Journal of Thermal Analysis and Calorimetry, Vol. 82 (2005) 483–489

THERMODYNAMIC PROPERTIES OF ASSOCIATION COLLOIDS

P. Garidel[1,2*] *and A. Hildebrand*[2]

[1]Institute of Physical Chemistry, Mühlpforte 1, Martin-Luther-University Halle/Wittenberg, Germany
[2]Institute of Pharmaceutical Technology and Biopharmaceutics, Wolfgang-Langenbeck-Str. 4, 06108 Halle/Saale, Germany

The single components of association colloids are amphiphilic molecules, which are held together by van der Waals forces and/or hydrogen interactions. The thermodynamic parameters associated with the aggregation behaviour of amphiphiles depend on the chemical nature of the molecules as well as their environmental conditions (temperature, ionic strength, etc.).

The systems studied and presented in this paper are association colloids, also known as micellar systems, which are formed of biological relevant detergents (e.g. bile salts, fatty acids). Information concerning the self-organisation (self-aggregation) of such micellar colloids can be easily obtained from isothermal titration calorimetry (ITC), as the critical micelle/aggregation concentration, the number of molecules (*n*) associated in the aggregate and the heat of aggregation. A complete thermodynamic description (ΔH, ΔS, ΔG, ΔC_p) of the micellar colloids can be derived from the ITC data, allowing insights into the formation and stability of these colloidal systems. Based on the mass action model, taking into account counter ion binding, the ITC titration curves were simulated, and the aggregation number *n* of the aggregates derived.

Isothermal titration calorimetry has a considerable advantage compared to other methods, because the critical micellisation concentration, the thermodynamic parameters of the aggregation process, and the aggregation numbers can be determined directly from one experiment.

Keywords: *association colloids, calorimetry, ITC, micelle, thermodynamic*

Introduction

The term colloid (derived from the Greek word ‘kolla’ meaning glue) applies broadly to systems containing at least two components, in any state of matter, one dispersed in the other, in which the dispersed component consists of large molecules or small particles [1–3]. A typical characteristic of colloidal systems is based on the particle size, which ranges between 10^{-9}–10^{-7} m [1, 2]. Lumière and Staudinger classified colloidal systems into two groups: molecular and association (micellar) colloids [1, 2]. The particles of molecular colloids are single macromolecules, and their structure is essentially the same as the structure of small molecules, i.e. the atoms are joined by true chemical bonds (e.g. starch). The particles of association colloids are not large molecules (e.g. bio-polymers), but aggregates of many small molecules (the monomers), which are held together by i.e. cohesive, van der Waals forces or hydrogen bondings.

The concentration at which the micelles are formed is termed the critical micellisation concentration (*cmc*) (Fig. 2b, and text below). A number of methods, including electrical conductivity [4–6], fluorescence depolarisation [7], light scattering [8, 9], hyper-Rayleigh scattering [10], gel filtration chromatography [11], density measurements [12], surface tension [13], viscosity measurements [14], spectrophotometry [15, 16], cyclic voltametry [17], nuclear magnetic resonance [18], capillary electrophoresis [19, 20] and others [21–23] have been used to determine the *cmc* of various amphiphiles.

The presented paper addresses the interactions involved in the self-association and driving forces for the formation of association colloids. The investigated systems are composed of biological relevant detergents like bile salts and fatty acids. Bile salts are found in mixed micelles, which are used e.g. as drug delivery systems [24].

The thermodynamic parameters associated with the self-organisation of detergents can be easily obtained from isothermal titration calorimetry (ITC). ITC is an extremely sensitive technique measuring the heat of reaction (in the range of a few microcalories) of two components after mixing. This corresponds to temperature differences of less than 10^{-6} K, compared to a reference system. A so-called demicellisation experiment is presented [25–30]. The thermodynamic parameters connected with the demicellisation, the change in demicellisation enthalpy ($\Delta H_{\mathrm{demic}}$), the change in demicellisation entropy ($\Delta S_{\mathrm{demic}}$), the change in Gibbs energy ($\Delta G_{\mathrm{demic}}$), as well as the change in heat capacity ($\Delta C_{\mathrm{p\ demic}}$) during demicellisation are obtained from one and the same ITC experiment. Additionally, the critical micellisation concentration (*cmc*) is gained. From the

---

[*] Author for correspondence: Patrick.Garidel@t-online.de

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

ITC data, information concerning the number of molecules forming the aggregate can also be derived.

Further applications of ITC in pharmaceutical and colloidal sciences have been reviewed recently and it is referred to these papers [31, 32].

