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Quantification of Cyclodextrins Fixed onto Cellulose Fibers

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Abstract Cyclodextrins are fixed onto different textiles using conventional finishing technologies to create new materials with a wide range of applications. One important problem in the textile finishing is evaluation of the amount of cyclodextrins accessible for complexation with guest substances. This research investigated the coordination and adsorption properties of cellulose materials with fixed monochlorotriazine substituted β-cyclodextrin for different primary, secondary and tertiary volatile aliphatic amines. The textiles showed high ability to complex formation from the gas phase due to molecular recognition between internal cyclodextrin cavity and hydrocarbon chains of the amines. The complexation reaction with cyclohexylamine is suggested for quantitative determination of the accessible cyclodextrins fixed on the surface of cellulose fibers.

Key words cyclodextrin, finished cellulose fibers, volatile amines, complexation, adsorption

Cyclodextrins are natural cyclic oligosaccharides, formed during the enzymatic degradation of starch. They are currently used commercially in the pharmacy, cosmetic and food industries. Due to their benign toxicological and ecological properties, in recent years cyclodextrins have also become important for textile finishing [1–3]. Permanent fixation of cyclodextrins onto fibers is one of the attractive possibilities of chemical modification of textile materials. Thus, permanent fixation on cotton is possible by reactive monochlorotriazinyl group or using the crosslinking agents. Molecular recognition and selective binding of dyes, perfumes, pharmaceuticals, etc. by cyclodextrins on the textile surface allow the creation of materials with odor-reducing, controlled release and other useful properties. Some textiles with fixed cyclodextrins e.g. underwear, bed linen and curtains are already offered on the European market. For example, in bed linen the cyclodextrins act as depot for aromatherapy oils and in towels as depot for fragrances. Unpleasant odors are masked with the aid of cyclodextrins in jackets and t-shirts or may be removed from the air by curtains containing cyclodextrins. Testing quality of these new materials as well as production control in the textile industry are in need of quantitative analytical methods for the determination of the amount of fixed cyclodextrins [4–6].

The simplest quantitative estimation of the overall amount of cyclodextrins fixed on the textile surface is gravimetric determination of weight of a sample before and after finishing procedure. Another possibility for cellulose materials with fixed monochlorotriazine substituted β-cyclodextrins is triazine test as well as elemental analysis with reference to nitrogen content. However, due to the high carbon background in textile samples, the precision of these methods is not sensitive enough for the quantitative determination of cyclodextrins. Furthermore, as a rule, only part of cyclodextrins fixed onto textile is available for inclusion of guest molecules due to unfavorable arrangement, steric hindrance, possible polymerization, etc.

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In this study, we investigated the interactions of volatile amines with cyclodextrin finished cellulose fibers in order to develop a more useful and informative method. The inclusion complexes between cyclodextrins and gaseous organic compounds (amines, alcohols, etc.) were formed at the conditions of solid-gas equilibrium as well as in aqueous solution [7–9]. The amount of accessible cyclodextrins fixed on the surface of cotton materials was allowed to be determined using a simple titration of the extracted amines in water.

Experimental

Samples of cellulose materials (S/400 TESTEX Prüftextilien, surface density 111 $g \cdot m^{-2}$) with different concentrations of fixed (f) monochlorotriazinyl-beta-cyclodextrin (MCT-β-CD) ("Cavasol W7 MCT", Wacker-Chemie GmbH) ($C_{\beta\text{-}CD(f)}$ =1.2–8.6 mass.%) were used. The preparation of the samples and the gravimetrical determination of the total amount of fixed cyclodextrin have been described previously [4]. All amines (Fluka) were of the highest purity commercially available. Distilled deionised water was used throughout the experiments.

Treatment of the textile samples with amine vapors, $R_3N_{(g)}$, was carried out in an exicator at room temperature (48 h).

$$R_3N_{(g)} + \beta\text{-}CD_{(f)} \Leftrightarrow [R_3N \subset \beta\text{-}CD]_{(f)} \text{ Complex 1:1} \quad (1)$$

After extraction of the complexed and adsorbed amine with water, the total amount of amine in aqueous solution was determined by acid-base volumetric titration using a Metrohm Dosimat 665 with standard 0.1 M HCl solution (Merck) and mixed methyl-red/-blue indicator 5 for ammonia titrations (Merck) according to equations (2)–(4),

$$R_3N + H^+ \Leftrightarrow R_3NH^+ \quad n_{HCl} = n_{amine(total)} = V_i(HCl) \cdot C(HCl) \quad (2)$$

$$n_{amine(total)} = n_{amine(complexed)} + n_{amine(adsorbed)} \quad (3)$$

$$n_{amine(complexed)} = (V_i(HCl) - V_0(HCl)) \cdot C(HCl) \quad (4)$$

where n is the amount of amine or hydrochloric acid (mole), C(HCl) is the concentration of titrant solution and V_i and V_0 are the volumes of titrant solution used for titration of the sample with fixed cyclodextrins and the reference sample (without cyclodextrins), respectively. The experiments were performed in triplicate.

