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Acoustical Spectroscopy of Carbohydrate Aqueous Solutions: Saccharides; Alkyl Glycosides; Cyclodextrins. Part II. Association and Complexation

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Results from broadband acoustical spectroscopy for aqueous solutions of mono- and disaccharides with salts added, of various alkyl glycosides, and of α-cyclodextrin with n-octyl-β-D-glucopyranoside added are briefly summarized in view of their relevance in the study of molecular association and complexation processes. Mono- and tridentate complexes of alkali earth ions with saccharides are discussed as well as the monomer exchange between micellar structures and the suspending phase in the alkyl glycoside surfactant solutions. Particular attention is given to the behaviour at solute concentrations close to the critical micelle concentration or aggregate concentration, respectively. Also described is the competition between inclusion complex formation and self-aggregation in solutions containing cyclodextrin and alkyl glycoside surfactant.

Keywords: acoustical spectroscopy, carbohydrate-cation complexes, alkyl glycosides, cyclodextrin, micelles, inclusion complexes.

1. Introduction

In the first part of this review (Kaatze, 2010) the potential of acoustical spectroscopy has been demonstrated to uncover structural isomerisation of carbohydrates in solution and to thus contribute to a better understanding of the conformational variety of this prominent class of molecules. In this second part of the review carbohydrates sharing in association and complex formation processes will be the focus. Acoustical relaxations highlighting three molecular mechanisms will be summarized. They will demonstrate direct monitoring of dynamic processes which are hardly accessible by another single method (Weingärtner *et al.*, 2001; Matsuoka *et al.*, 2002; Fuchs, Kaatze, 2002; Upadhya *et al.*, 2003; Lee *et al.*, 2005; Pomata *et al.*, 2009; Lelong *et al.*, 2009; Gallina *et al.*, 2010; Sajadi *et al.*, 2010).

Complexation with metal ions is suspected to affect the conformational flexibility of carbohydrates. Until now equilibrium studies have been primarily performed on this subject (Rongère *et al.*, 1995). They indicated promotion of interactions between saccharides and metal ions by special hydroxyl group sequences (Angyal, 1989). Only recently acoustical relaxation studies have elucidated the kinetics of such interactions (Cowman *et al.*, 1999; Baucke *et al.*, 2004a). Some results for the complexation of physiologically important calcium ion will be given.

Recently, much attention has been directed towards environmentally friendly alkyl glycoside surfactants. Besides synthesis optimization, most work has been devoted to phase diagrams and the structure of different phases of alkyl glycoside solutions (Nickel *et al.*, 1993; Platz *et. al.*, 1995; Bonicontro *et al.*, 1996; Nilsson *et al.*, 1996; Bonicelli *et al.*, 1998; Schulte *et al.*, 1999; Häntschel *et al.*, 1999; Bogusz *et al.*, 2000). The kinetics of self-aggregation, however, has been far less regarded. Here results from broadband ultrasonic spectroscopy (Haller, Kaatze, 2009a; 2009b) on the micelle formation of some alkyl glycosides will be reported. Attention will be especially directed to the similarity with poly(ethylene glycol) monoalkyl ethers, the other popular class of non-ionic surfactants, and to the compatibility of the ultrasonic relaxation data with the well-established Teubner-Kahlweit-Aniansson-Wall model (Aniansson, 1978; 1985; Aniansson, Wall, 1974; Teubner, 1979; Kahlweit, Teubner, 1980) of stepwise formation of micelles will be considered.

The third mechanism under consideration is the formation of inclusion complexes by α-cyclodextrin. Cyclodextrins are cyclic glycosyl oligomers, receiving current wide interest (Liu, Guo, 2002) because of their ability to form inclusion complexes with guest molecules or ions. Cyclodextrin complex formation with a wide range of guests has been studied, including inorganic ions and ion complexes (Minns, Khan, 2002; Papaioannou, Ghikas, 2003; Haller *et al.*, 2006), organic ions (Yamaguchi *et al.*, 2005), surfactants (Balcerzak *et al.*, 2002; Valente *et al.*, 2005; Balcerzak, 2008; Haller, Kaatze, 2008; 2009c) polymers (Panneer Selvam, Geetha, 2008), alcohols (Nishikawa *et al.*, 2001; Fukahori *et al.*, 2004a), carboxylic acids (Nishikawa *et al.*, 2002), amino acids (Ugawa, Nishikawa, 2001; Fukahori *et al.*, 2004b), nucleotides (Bae, Lee, 2009), cholesterol (Yu *et al.*, 2006), and drugs (Jutunen *et al.*, 2005; Hazekamp, Verpoorte, 2006; Fukahori *et al.*, 2006). Most studies aim at the dynamical specifity of cyclodextrin, opening pathways of molecular recognition mechanisms. This contribution will be restricted to the interplay of self-aggregation and complex formation in aqueous solutions of alkyl glycoside and α-cyclodextrin.

2. Carbohydrate-cation interactions

Interactions between carbohydrates and Ca^{2+} ions are ubiquitous in nature and are thus taken an example to show their kinetic properties. Studying car-

bohydrate solutions with added salt, potential cation-anion complexes have to be carefully considered. In order to reduce effects from such complexes monovalent anions are preferably used. As illustrated by the acoustical spectra in Fig. 1, however, even 2:1 valent salts may reveal relaxation behaviour within the frequency range of interest (Baucke *et al.*, 2004b). The relaxation amplitude is substantially larger with spectra for $Ca(NO_3)_2$ solutions than for $CaCl_2$ solutions, probably because interactions of Ca^{2+} with lone electron pairs and/or the delocalized π orbital of the nitrate ion are stronger than with the chloride ion. Carbohydrate-cation complexation studies, therefore, have been preferably performed with chlorides, displaying negligibly small effects from cation-anion structures.

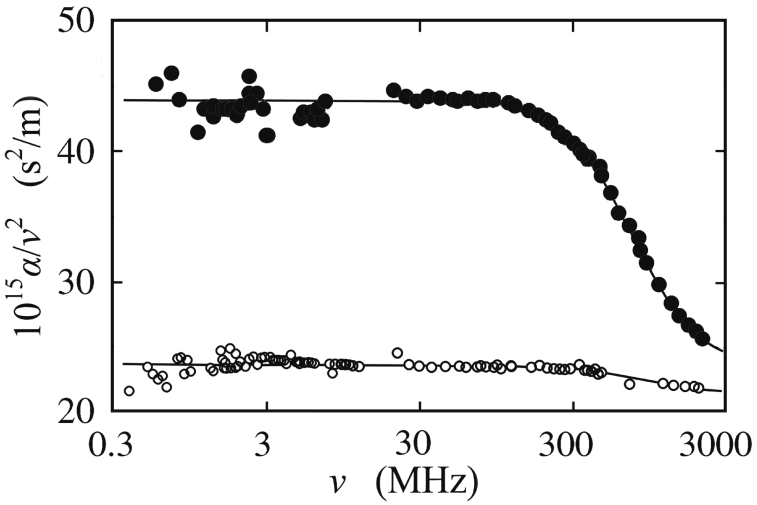

Fig. 1. Acoustical attenuation coefficient α per ν^2 *versus* frequency ν for 1 mol/l solutions of calcium nitrate (•) and calcium chloride (○) in water at 25°C (Baucke *et al.*, 2004b).

