## List of figures

- Fig. 1.1 The glucose residue in cyclodextrins.
- Fig. 1.2 Crystallographic structures of β-CD and per(2,6-O-methyl)-β-CD(DIMEB).
- Fig. 1.3 The geometry of the  $\beta$ -CD macrocycle.
- Fig. 2.1 The scheme of the neutron scattering experiment for the direct geometry time-of-flight spectrometer.
- Fig. 2.2 A hypothetical example showing the significance of the experimental energy resolution,  $\Delta E$ .
- Fig. 3.1 The geometry of the small-angle scattering experiment.
- Fig. 5.1 The definition of the hydration shell employed in the "hydrated solute model".
- Fig. 6.1 The comparison of the experimental,  $I_{\text{EXP SAXS}}(Q)$ , and theoretical,  $I_{\text{THEO SAXS}}(Q)$ , SAXS curves of D<sub>2</sub>O solutions of CDs and mCDs.
- Fig. 6.2 Temperature and concentration dependence of the experimental SAXS curves of  $\beta$ -CD and  $\gamma$ -CD solutions in D<sub>2</sub>O.
- Fig. 6.3 Temperature and concentration dependence of the experimental SAXS curves of DIMEB solutions in D<sub>2</sub>O.
- Fig. 6.4 Temperature and concentration dependence of the experimental SAXS curves of TRIMEG solutions in D<sub>2</sub>O.
- Fig. 6.5 SANS results for DIMEB solutions in D<sub>2</sub>O.
- Fig. 7.1 Scaling factor Sc.F( $Q_{\rm EL}$ ) determined in the fits to QENS spectra of D<sub>2</sub>O and H<sub>2</sub>O.
- Fig. 7.2 Values of  $D_{TR \, SOL}$  for DIMEB solutions in  $D_2O$  as obtained from QENS and PFG-NMR experiments.
- Fig. 7.3 Values of the rotational structure factors,  $A_l(Q)$ , for DIMEB.
- Fig. 7.4 Influence of the rotational diffusion coefficient,  $D_{r \, SOL}$ , (kept at various fixed values) on the translational diffusion coefficient,  $D_{TR \, SOL}$ , values determined from the fits of QENS spectra.
- Fig. 7.5 Examples of fits of the "standard solute model" to spectra of DIMEB solutions in  $D_2O$  with the concentration 39.8 mM,  $\Delta E$ =30  $\mu eV$ .
- Fig. 7.6 Examples of fits of the solute model with the additional "broad" component to spectra of DIMEB solutions in  $D_2O$  with the concentration 39.8 mM,  $\Delta E$ =30  $\mu eV$ .
- Fig. 7.7 The intensity of the component describing the motion of -CH<sub>3</sub> and -CH<sub>2</sub>-OCH<sub>3</sub> groups,  $A_{MET}(Q)$ , as determined from the fit to the spectra of DIMEB solution in D<sub>2</sub>O with the concentration 39.8 mM.
- Fig. 7.8 Values of the rotational diffusion coefficient, D<sub>r SOL</sub>, and the width of the component due to the motion of -CH<sub>3</sub> and -CH<sub>2</sub>-OCH<sub>3</sub> groups, W<sub>MET</sub>, as determined from the fit to the

spectra of DIMEB solution in D<sub>2</sub>O with the concentration 39.8 mM.

Fig. 7.9 Behavior of QENS intensity towards low Q region in the {NEAT(3)} spectra of D<sub>2</sub>O and  $\gamma$ -CD, DIMEB and TRIMEG solutions in D<sub>2</sub>O.

Fig. 7.10 Results of the application of the "hydrated solute model".

Fig. A1 Fit of {NEAT(4)} D<sub>2</sub>O spectra,  $\lambda_0$ =5.1 Å,  $\Delta$ E=90  $\mu$ eV, low Q region.

Fig. A2 Fit of {NEAT(4)}  $D_2O$  spectra,  $\lambda_0=5.1$  Å,  $\Delta E=90$  µeV, high Q region.

Fig. A3 Fit of {IN5(1)} D<sub>2</sub>O spectra,  $\lambda_0$ =7.6 Å,  $\Delta$ E=30  $\mu$ eV, low Q region.

Fig. A4 Fit of {IN5(1)} D<sub>2</sub>O spectra,  $\lambda_0$ =7.6 Å,  $\Delta$ E=30  $\mu$ eV, high Q region.

Fig. A5 Fit of {NEAT(3)} D<sub>2</sub>O spectra,  $\lambda_0$ =15.3 Å,  $\Delta$ E=10  $\mu$ eV.