Experimental

Materials and methods

The detergents were obtained from Sigma and were used without further purification. Detergent solutions of a definite concentration were freshly prepared by weighting a certain amount of detergent and dissolving it in an appropriate buffer or water (see text).

ITC measurements were performed with a MicroCal Omega titration calorimeter, an MCS ITC and a VP-ITC unit (MicroCal, Inc., Northampton, MA, USA). Technical details are given elsewhere [24, 27, 28]; the experimental procedure is the follow [33]: The experimental cell is filled with degassed water or buffer solution. A removable syringe (e.g. 250 μL) is filled outside the instrument with a colloidal (micellar) solution at a concentration, which is expected to be much higher than the critical micellisation/aggregation concentration (*cmc*). Defined aliquots (normally 5–10 μL) of the micellar solution are injected stepwise into the reaction cell and the heat flow is measured as a function of time. During the titration experiment the syringe rotates, allowing appropriate mixing. Data evaluation is performed as described recently [27, 28]. With the used set-up the heat of reaction can be determined in temperature ranges between 5–70°C.

Results and discussion

The demicellisation experiment into pure buffer represents the dilution of association colloids (micelles) and, as a consequence of the dilution, the stability of the colloids is altered leading to a disintegration of the micellar colloids. The related heat flows are registered by ITC. From these experiments information concerning the stability and self-organisation of the micellar colloids are derived.

A typical ITC detergent dilution experiment of sodium cholate (NaC), a trihydroxy bile salt, in water at pH 7.5 (15°C) is shown in Fig. 1a. The titration consists of 25 injections of 10 μL aliquots of a highly concentrated micellar solution. Each injection induces a heat flow as a function of time and, thus a deviation from the baseline. The next injection is performed after the baseline has reached its initial value, which usually takes a few minutes. The reaction heat of each injection is obtained by integration, as can be seen in Fig. 1b. Exothermic heat flows are measured (Fig. 1). With increasing detergent concentration in the sample cell, the heat flow decreases and becomes constant, i.e. almost zero at the end of the experiment (Fig. 1a). As is obvious from Fig. 1b, the integration of the heat effects as a function of total detergent in the measuring cell has a sigmoidal shape.

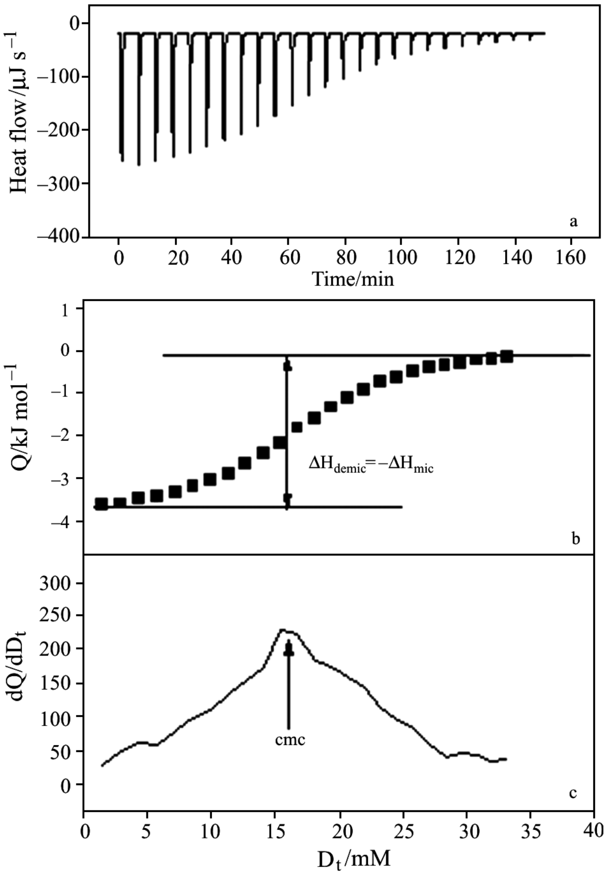

Fig. 1 Titration of 200 mM sodium cholate (NaC) in water at pH 7.5 into 1.34 mL water at pH 7.5 at 15°C. a – Calorimetric traces (25 injections a 10 mL aliquots), b – reaction enthalpy (Q) *vs*. the total detergent concentration D_t in the reaction cell, c – first derivative (dQ/dD_t) of curve shown in b calculated numerically from interpolated values. *cmc*: critical micellisation concentration

Figure 2a schematically represents the processes involved during the demicellisation experiment. The concentration of the detergent in the syringe is much larger than the expected *cmc* of the detergent (c_{syr}>>*cmc*), implicating that the solution in the syringe is composed of micelles in equilibrium to monomers. As a consequence, for the first injection into the measuring cell, which is filled with water, all micelles disintegrate and the corresponding reaction heat for the demicellisation process is measured (Fig. 2a), in addition to the enthalpy of monomer dilution. This process is temperature dependent. At 15°C, the dilution of NaC (water,