It is only briefly mentioned that independence of the relaxation time τ from the salt concentration of $CaCl_2$ aqueous solutions as well as independence of τ from the radius and electronic structure of the cation, when Ca^{2+} is exchanged for another two-valent metal ion, suggests the relaxation in the acoustical spectra (Fig. 1) to be due to a unimolecular reaction. Hence the ultrasonic relaxation reflects the equilibrium

$$(\mathrm{Me}\cdots\mathrm{L})^+ \leftrightarrow (\mathrm{Me}-\mathrm{L})^+ \tag{1}$$

between a complex of encounter, $(\mathrm{Me}\cdots\mathrm{L})^+$, and a solvent separated outer sphere complex, $(\mathrm{Me}-\mathrm{L})^+ = \mathrm{Me}^{2+}(\mathrm{H_2O})\mathrm{L}^-$. Here Me^{2+} denotes the metal ion and L^- the ligand. The above suggestion is supported by an estimation of the relaxation rate for the process of encounter

$$\mathrm{Me}^{2+} + \mathrm{L}^- \leftrightarrow (\mathrm{Me}\cdots\mathrm{L})^+ \tag{2}$$

using Debye-Eigen-Fuoss theory (Debye, 1942; Eigen, 1954; Fuoss, 1958), from which relaxation rates well above the frequency range of measurement follow.

Acoustical attenuation spectra identify two groups of saccharide solutions. Within one group, to which belong D-glucose and D-maltose, reveal somewhat enhanced relaxation amplitudes when salt is added, but do not indicate additional effects. The other group exhibits significant changes in the relaxation times of the carbohydrate relaxation terms (Baucke *et al.*, 2004a). This group includes D-xylose and D-fructose, for which also an additional relaxation term emerges on addition of salt. Figure 2 shows the noticeable effect of $CaCl_2$ in the spectra of a D-fructose solution. The data are presented in the excess attenuation per wavelength format

$$(\alpha\lambda)_{\mathrm{exc}} = \alpha\lambda - B\nu, \tag{3}$$

since the asymptotic high-frequency background contributions $B\nu$ are of low interest (Kaatze, 2010). Here $\lambda = c_s/\nu$, with c_s denoting the sound velocity, and B is independent of frequency ν.

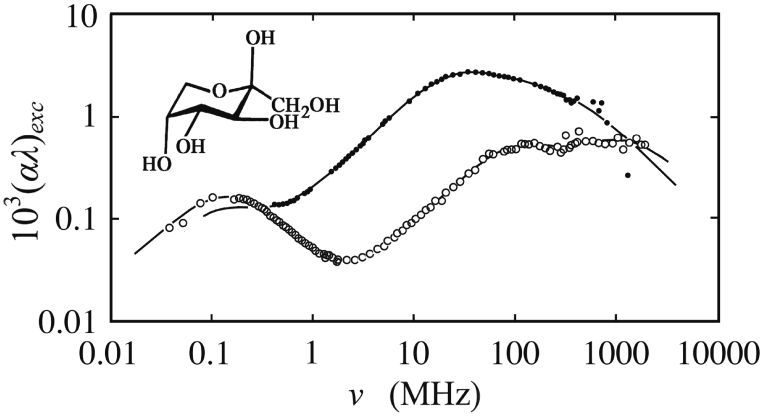

Fig. 2. Acoustical excess attenuation spectra for solutions of 0.5 mol/l D-fructose in water at 25°C without (○) and with (●) $CaCl_2$ added (Baucke *et al.*, 2004a). The salt concentration is 0.5 mol/l.

Whereas the low-frequency chair – chair relaxation term in this spectrum (Kaatze, 2010) remains probably unchanged, the relaxation term due to the pseudorotation of D-xylose is shifted to considerably lower frequencies, clearly pointing at vital carbohydrate-cation interactions (Baucke *et al.*, 2004a). Obviously the Ca^{2+} ion tends to stiffen the saccharide ring, thus increasing the potential energy barrier between a chair conformer and labile boat or skewed boat conformers (Kaatze, 2010).

Explicit evidence of carbohydrate-cation interactions is provided by an additional relaxation term in the spectra of monosaccharides with calcium salts added. Relaxation times in a rather small range between 3.5 and 6.8 ns have been obtained from a regression analysis of the acoustical spectra of D-xylose,

D-fructose and methyl-β-D-arabinopyranoside solutions (Cowman *et al.*, 1999; Baucke *et al.*, 2004a). As bicyclic 1,6-anhydro-β-glucopyranoside does not reveal acoustical excess attenuation within the frequency range under consideration (Kaatze, 2010) a clear-cut discussion of the additional relaxation behaviour is possible for the spectra of its solutions with salt added (Fig. 3). Surprisingly, the excess attenuation spectrum discloses two relaxation terms, suggesting a multi-step association. In correspondence with the conformational variations of carbohydrates described in part I of this review and with the cation-anion complexation term mentioned above, relaxation times τ_1 and τ_2 are roughly independent of carbohydrate and salt concentrations. Hence the relaxation terms in the spectra of 1,6-anhydro-β-glucopyranoside-calcium perchlorate solutions do not reflect the process of encounter but two equilibria in the general multi-step association scheme (Eigen, Winkler, 1970)

$$\mathrm{ch} + \mathrm{Ca}^{2+} \leftrightarrow (\mathrm{ch} \cdots \mathrm{Ca}^{2+}) \leftrightarrow (\mathrm{ch} - \mathrm{Ca}^{2+}) \leftrightarrow (\mathrm{ch} \equiv \mathrm{Ca}^{2+}). \qquad (4)$$

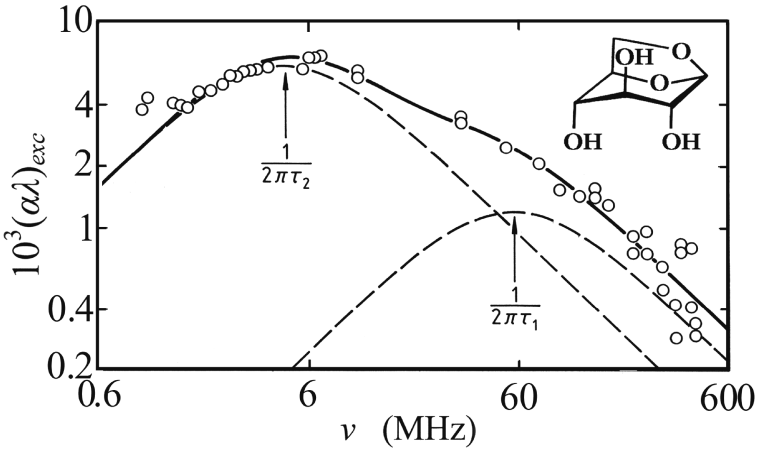

Fig. 3. Excess attenuation spectrum for an aqueous solution of 1,6-anhydro-β-glucopyranoside (0.75 mol/l) and $Ca(ClO_4)_2$ (0.77 mol/l) at 25°C. Dashed lines indicate the subdivision of the spectrum into two Debye-type relaxation terms with discrete relaxation times τ_1 and τ_2, respectively. The full line represents the sum of these terms (Cowman *et al.*, 1999).