Fig. A6 Fit of {IN16}  $D_2O$  spectra,  $\lambda_0=6.27$  Å,  $\Delta E=1$   $\mu eV$ .

Fig. A7 Fit of {NEAT(2)} H<sub>2</sub>O spectra,  $\lambda_0$ =5.1 Å,  $\Delta$ E=90  $\mu$ eV, low Q region.

Fig. A8 Fit of {NEAT(2)} H<sub>2</sub>O spectra,  $\lambda_0$ =5.1 Å,  $\Delta$ E=90  $\mu$ eV, high Q region.

Fig. A9 Fit of {IN5(2)} H<sub>2</sub>O spectra,  $\lambda_0$ =7.6 Å,  $\Delta$ E=30  $\mu$ eV, low Q region.

Fig. A10 Fit of {IN5(2)} H<sub>2</sub>O spectra,  $\lambda_0$ =7.6 Å,  $\Delta$ E=30  $\mu$ eV, high Q region.

Fig. B1 Examples of the fit of the "standard solute model" to  $\{IN16\}$  spectra of DIMEB solutions in heavy water, 39.8 mM,  $\phi$ =10.96° and 16.80°.

Fig. B2 Example of the fit of the "standard solute model" to {IN16} spectra of DIMEB solutions in heavy water, 39.8 mM,  $\varphi$ =25.0°.

Fig. B3 Example of the fit of the "standard solute model" to  $\{IN16\}$  spectra of DIMEB solutions in heavy water, 20.3 mM,  $\varphi$ =16.8°.

Fig. B4 Examples of the fits of the "standard solute model" to the {NEAT(3)} spectra of DIMEB solutions in heavy water, 37.6 mM,  $\varphi$ =76°.

Fig. B5 Examples of the fits of the "standard solute model" to the {NEAT(3)} spectra of DIMEB solutions in heavy water, 37.6 mM,  $\varphi=128.5^{\circ}$ .

Fig. C1 Geometry of scattering and angle definitions.

Fig. E1 Wave vectors relationship for double scattering.

## List of tables

- Tab. 1.1 Characteristics of  $\alpha$ -,  $\beta$  and  $\gamma$ -CD.
- Tab. 1.2 The abbreviations employed for the designation of per-dimethylated and per-trimethylated cyclodextrins.
- Tab. 2.1 Neutron scattering lengths and cross sections for selected elements/sotopes.
- Tab. 3.1 Samples measured in QENS experiments.
- Tab. 3.2 The details of the QENS experiments.
- Tab. 5.1 Neutron scattering cross sections for water and native and methylated cyclodextrins [barn].
- Tab. 6.1 Average electron densities ( $\rho_{AV}$ ) and contrast ( $\Delta \rho_{AV}$ ) for CDs and mCDs; experimental and computed values of the square of gyration radius, maximum diameter of the solute molecule and volume estimate.
- Tab. 6.2 Values of the second virial coefficient (A<sub>2</sub>) for DIMEB and TRIMEG in D<sub>2</sub>O at room temperature (24 °C) as function of concentration (determined from the experimental SAXS curves).
- Tab. 7.1 Parameter values as determined from fitting of the theoretical model to the spectra of  $D_2O$  and  $H_2O$ .
- Tab. 7.2 Magnitudes of the translational spectral broadening (example).
- Tab. 7.3 Magnitudes of the rotational spectral broadening (example).
- Tab. 7.4 Values of translational diffusion coefficients of DIMEB in D<sub>2</sub>O solutions as determined by QENS and PFG-NMR.
- Tab. 7.5 Values of the rotational diffusion coefficient,  $D_{r SOL}$ , of DIMEB-molecule found from the QENS spectra of DIMEB solution in  $D_2O c = 50 \text{ mg/mL} \{37.6 \text{ mM}\}$ .
- Tab. 7.6 Values of the translational and rotational diffusion coefficients,  $D_{TR SOL}$  and  $D_{r SOL}$ , respectively, as determined from the QENS spectra of  $\beta$ -CD solution in  $D_2O$ .

