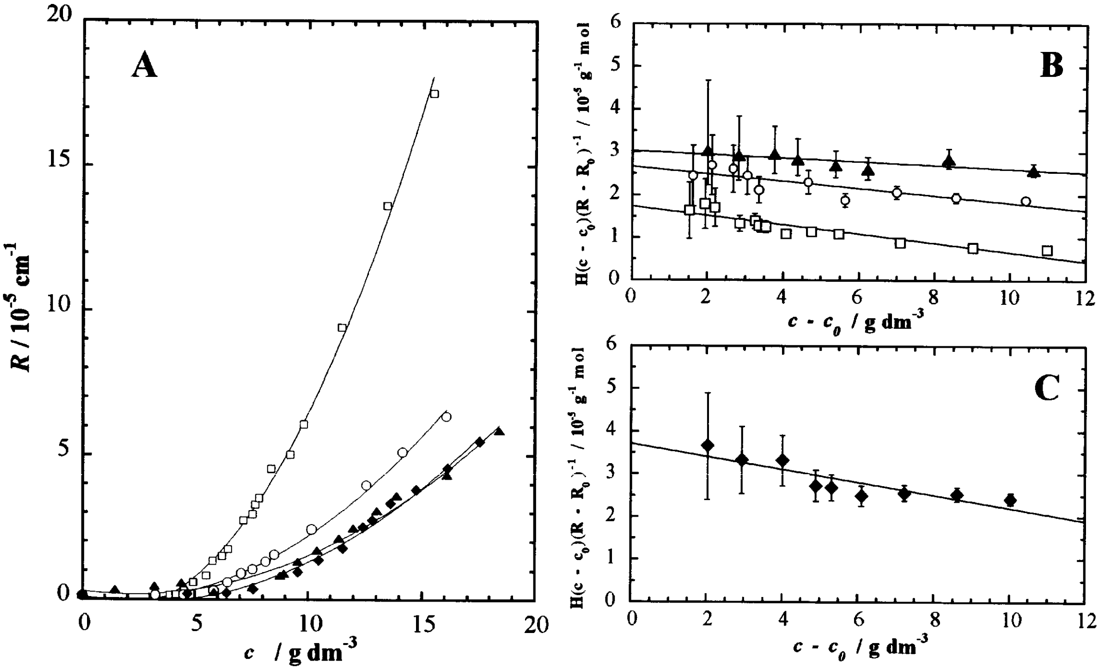

Fig. 4 **A** Concentration dependence of reduced light scattering intensity α-MOnG (□), β-MOnG (○), and β-OG (▲) at 35 °C. β-OG (◆) at 25 °C. Debye plots for the sugar surfactants at 35 °C (**B**) and at 25 °C (**C**). *Symbols* are the same as in **A**

tion is suggested. When the surfactants form micelles, however, the hydrophobic hydration around the alkyl chain disappears and the compressibility of the micellar aggregates becomes the dominant factor. It has been reported that partial molar compressibility of methyl α-glucopyranoside is more negative than the corresponding β-anomer, suggesting the hydration of the former is stronger than that of the latter [18], but our results for α-MOnG and β-MOnG indicate almost the same value of K_0. It is supposed that the ester linkage at the C-6 carbon strongly affects the water structure around glucopyranoside, and the difference between the α- and β-anomers diminishes. It is also to be noted that the hydration layer around the alkyl chain is usually less compressible than bulk water, but K_0 of α-MOnG and β-MOnG is positive at 35 °C. This suggests that hydrated water around the α-MOnG and β-MOnG molecules is more easily compressed than bulk water.

Aggregation number of the micelles

The results of the static light scattering experiments are shown in Fig. 4A in terms of the Rayleigh ratio, R, as a function of surfactant concentration, c. The scattering intensity increased sharply above the cmc. The weight-average aggregation number of the micelles at the cmc, N, was estimated from the Debye plot according to the following equation

$$H(c - c_0)(R - R_0)^{-1} = (MN)^{-1} + 2B_2(c - c_0) \ , \qquad (5)$$

where c_0 represents the cmc, R_0 the Rayleigh ratio at the cmc, M the molecular weight of surfactant, B_2 the second virial constant, and H is denoted as

$$H = [4\pi^2 n_0^2 / N_A \lambda^4](\mathrm{d}n/\mathrm{d}c)^2 \ . \qquad (6)$$

Table 2 Summary of the results of the light scattering experiments for sugar-based surfactants in water

Surfactant	T/°C	dn/dc (cm^3 g^{-1}) below the critical micelle concentration	dn/dc (cm^3 g^{-1}) above the critical micelle concentration	B_2/10^{-4} mol cm^3 g^{-2}	Micellar aggregation number
β-MOnG	35	0.1361	0.1247	−9	117
α-MOnG	35	0.1380	0.1246	−11	179
β-OG	35	0.1446	0.1354	−4	112
	25	0.1483	0.1322	−15	92
	22[a]	0.147	0.138	−4	87

[a] Ref. [21]

Here n and n_0 are the refractive indices of the solution and the solvent, N_A is Avogadro's number and λ is the wavelength of the incident light in a vacuum.

The Debye plots are shown in Fig. 4B and C and the results of the static light scattering experiments are summarized in Table 2. One can see that the micellar aggregation number of these sugar surfactants is significantly larger than those of other typical surfactants with an octyl group (usually it is below 50 [22]) and that the aggregation number of α-MOnG is 1.5 times larger than that of β-MOnG. From geometrical considerations of amphiphilic molecules [23], one may expect that the inter-head-group repulsion of β-MOnG is stronger than that of α-MOnG. In connection with this, we should note that the area per molecule at the air–water interface, which was estimated from the surface tension data obtained around the cmc, was 0.42 and 0.38 nm^2 for β-MOnG and α-MOnG, respectively. It should be stressed that small changes in an amphiphile head group, which leave the thermodynamic properties virtually unchanged, can greatly affect the micelle size and shape [24].

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