In this scheme, ch denotes the carbohydrate, $(\mathrm{ch} \cdots \mathrm{Ca}^{2+})$ a solvent-separated complex, $(\mathrm{ch} - \mathrm{Ca}^{2+})$ a monodentate and $(\mathrm{ch} \equiv \mathrm{Ca}^{2+})$ a tridentate complex. In the latter the cation interacts with three electron lone pairs of carbohydrate hydroxyl or ether groups. A graphical representation of reaction scheme (4) is given in Fig. 4.

Because of the presence of relaxation terms due to carbohydrate isomerisation, a second term from cation complexation may sometimes be hidden in the spectra. An unambiguous example for the existence of only one relaxation (with relaxation time τ_1) is solutions of 1-methyl-β-D-arabinopyranoside with

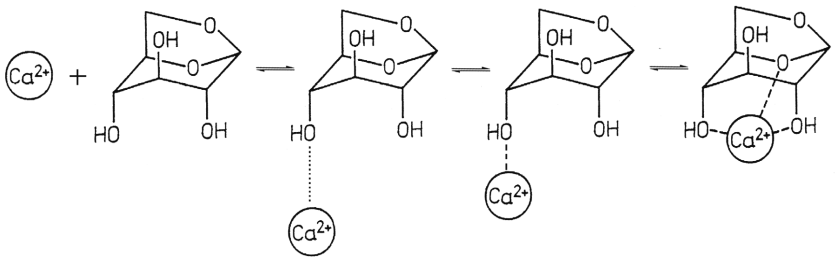

Fig. 4. Scheme of stepwise association/dissociation of 1,6-anhydro-β-glucopyranoside – calcium ion complexes.

$Ca(ClO_4)_2$ added (Cowman *et al.*, 1999). Like 1,6-anhydro-β-glucopyranoside, the monosaccharide solution without salt does not reveal acoustical excess attenuation (Polacek *et al.*, 2002). Hence the Debye-type relaxation term in the carbohydrate-salt solution clearly reflects the complex formation. Obviously, however, with 1-methyl-β-D-arabinopyranoside the Ca^{2+} ion does not bind to three oxygen atoms, since the hydroxyl groups of that monosaccharide do not provide the necessary arrangement for optimal complexation of a cation with ionic radius near 0.1 nm (Angyal, 1980). This is an example of the specific selectivity of carbohydrates.

3. Alkyl glycoside micelle formation

In Fig. 5 the ultrasonic excess attenuation spectrum for a solution of an alkyl monoglucoside is compared to that for a solution of D-glucose, essentially the head group moiety of the surfactant. The solute concentrations are identical for both solutions. Nevertheless, the acoustical spectra deviate markedly in the lower part

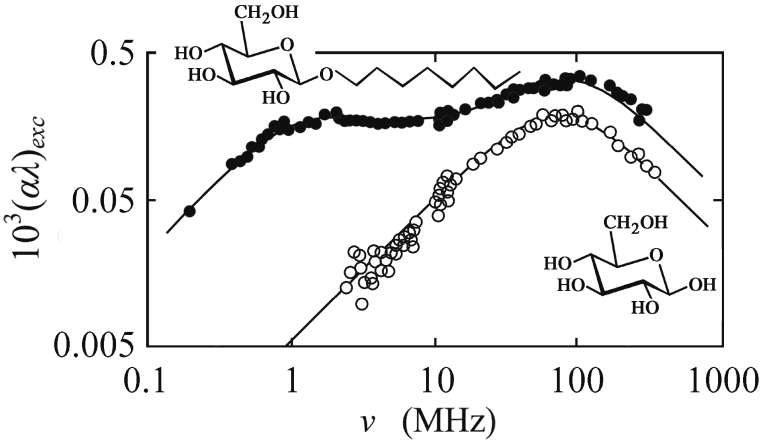

Fig. 5. Acoustical excess attenuation spectra for aqueous solutions of n-hexyl-β-D-glucopyranoside (•, cmc = 0.25 mol/l) and of D-glucose (○) at 25°C (Haller, Kaatze, 2009a). With both spectra the solute concentration is 0.2 mol/l.

of the frequency range. The additional contributions to the low-frequency part of the surfactant solution spectrum are self-evidently related to the formation of micellar structures. Quite remarkably, these contributions exist already at solute concentration (c = 0.2 mol/l) somewhat below the cmc (= 0.25 mol/l) of the surfactant. This behaviour is known from ionic (Telgmann, Kaatze, 1997a) as well as non-ionic (Telgmann, Kaatze, 2000a) surfactant solutions and is assumed to be due to the high content of oligomers as will be discussed with more details below in Sec. 4.

At $c <$ cmc the spectrum for an alkyl maltoside surfactant solution shown in Fig. 6 possesses contributions just in the frequency range where D-maltose

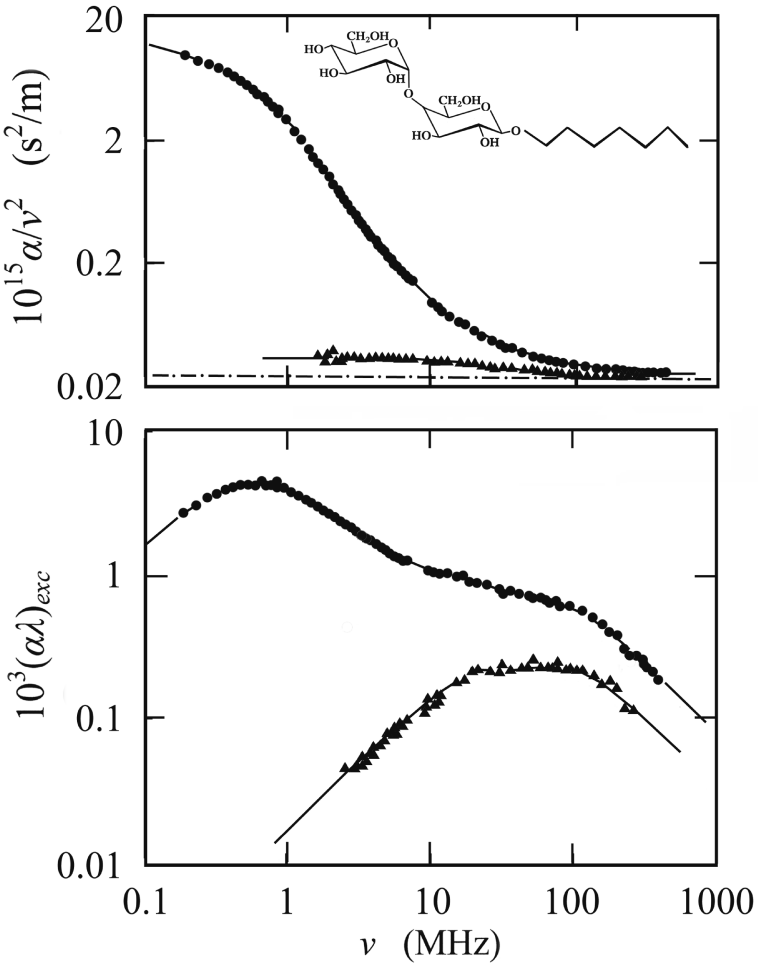

Fig. 6. Acoustical attenuation spectra in the frequency normalized format (top) and as excess attenuation per wavelength (bottom) for two aqueous solutions of n-hexyl-β-D-maltopyranoside at 25°C (cmc = 0.201 mol/l): ▲, c = 0.150 mol/l; ●, c = 0.225 mol/l (Haller, Kaatze, 2009b).

solutions also display acoustical excess attenuation. At higher surfactant concentration ($c <$ cmc), however, remarkably strong sonic attenuation exist. The mechanisms underlying this excess attenuation will be the focus of this section since the other (high-frequency) contributions have been already examined in Part I of the review (KAATZE, 2010), where they have been discussed in terms of rotations around glycosidic angles and of exocyclic hydroxymethyl group isomerisation.