The weight fraction (mass.%) of the accessible cyclodextrins, $\omega^*_{\beta\text{-}CD(f)}$, is given by equation

$$\omega^*_{\beta\text{-}CD(f)} = \frac{n_{amine(complexed)} \cdot M_{\beta\text{-}CD(f)} \cdot 100}{m_{textile}} \quad (5)$$

and the accessibility ratio, R, may be calculated from

$$R = \frac{\omega^*_{\beta\text{-}CD(f)}}{\omega_{\beta\text{-}CD(f)}} \quad (6)$$

where $\omega_{\beta\text{-}CD(f)}$ is the overall (gravimetric) weight fraction (mass.%) of fixed (f) β-cyclodextrins. Most of the adsorbed amines and water were eliminated by drying the textiles for two h at 120°C before and after treatment at the amine atmosphere.

Results and Discussion

Due to different arrangements of cyclodextrin molecules on the textile surface, only cyclodextrins with "open" cavities are capable to coordination of guest substances. The number of accessible for complexation cyclodextrins is not an absolute value; it depends on both the geometrical features (size and shape) and chemical reactivity of guest molecules. Cyclodextrins form complexes mainly with molecules or functional groups of molecules having hydrophobic nature [10]. Thus, aliphatic amines seemed to be very suitable as model substances for this study. On the one hand, amine molecules have a hydrophobic alkyl chain capable to complexation within the hydrophobic cyclodextrin cavity (Figure 1). On the other hand, they have basic amino groups, providing a possibility for simple and rapid analytical determination in aqueous solution.

Assuming exactly stoichiometric 1:1 binding of amines by cyclodextrin, weight fractions of cyclodextrins, capable to complexation with several primary, secondary and tertiary amines, $\omega^*_{\beta\text{-}CD(f)}$, were calculated (Figure 2a–c). The total weight fraction of cyclodextrins on the surface of cellulose, $\omega_{\beta\text{-}CD(f)}$, was determined gravimetrically by the precise weighting of the textile samples before and after fixation of MCT-β-CD. The dotted lines in Figure 2 correspond to the highest possible i.e. 100% "activity" of fixed

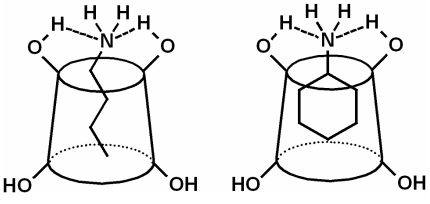

Figure 1 Schematic representation of β-cyclodextrin complexes with n-butylamine and cyclohexylamine.

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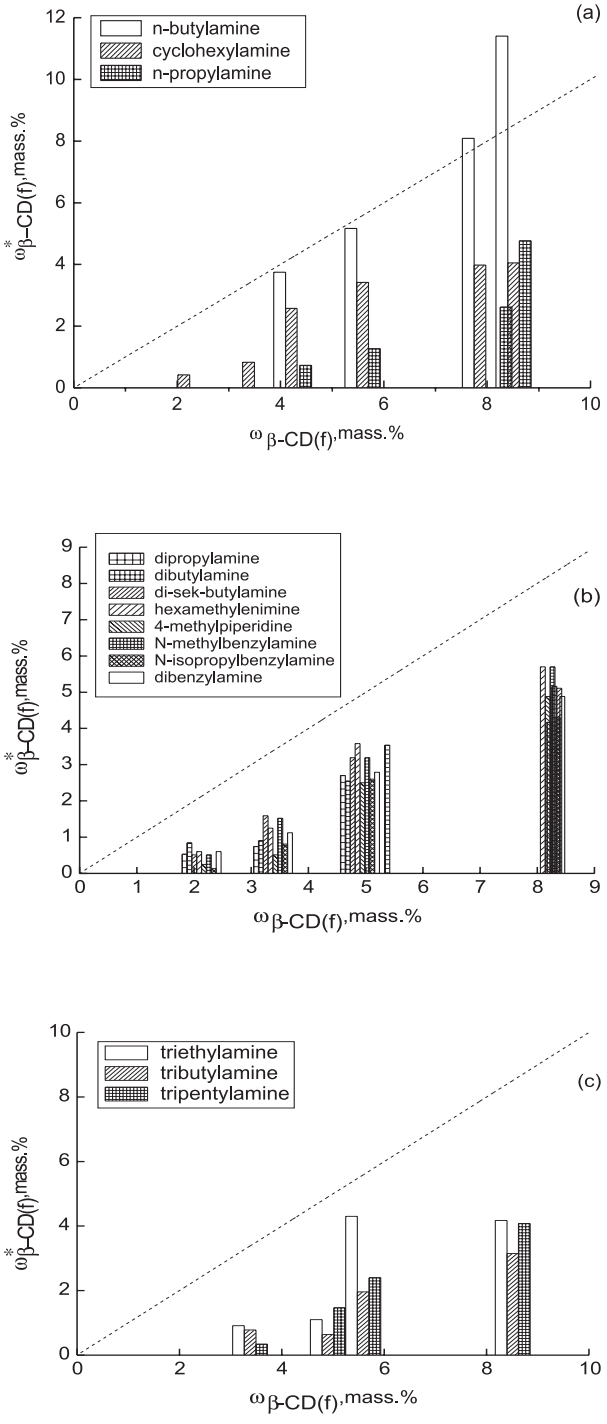