## List of important symbols and notations

 $\otimes$  convolution operator

A<sub>2</sub> the second virial coefficient

< b > coherent neutron scattering length [10<sup>-12</sup> cm]

c concentration [mg/mL]

CM (or c.m.) center of mass

D maximum particle diameter [Å]

DHO damped harmonic oscillator

DWF Debye-Waller factor

 $D_{TR}$  translational diffusion coefficient [10<sup>-5</sup> cm<sup>2</sup>/s]

D<sub>r</sub> rotational diffusion coefficient [meV]

EC empty container

FWHM full width at half maximum  $G(\mathbf{r}, t)$  pair correlation function  $G_S(\mathbf{r}, t)$  self correlation function

 $g_{CM}(r)$  static pair correlation function of the center of mass of the molecule

 $H_1(\mathbf{k}_{\theta}, \mathbf{k})$  1<sup>st</sup> order transmission factor HWHM half width at half maximum h thickness of the hydration shell

ħ reduced Planck constant,  $\hbar = (6.62607 \times 10^{-34} / 2\pi) \text{ J} \cdot \text{s} \approx 0.6583 \text{ meV} \cdot \text{ps}$ 

 $\hbar\omega$  energy transfer suffered by the neutron [meV] I(Q) scattering intensity (at infinite dilution) in the small-angle scattering experiment

I(Q, c) scattering intensity in the small-angle scattering experiment

 $I(\mathbf{Q}, t)$  intermediate scattering function  $I_{SELF}(\mathbf{Q}, t)$  self intermediate scattering function

 $I_{QENS}(Q_{EL})$  QENS integral (i.e. integral of  $S_{EXP}(\varphi, \omega)$ )

 $m{k}$  wave vector  $[\AA^{-1}]$   $m{k}_{m{\theta}}$  incident wave vector  $[\AA^{-1}]$ 

Lor Lorentzian

M molecular mass [g/mol]

MSC multiple scattering

N<sub>HYD</sub> number of water molecules in the hydration shell

n number density [cm<sup>-3</sup>]

PFG-NMR pulsed field gradient nuclear magnetic resonance

 $m{Q}$  momentum transfer  $[\mathring{A}^{-1}]$   $Q_{\text{EL}}$  modulus of the elastic momentum transfer  $[\mathring{A}^{-1}]$ 

 $R(\phi, \omega)$  energy resolution function

$R^2_{g}$	square of the radius of gyration	$[\AA^2]$	
$S(Q, \omega)$	scattering function	$[meV^{-1}]$	
$S_{INC}(Q, \omega)$	incoherent scattering function	$[meV^{-1}]$	
S(Q)	intermolecular structure factor of the center of mass		
S(Q, c)	the same as $S(Q)$ , in this notation the concentration dependence is stressed		
SC	sample container		
Sc.F.	Scaling factor		
T	absolute temperature	[K]	
$T_{S,}T_{EC}$	transmission of the sample and empty cell, respectively		
$< u^2 >$	mean square displacement	$[\AA^2]$	

## **Greek letters**

Greek letters		
α	sample angle	
Γ	damping constant of the DHO	[meV]
$\gamma_{\mathrm{CM}}(oldsymbol{\mathcal{Q}})$	the space-Fourier transform of $g_{CM}(r)$	
$\gamma(r)$	correlation function of the excess scattering density	
δ	delta function	
$\delta_{ij}$	Kronecker symbol	
ΔΕ	full width at half maximum (FWHM)	[meV]
λ	wavelength	[Å]
$\lambda_0$	incident neutron/X-ray wavelength	[Å]
П	osmotic pressure	
$ ho_0$	solvent scattering density	[cm <sup>-2</sup> ]
$ ho_{AV}$	average solute scattering density	[cm <sup>-2</sup> ]
$\Delta \rho_{AV}$	scattering contrast	[cm <sup>-2</sup> ]
$\rho(\mathbf{r})$	scattering density	[cm <sup>-2</sup> ]
$\sigma_{\text{INC}}$	incoherent scattering cross section	[barn=10 <sup>-24</sup> cm <sup>2</sup> ]
$\sigma_{\text{COH}}$	coherent scattering cross section	[barn=10 <sup>-24</sup> cm <sup>2</sup> ]
$\sigma_{\scriptscriptstyle S}$	scattering cross section, $\sigma_{INC} + \sigma_{COH}$	[barn=10 <sup>-24</sup> cm <sup>2</sup> ]
$\sigma_{A}$	absorption scattering cross section	[barn=10 <sup>-24</sup> cm <sup>2</sup> ]
$\sigma_{R}$	standard deviation of the Gaussian function	
$ au_{TR}$	time between the successive jumps (in translational diffusion)	[ps]
$\tau_{ROT}$	rotational correlation time	[ps]
Ψ	polar angle	
φ	scattering angle	
Ω	solid angle	
ω	circular frequency	