Most spectra of alkyl glycoside solutions can be well represented by a sum of three Debye- type relaxation terms ($\omega = 2\pi\nu$)

$$(\alpha\lambda)_{\text{exc}} = \sum_{n=1}^{3} \frac{A_n \omega\tau_n}{1 + (\omega\tau_n)^2}, \tag{5}$$

with discrete relaxation times τ_n, $n = 1, 2, 3$ (HALLER, KAATZE, 2009a; 2009b). With some monoglycosides, however, the low-frequency term with relaxation frequency at around 1 MHz (Fig. 6) is broadened. A consistent analysis of this finding comes from the assumption of two overlapping Debye terms, assigned to two modes of monomer exchange in the micelle solutions (HALLER, KAATZE, 2009a). Following this assumption, one mode reflects the exchange kinetics of systems with Gaussian size distribution, as presumed in the Teubner-Kahlweit-Aniansson-Wall model (ANIANSSON, 1974; 1985; ANIANSSON, WALL, 1978; TEUBNER, 1979; KAHLWEIT, TEUBNER, 1980) of micelle formation. The other mode is considered to be due to the monomer exchange from non-globular micelles with closer packing of surfactant molecules. Such surfactants likely exist at high solute concentration. It is, however, unclear, whether large non-globular micelles are formed in addition to or by growth and accompanying deformation of existing globular micelles. Independent of this open feature of aggregate structure, indication of a second exchange term is an interesting aspect of ultrasonic spectra, offering a potential for future more detailed investigations of highly concentrated micelle solutions.

The commonly accepted theory of micelle formation predicts one monomer exchange term in the acoustical spectra (TEUBNER, 1979; KAHLWEIT, TEUBNER, 1980). Proceeding from an isodesmic scheme of coupled equilibria

$$\mathrm{S} + \mathrm{S}_{i-1} \leftrightarrow \mathrm{S}_i, \qquad i = 1, 2, 3, \ldots, \tag{6}$$

theory predicts the relaxation rate and relaxation amplitude of the dominating relaxation term to be given by

$$\frac{1}{\tau_1} = k_b \left(\frac{1}{\sigma^2} + \frac{X}{\overline{m}} \right) \tag{7}$$

and

$$A_1 = \frac{\pi(\Delta V)^2}{\kappa_S^{\infty} RT} \,\text{cmc}\, \frac{(\sigma^2/\overline{m})X}{1 + (\sigma^2/\overline{m})X}, \tag{8}$$

respectively. In these equations, S_1 is a surfactant monomer and S_i is an oligomer or micelle made of i monomers. $X = (c - \mathrm{cmc})/\mathrm{cmc}$ is a reduced concentration, $\overline{m}$ and σ^2 denote the mean aggregation number and the variance, respectively, in the size distribution of micelles, assumed to be Gaussian, and k_b is the backward rate constant at micelle sizes around the mean ($i \approx \overline{m}$). Quantity κ_S^∞ is the adiabatic compressibility extrapolated to frequencies well above the relaxation region, R is the universal gas constant, and ΔV is the reaction volume associated with the monomer exchange. Deriving Eq. (8) it has been assumed that the reaction volume is identical for all steps ($\Delta V = \Delta V_i$, $i = 2, 3, \ldots$) in the isodesmic reaction scheme (Eq. (6)).

Let us consider the low-frequency relaxation term with relaxation time τ_1 and amplitude A_1 in the light of the above theoretical model. When plotted *versus* reduced concentration the relaxation rates $1/\tau_1$ for both, alkyl glycoside and alkyl maltoside solutions reveal significant differences of their slopes $k_b/\overline{m}$, ranging from $3 \cdot 10^4$ s^{-1} to $4.1 \cdot 10^6$ s^{-1} (Fig. 7). Linear regression of relaxation rate data in terms of Eq. (7) yields $k_b/\overline{m}$ values which, with the aid of $\overline{m}$ data from the literature (Lorber *et al.*, 1990; Products and Services Catalog, n.d.), have been evaluated to obtain k_b values. Along with results for cationic, anionic and nonionic surfactants, k_b values for alkyl monoglycosides and alkyl maltosides are presented in Fig. 8. The alkyl glycoside data are in line with the reasonable overall tendency of k_b to increase with cmc. At decreasing length of alkyl chain the cmc increases but the probability of a molecule to escape from a micelle

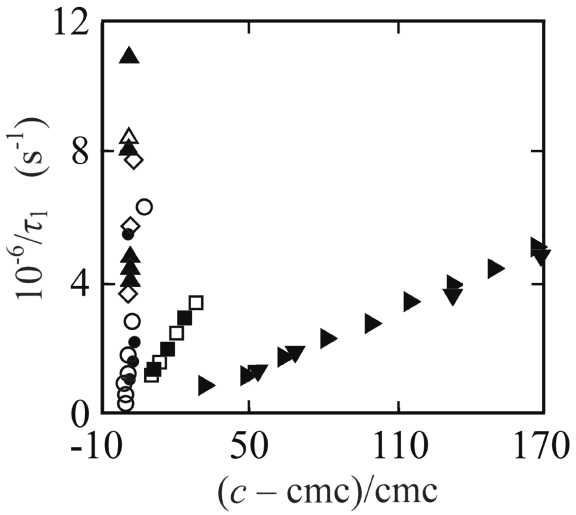

Fig. 7. Relaxation rates τ_1^{-1} of the dominating monomer exchange relaxation term for aqueous solutions of alkyl glucosides (C_iG_1; Haller, Kaatze, 2009a); i denotes the number of methyl groups C per alkyl chain, G denotes a glucopyranoside moiety), and alkyl maltosides (C_iG_2; Haller, Kaatze, 2009b) at 25°C: Δ, C_6G_1; ◇, C_7G_1; ○, C_8G_1; □, C_9G_1; ▲, C_6G_2; ●, C_8G_2; ■, C_9G_2; ▼, $C_{10}G_2$; ►, α-$C_{10}G_2$. α-$C_{10}G_2$ is the abbreviation of the α-anomer of *n*-decyl-D-maltopyranoside. All other alkyl glycosides are β-anomers.