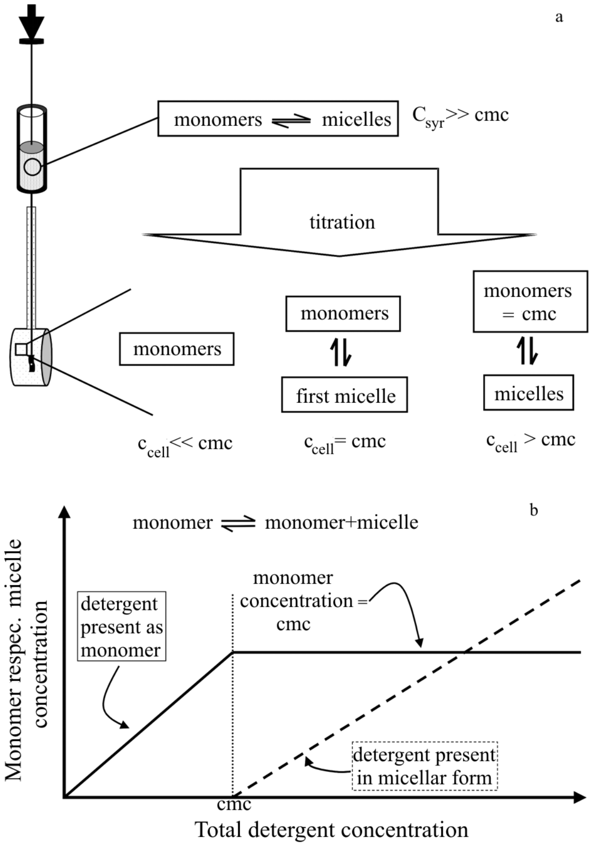

Fig. 2 a – Schematic representation of the demicellisation experiment; b – concentration dependence of monomers and micelles as a function of the total detergent concentration

pH 7.5) is exothermic (Fig. 1) and decreases continuously [28]. During the titration experiment, the amount of detergent in the sample cell increases and at a critical concentration, the so-called critical micellisation concentration (*cmc*), the first aggregates are formed (Fig. 2b). This critical concentration is easily determined in the ITC experiment by calculating the first derivative of the reaction heat with respect to the total detergent concentration D_t in the cell (Fig. 1c) [26–30].

The molar reaction heat ΔH is obtained as shown in Fig. 1b. The enthalpy of the demicellisation process ($\Delta H_{\mathrm{demic}}$) is equal to the enthalpy for the micellisation process (ΔH_{mic}), but opposite in sign.

The large exothermic peak observed for the first injection is the sum of three processes [28]: 1. dilution of monomers ($\Delta H_{\mathrm{mon,dil}}$), 2. dilution of micelles ($\Delta H_{\mathrm{mic,\ dil}}$) and 3. demicellisation, i.e. decomposition of micelles ($\Delta H_{\mathrm{demic}}$) (Fig. 2a).

$\Delta H_{\mathrm{mon,\ dil}}$ is obtained by titrating a highly diluted detergent solution (monomeric solution) to buffer, whereas the second heat contribution $\Delta H_{\mathrm{mic,\ dil}}$ is obtained by the injection of a micellar solution into the sample cell containing also a micellar solution (Fig. 2).

From this type of experiments the demicellisation enthalpy as well as the *cmc* is obtained and the thermodynamic parameters are derived. The change in free enthalpy for the demicellisation process $\Delta G_{\mathrm{demic}} = -R\,T \ln cmc'$, with the gas constant R, the temperature T and *cmc*' being the *cmc* expressed in mole fraction units, is calculated from the *cmc* data. Using the Gibbs–Helmholtz relation, the change in entropy ($\Delta S_{\mathrm{demic}}$) is obtained. In Fig. 3 the *cmc*'s of NaC (water, pH 7.5) are represented at various temperatures. As observed for a number of detergents, the *cmc* has a minimum at room temperature [26, 28, 33].