Figure 2 Dependence of the weight fraction of accessible β-cyclodextrins on the surface of cellulose fiber at complexation with primary (a), secondary (b) and tertiary (c) amines on the overall (gravimetric) weight fraction (mass.%) of fixed β-cyclodextrins.

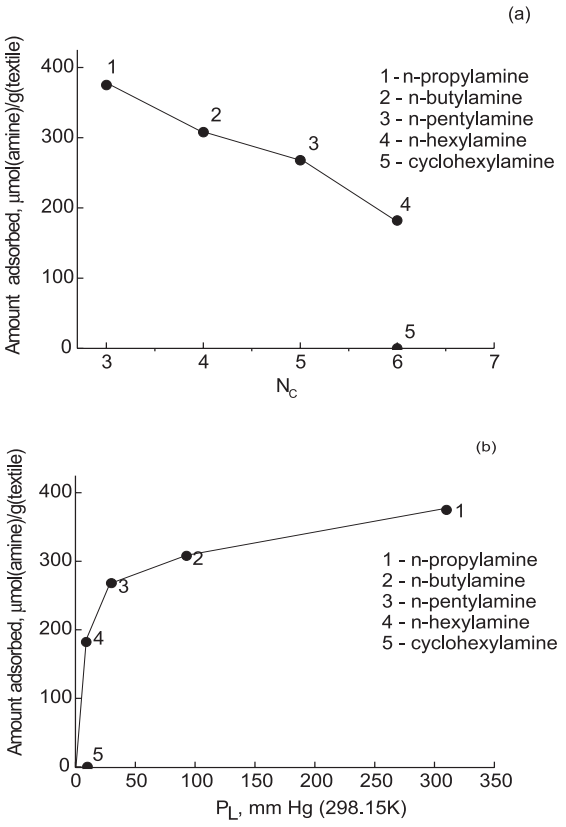

Figure 3 Adsorption of amines onto pure cellulose textile material as a function of the number of carbon atoms in amine molecules N_C (a) and saturated vapor pressure of amines P_L at 298.15 K (b).

β-cyclodextrins. The values of accessibility ratio, equation (6), demonstrated that more than 50% of cyclodextrins on the surface were able to complexation with amines studied.

The precision of the results was strongly influenced by adsorption of amines on cellulose. To take into account the rest adsorption, all $\omega^*_{\beta\text{-}CD(f)}$ values were corrected in relation to the untreated material i.e. without cyclodextrin (equation (4)). Nevertheless, the amount of amine adsorbed on the reference material and finished samples may be different, so that the correction made did not exclude an indefinite error. Strong adsorption of amines on the textile surface was probably the result of hydrogen bond formation between hydroxyl groups of cellulose and amino groups. This was confirmed by the acid-base titration of several amines extracted by water from the pure cellulose textile material after treatment 24 h with amine vapors and drying two h at 120 ^{0}C. With increasing size of the hydrocarbon chain, the rest adsorption of primary amines decreased (Figure 3a). The dependence of adsorption from the saturation vapor pressure of amines (at

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standard temperature 298.15 K) was similar with classical adsorption isotherm for gases (Figure 3b). However, inductive and steric influences of alkyl groups on amino group seemed to be more important factors. Thus, cyclohexylamine was not adsorbed by cellulose in spite of almost the same vapor pressure as for n-hexylamine. Although some secondary and tertiary amines were not adsorbed by cellulose as well, they had a much less vapor pressure requiring a longer time of equilibration. Screening all the amines studied, one can conclude that cyclohexylamine seems to be a most suitable model compound for quantitative determinations of fixed cyclodextrins, since it had sufficiently high vapor pressure at room temperature and formed stable complexes from the gas phase without adsorption on cellulose.

Conclusions

A new quantitative analytical method is described for analysis of cellulose fibers with fixed monochlorotriazine substituted β-cyclodextrins. The amounts of cyclodextrins accessible for inclusion of guest substances were determined by using the complexation reaction with volatile amines of different nature. Cyclohexylamine was selected as a most suitable model compound complexed without adsorption on textile surface. Suggested procedure including treatment of textiles in amine atmosphere followed by acid-base titration of extracted amine in aqueous solution may be directly applied in industrial practice. Further research is needed on the possible influence of different cyclodextrin fixation additives (cross-linking agents, etc.) incorporating into textile material by finishing with unsubstituted cyclodextrins.

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