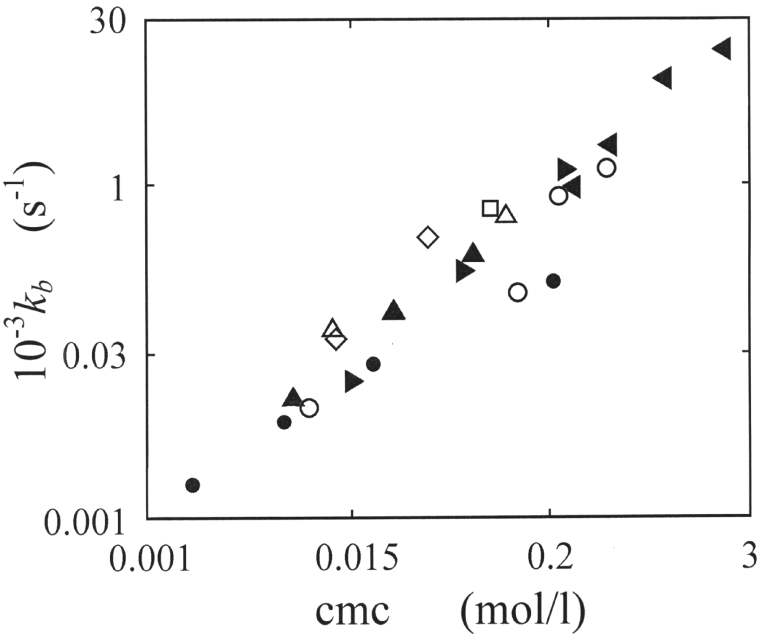

Fig. 8. Log-log plot of the backward rate constant at micellar sizes around the mean, $k_b(= k_m^b)$, *versus* critical micelle concentration, cmc, for aqueous solutions of alkyl glucosides (▲, C_iG_1; Haller, Kaatze, 2009a), alkyl maltosides (●, C_iG_2; Haller, Kaatze, 2009b), poly(ethylene glycol) monoalkyl ethers (□, C_iE_3; ◇, C_iE_4; Δ, C_iE_5; Frindi *et al.*, 1992; Kato *et al.*, 1995; Telgmann, Kaatze, 2000a; 2000b), alkylammonium chlorides (◀, C_iACl; Telgmann, Kaatze, 1997b; Hagen, 1998; Polacek, 2003), alkyltrimethylammonium bromides (▶, C_iTABr; Nomura *et al.*, 2000), and sodium alkyl sufates (○, C_iSO_4Na; Hall, Wyn–Jones, 1986; Polacek, Kaatze, 2007).

and likewise the probability of a surfactant molecule to be solved as monomer increases. A small head group effect is also indicated by the data in Fig. 8. According to our expectations, at given number i of methyl groups per chain, surfactants with more hydrophilic ionic head groups reveal larger k_b values than less hydrophilic nonionic surfactants.

The relaxation rates of the alkyl monoglycoside solutions have been extrapolated back to yield k_b/σ^2 at $c =$ cmc. No such extrapolation was possible with the alkyl maltoside solutions since, likely due to somewhat incorrect cmc values, meaningless negative k_b/σ^2 result for some series of data. For this reason, the discussion of the relaxation amplitude A_1 (Eq. (8)) may be first restricted to the monoglycosides. With $\kappa_S^\infty = \rho^{-1}c_s^{-2}$, reaction volumes ΔV follow, which in Fig. 9 are displayed along with data for poly(ethylene glycol) monoalkyl ether surfactants The value for *n*-heptyl-β-D-glucopyranoside (C_7G_1) fits well to the chain length dependence in the monomer exchange reaction volume of nonionic surfactants. With the higher homologues C_8G_1 and C_9G_1, the ΔV values are smaller than predetermined by the general trend (Fig. 9). This finding is taken

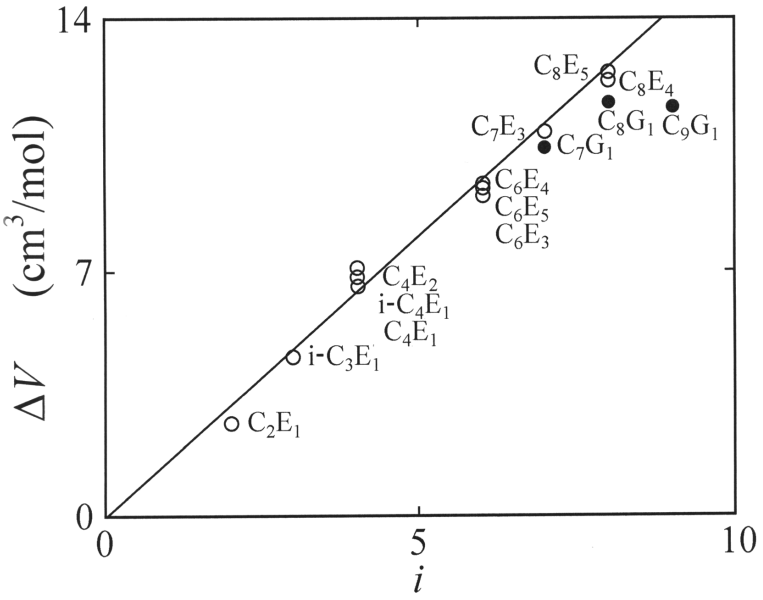

Fig. 9. Reaction volume as following from Eq. (8), ΔV, *versus* number of methyl/methylene groups per alkyl chain, i, for solutions of alkyl glucosides (•, C_iG_1; Haller, Kaatze, 2009a) and poly(ethylene glycol) monoalkyl ethers (○, $CH_3(CH_2)_{i-1}(OCH_2CH_2)_jOH$, C_iE_j; Telgmann, Kaatze, 2000a; 2000b). Only the largest values of concentration series are shown, respectively.

another indication for the existence of a second monomer exchange relaxation. As part of the surfactant molecules has a share in the second monomer exchange process, only the remaining part is essentially involved in the dominating process. Consequently, using the total surfactant concentration c in the evaluation of relaxation amplitude A_1 must produce reaction volumes which are too small when compared to such of proper globular micelle systems.

At unknown variance in the Gaussian distribution of micelle sizes, relaxation amplitudes may still be evaluated to yield apparent reaction volumes, $\Delta V_{\mathrm{app}} = \lim_{X\to\infty} \Delta V$, from Eq. (8). In Fig. 10 such apparent reaction volumes per methylene group of the alkyl chains are shown for both series of alkyl glycosides. Obviously, the $\Delta V_{\mathrm{app}}/i$ data (i = number of methyl groups per alkyl chain) reach a plateau not before $X = 2$, that is not before $c = 3$ cmc. The initial increase in the $\Delta V_{\mathrm{app}}/i$ values is explained by the fact that, close to the cmc, rather open water-rich oligomeric micellar structures are formed. The exchange of monomers is thus accompanied by a comparatively small change in the molar volume of the hydration water. At $c > 3$ cmc larger micelles with closer packing of surfactant molecules are formed, thereby causing a larger reaction volume. At higher surfactant content ($c > 3$ cmc) $\Delta V_{\mathrm{app}}/i = 1.5$ cm^3/mol with the maltoside solutions, in close agreement with the volume change per methylene group of for poly(ethylene glycol) monoalkyl ether surfactant solu-

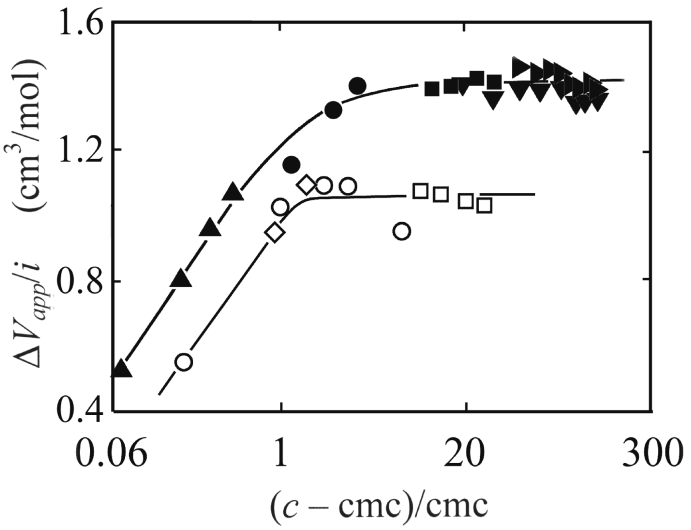

Fig. 10. Lin-log plot of the apparent reaction volume per methylene group, $\Delta V_{\mathrm{app}}/i$, *versus* reduced concentration, c/cmc-1, for alkyl glucoside (open symbols) and alkyl maltoside (filled symbols) solutions at 25°C (Haller, Kaatze, 2009b). See Fig. 7 for the figure symbols.

tions ($\Delta V_{\mathrm{app}}/i = 1.6$ cm^3/mol). The fact that the volume change is smaller with alkyl glucoside solutions ($\Delta V_{\mathrm{app}}/i = 1.1$ cm^3/mol) than with alkyl maltoside solutions is, at least in parts, due to the formation of non-globular micelles, as revealed by the second low-frequency relaxation term in the spectra for solutions of *n*-hepty-, *n*-octyl-, and *n*-nonyl-β-D-glucopyranoside. Taking the amplitude of this second relaxation term also into account leads to $\Delta V_{\mathrm{app}}/i = 1.3$ cm^3/mol. The still remaining difference to the value for alkyl maltoside solutions likely reflects different hydratisation of the first alkyl groups of the chains in non-globular micelles.

4. Complex formation and self-association

As briefly mentioned in the Introduction, investigations into the formation of inclusion complexes of cyclodextrins (CD's) have been performed with a broad variety of "guests". Here the interest will be directed towards the complexation of CD with *n*-octyl-β-D-glucopyranoside surfactant (S), with the appealing competition between complex formation and self-association of the amphiphile. Interestingly, for aqueous solutions of octy-glucopyranoside (C_8G_1) with α-cyclodextrin (CD, 0.05 mol/l) added, the plot of the sound velocity *versus* surfactant concentration (Fig. 11) exhibits an inflection point at a surfactant concentration ($[C_8G_1] = 0.07$ mol/l) noticeably above the critical micelle concentration (cmc = 0.018–0.026 mol/l (Lorber *et al.*, 1990; Shinoda *et al.*, 1961; Aoudia, Zana, 1998; López *et al.*, 2001). Following a previous suggestion (Valente *et al.*, 2005), the

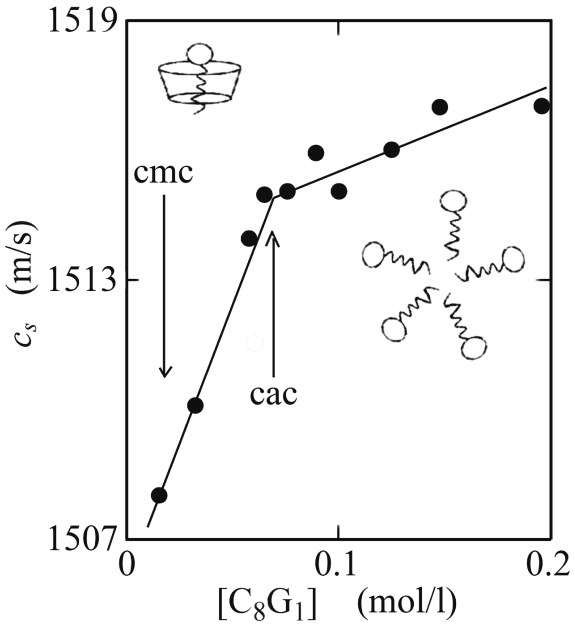

Fig. 11. Sound velocity c_s as a function of total surfactant concentration $[C_8G_1]$ for solutions of *n*-octyl-β-D-glucopyranoside in water with α-cyclodextrin (c(CD) = 0.05 mol/l, 25°C) added (Haller, Kaatze, 2009c). Above the inflection point cac micelles are formed, whereas cmc marks the critical micelle concentration of C_8G_1 aqueous solutions without CD (Shinoda *et al.*, 1961; Lorber *et al.*, 1990; Aoudia, Zana, 1998; López *et al.*, 2001).

surfaction concentration at this inflection point will be named "critical aggregation concentration" (cac, Fig. 11).

The finding of cac ≈ cmc+c(CD) indicates C_8G_1 molecules, at concentrations up to c(CD), to preferably form complexes with cyclodextrin. Previous studies of cyclodextrin-surfactant solutions were based on the idea of surfactant molecules to exist in either state: as monomers, 1:1-, 2:1-, and 1:2-complexes with CD, as well as associated as micelles (Junquera *et al.*, 1993; Cunha–Silva, Teixera–Dias, 2002; Reinsborough, Stephenson, 2004; Valente *et al.*, 2005; Cabaleiro–Lago *et al.*, 2006; Piñeiro *et al.*, 2007; Haller, Kaatze, 2008). Therefore, the overall coupled reaction scheme of the CD – S solutions may be written as

$$\mathrm{CD} + \mathrm{S} \overset{K_{11}}{\longleftrightarrow} \mathrm{CD \cdot S}, \tag{9}$$

$$\mathrm{CD \cdot S} + \mathrm{S} \overset{K_{21}}{\longleftrightarrow} \mathrm{CD \cdot S_2}, \tag{10}$$

$$\mathrm{CD \cdot S} + \mathrm{CD} \overset{K_{12}}{\longleftrightarrow} \mathrm{CD_2 \cdot S}, \tag{11}$$

$$\mathrm{S} + \mathrm{S}_i \overset{K_i}{\longleftrightarrow} \mathrm{S}_{i+1}, \tag{12}$$

with $i = 1, 2, 3, \ldots$ and with $K_{p,q}$, $p, q = 1, 2$, as well as K_i denoting equilibrium constants. Applying law of conservation of mass and utilizing equilibrium constants from the literature (Piñeiro *et al.*, 2007), concentrations for the different species as shown in Fig. 12 have been calculated (Haller, Kaatze, 2009). CD·S_2 complexes are completely missing in that diagram, since the literature value of the relevant equilibrium constant vanishes ($K_{21} = 0$; Piñeiro *et al.*, 2007). Acoustical attenuation spectra, however, indicate presence of a small amount of $CD(C_8G_1)_2$ complexes (Haller, Kaatze, 2009).

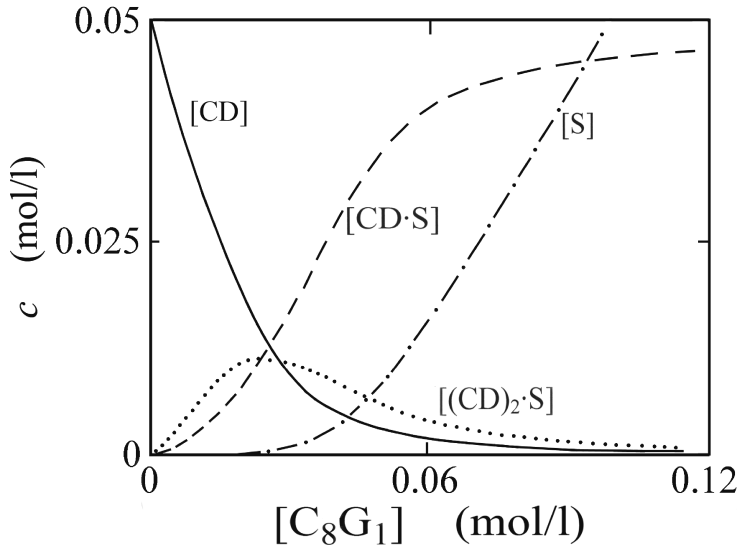

Fig. 12. Dependencies of the concentrations of uncomplexed cyclodextrin CD, uncomplexed surfactant S, as well as of CD·S and $(CD)_2$·S complexes upon total surfactant concentration for solutions of *n*-octyl-β-D-glucopyranoside in water with α-cyclodextrin (c(CD) = 0.05 mol/l, 25°C). Calculating the data (Haller, Kaatze, 2009c) the following values for the equilibrium constants have been used (Piñero *et al.*, 2007): $K_{11} = 1700$ $(\text{mol/l})^{-1}$, $K_{21} = 0$, $K_{12} = 64$ $(\text{mol/l})^{-1}$.

Examples of acoustical spectra are given in Fig. 13 where results for aqueous solutions of 0.05 mol/l α-cyclodextrin without (open symbols) and with octyl glucopyranoside added are shown. Without surfactant the spectrum reflects two processes of structural isomerisation of the cyclodextrin molecule. At small surfactant concentration ($[C_8G_1] \approx 0.44$ cac) an additional low-frequency relaxation regime emerges which is already due to both, complex formation with cyclodextrin and formation of micellar structures. The low-frequency excess attenuation increases substantially as surfactant concentration exceeds cac (Fig. 13). The relaxation times of both relaxation terms underlying the low-frequency excess attenuation differ by more than a factor of 6 (Haller, Kaatze, 2009). This difference facilitates evaluation of the spectra in terms of relevant relaxation

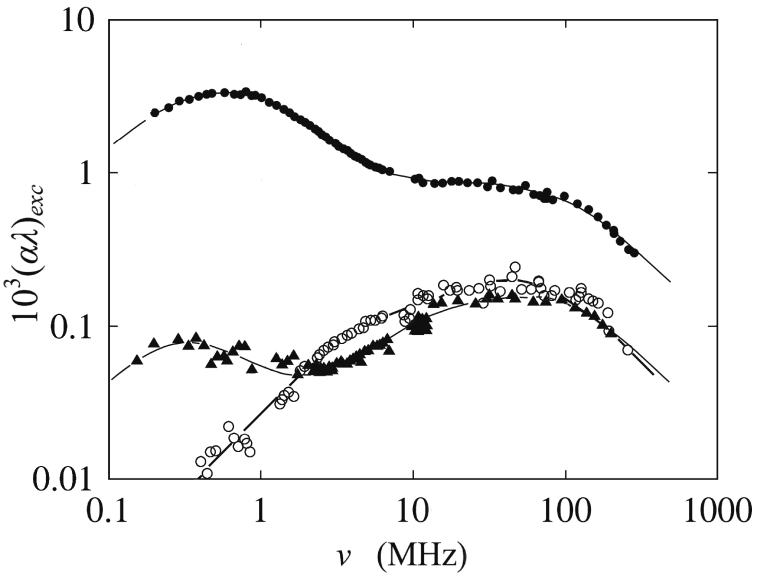

Fig. 13. Acoustical excess attenuation spectra at 25°C for 0.05 mol/l aqueous solutions of α-cyclodextrin without (○) and with *n*-octyl-β-D-glucopyranoside (▲, 0.016 mol/l ≙ 0.44 cac; ●, 0.20 mol/l ≙ 2.8 cac) added (Haller, Kaatze, 2009c).

parameters and it also suggests, at least in a first approach, to consider the formation of complexes decoupled from the micelle formation. But on these assumptions the concentration dependence of the relaxation times and amplitudes is incompatible with K_{21} being strictly zero as following from literature (Haller, Kaatze, 2009c). If, however, allowance is made for an only small amount of CD·S_2 complexes, a reasonable description of relaxation parameters is reached. An equilibrium constant K_{21} just on the order of 1 $(\text{mol/l})^{-1}$ is required, which leaves the concentrations of the other species shown in Fig. 12 essentially unaltered.

Another noteworthy aspect is the initial slope in the concentration dependence of the relaxation rate τ_1^{-1} related to the monomer exchange of micelles (Fig. 14). As briefly mentioned above, a monomer exchange relaxation term exists already at solute concentrations slightly below the cac. Unlike the prediction from the Teubner-Kahlweit-Aniansson-Wall model for proper micelle systems (Eq. (7)), however, the relaxation rate first decreases to linearly increase with c at higher surfactant content. Such initial negative slope has been reported for various ionic and non-ionic surfactants (Adair *et al.*, 1976; Hall, Wyn–Jones, 1986; Frindi *et al.*, 1994a; 1994b; Telgmann, Kaatze, 1997b; 2000a; Polacek, Kaatze, 2007) and has been discussed in terms of an extended model of micelle formation/disintegration (Telgmann, Kaatze, 1997a).

In order to more adequately account for surfactant solutions around the cmc or cac, respectively, the extended model does not proceed from an empirical size distribution of aggregates but from reasonable assumptions on the forward (k_i^f)

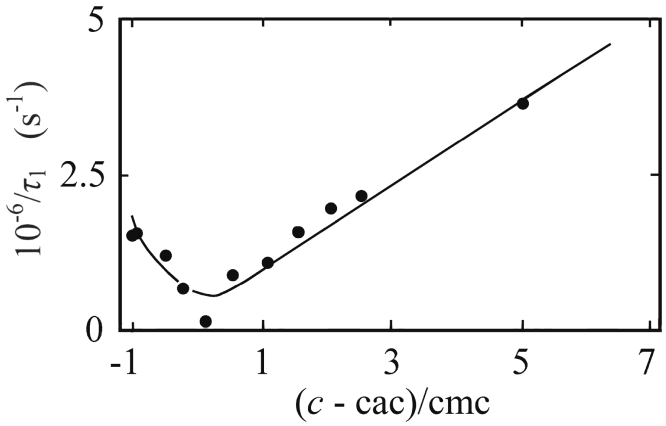

Fig. 14. Relaxation rate τ_1^{-1} of relaxation term due to surfactant monomer exchange in the micelle formation/disintegration kinetics *versus* scaled concentration (c – cac)/cmc for aqueous solutions of C_8G_1 and CD (c(CD) = 0.05 mol/l; c = [C_8G_1]; 25°C).

and backward (k_i^b) rate constants ($K_i = k_i^f/k_i^b$, $i = 1, 2, 3, \ldots$) in Eq. (12). The following aspects have been taken into account when modelling k_i^f and k_i^b: (i) at small aggregation numbers i the backward rate constants k_i^b have to strongly decrease with i in order to promote micelle formation; (ii) at large i the k_i^b should strongly increase, whereas the k_i^f should decrease with aggregation number in order to restrict the micelle sizes; (iii) near the relative maximum of the size distribution ([S_i] ≈ [S_{i-1}]), in conjunction with the law of mass action, [S_i] = $k_i^b/k_i^f = 1/K_i$ holds, and (iv) a linear dependence of k_i^f and k_i^b upon i should be preferred in the micelle regime in order to induce a Gaussian distribution of micelles. The following analytical forms have been proven adequate (Telgmann, Kaatze, 1997a):

$$k_{i+1}^f = k_{\overline{m}}^f \left(1 - s_f(i - \overline{m})\right), \tag{13}$$

$$k_{i+1}^b = k_{\overline{m}}^b \left(1 + s_b(i - \overline{m})\right) + k_0^b \frac{1 + \exp\left(\dfrac{1 - i_c}{d}\right)}{1 + \exp\left(\dfrac{i - i_c}{d}\right)}. \tag{14}$$

In these equations, $k_{\overline{m}}^f$ and $k_{\overline{m}}^b$ allow the forward and backward rate constants, respectively, to be matched at the mean aggregation number $\overline{m}$. Parameter i_c defines the aggregation number at which the backward rate constants change from a linear dependence upon i to a Fermi-distribution behaviour. The slope parameters s_f and s_b ($\approx s_f$) define the point of intersection of the functions given by Eqs. (13) and (14) and thus establish $\overline{m}$. Quantities k_0^b and d, modelling the aggregation number dependence in the backward rate constants at small i, like i_c are related to the cmc.

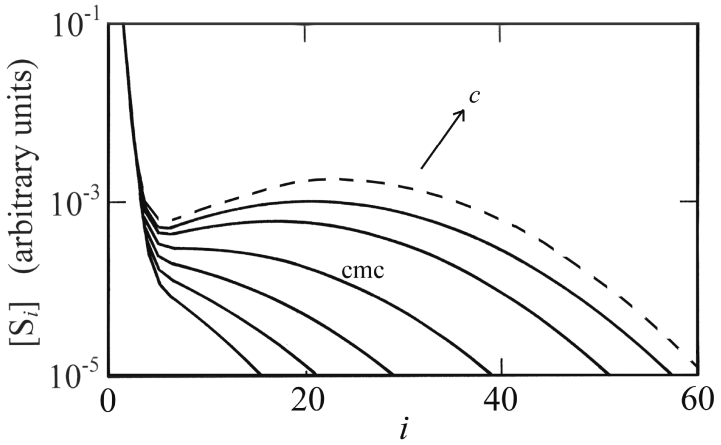

Fig. 15. Logarithmic plot of concentrations $[S_i]$ of aggregates containing i monomers *versus* aggregation number i with surfactant concentration c as a parameter: results from model calculations of an extended Teubner-Kahlweit theory (Telgmann, Kaatze, 1997a).

Using reasonable values for the parameters of Eqs. (13) and (14), the equilibrium concentrations as shown in Fig. 15 at various surfactant concentrations have been obtained from a computer simulation of the isodesmic reaction scheme of micelle formation/ disintegration (Eqs. (6), (12)). The dashed curve shows the size distribution at surfactant concentration well above the critical micelle (or aggregate) concentration. Notice the logarithmic scale of the aggregate concentration which makes the curve to look different from a Gaussian. In fact it follows closely a Gaussian size distribution. At decreasing surfactant concentration the minimum in the oligomeric region more and more vanishes. This tendency is correlated with increasing degeneration of the acoustical relaxation terms associated with the micelle formation kinetics. Whereas in proper micelle systems, in addition to the fast monomer exchange term, another term exists, representing the slow relaxation of the system into final equilibrium, the relaxation times of both terms approach when surfactant concentration decreases. Finally, at vanishing minimum in the oligomer regime of the size distribution, both relaxation terms merge. At those concentrations, almost no proper micelles but open water-rich oligomeric structures exist in the solutions. They allow for a faster monomer exchange than closer packed micelles. For this reason the relaxation rate $1/\tau_1$ increases when, coming from large c values, the surfactant concentration approaches or even falls below the cmc or cac, respectively (Fig. 14).

5. Conclusions

Complementary to the first part of this review, exposing the ability of broadband acoustical spectroscopy to examine structural isomerisation of molecules

in solution, the suitability of the method also for the inspection of association and complex formation processes has been depicted in this part. Results for carbohydrate solutions demonstrate the general usability of broadband acoustical measurements for the study of ion-saccharide complexation, amphiphile self-association, and inclusion complex formation. It has been shown that mono- and disaccharides interact with 2-valent alkaline earth metal ions in a specific manner. Addition of cations may leave the acoustical relaxation spectra of saccharide solutions almost unaltered, they may affect relaxation terms reflecting structural isomerisation of carbohydrate, and they may lead to additional relaxation terms due to complex formation. Variations of fine details in the structure of the saccharide molecule may generate substantially different complexation characteristics. As an example, the formation of monodentate and tridentate complexes with calcium ions, depending on the availability of suitably arranged electron lone pairs of carbohydrate hydroxy or ether groups, have been presented.

At sufficiently high solute concentration acoustical spectra of alkyl mono- and maltoglycosides in water reveal a low-frequency relaxation term due to the exchange of surfactant monomers between micelles and the suspending phase. With some alkyl monoglycoside solutions an additional low-frequency relaxation term emerges which is assigned to the exchange of monomers from micelle sites with closer packing of molecules. At high solute concentration such sites likely exist due to the formation of large nonglobular micelles. Nonglobular aggregates may form in addition to or by growth and deformation of proper globular micelles. Characteristic parameters of the monomer exchange process, such as the backward rate constant at micelle sizes around the mean and the reaction volume, correspond with data for other non-ionic surfactant systems. The former parameter follows the common trend to increasing with increasing cmc, the latter one meets the trend to increasing with increasing length of the surfactant alkyl chain.

Addition of cyclodextrin (CD) to aqueous solutions of octyl glucopyranoside surfactant (S) shifts the onset of micelle formation to a critical aggregate concentration cac that exceeds the cmc of the surfactant almost for the CD concentration. Hence at surfactant concentration $c <$ cac octyl glucopyranoside preferably forms inclusion complexes with cxclodextrin. The acoustical relaxation term due to the complexation reveals the existence of CD·S, CD_2·S, and CD·S_2 complexes. The concentration of the latter is in fact small but does not vanish at all, as predicted from literature data for the equilibrium constants. An acoustical relaxation term with its amplitude distinctly increasing at $c >$ cac reflects the monomer exchange between micelles and the suspending phase. The relaxation parameters for octyl glucopyranoside solutions with and without CD added show identical behaviour when in the relevant relations the cmc is exchanged for the cac. At low c the relaxation rates follow the extended Aninsson-Wall-Teubner-Kahlweit model that includes the variation of the aggregate size distribution as the cmc or cac, respectively, is approached.

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