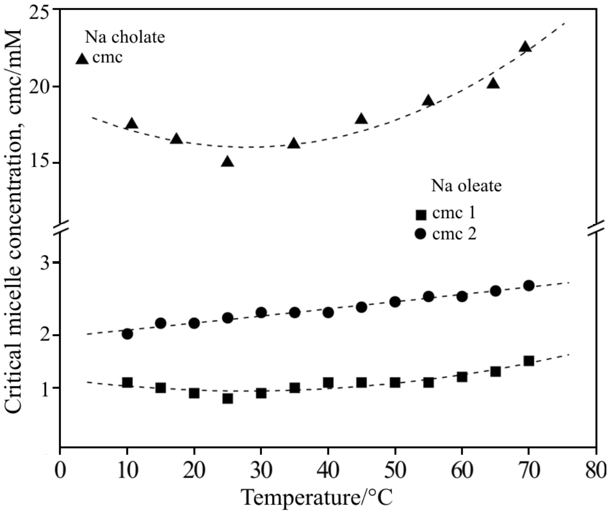

Fig. 3 Temperature dependence of the critical micellisation concentration (*cmc*) of sodium cholate (NaC) and sodium oleate (NaO) in water at pH 7.5. The lines are obtained using a second order polynomial fit. Note, that for NaC only one *cmc* is detected, whereas two *cmc*'s are found for NaO

Figure 4 represents two ITC dilution experiments of sodium oleate (NaO) in water (pH 7.5) at 15 and 70°C. At low temperature the heat flow is exothermic compared to data obtained at high temperature: $\Delta H = -16.3$ kJ mol^{-1} (15°C) and $\Delta H = +20.6$ kJ mol^{-1} (70°C) (Fig. 4).

Most detergents, like sodium dodecyl sulphate [26], octyl glucoside [27], bile salts [28, 30], oligo(ethylene oxide) alkyl ethers [25, 29], or the steroid CHAPS [34] show only one extremum in the dQ/dD_t curve of the demicellisation experiment, which corresponds to one *cmc* value. However, analysing the first derivative (Fig. 4) dQ/dD_t of NaO clearly shows the appearance of two extrema, indicating two *cmc* values denoted by *cmc*1 and *cmc*2. The *cmc* data of NaO are shown in Fig. 3 and are fitted with a second order polynomial [35]. Compared to the *cmc* of NaC, the *cmc*'s of NaO are much smaller, due to the different chemical structures of the amphiphiles. The temperature dependence of the *cmc*'s of NaO is reported in Fig. 3.

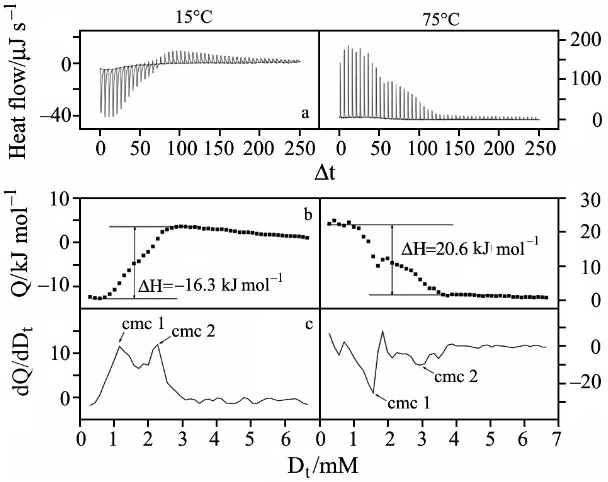

Fig. 4 ITC demicellisation experiment for the determination of the critical micellisation concentration (*cmc*) of sodium oleate (NaO) in water at pH 7.5 at 15°C and 75°C: titration of 40 mM NaO in steps of 50 per 5 μL. a – Calorimetric traces (heat flow *vs*. time), b – reaction enthalpy (*Q*) *vs*. the total detergent concentration (D_t) in the reaction cell, and c – first derivative (dQ/dD_t) of curve b calculated numerically from interpolated values

Usually, the temperature dependence of the *cmc* of a number of amphiphiles shows a minimum at room temperature [33], as is observed for the first *cmc*1 of NaO or the *cmc* of NaC. The second *cmc*2 of NaO, however, increases continuously with increasing temperature (Fig. 4). This means, that the second dissociation step of NaO is accompanied by an endothermic process over the whole temperature range, whereas the enthalpy change for the first dissociation is temperature dependent. A careful analysis of the ITC titration curve gives indeed an indication that even at low temperature the second *cmc* is connected with a slight endothermic effect, because the reaction enthalpy is positive at intermediate concentrations [36].

The two *cmc*'s for the demicellisation of NaO as observed by ITC can be explained by a two-step self-aggregation mechanism. Using proton longitudinal magnetic relaxation times and self-diffusion measurements similar results were obtained [37]. Mahieu *et al*. [37] detected two types of aggregates at a concentration of 1.5 and 3.0 mM at room temperature, with the first micelles having a spherical shape, whereas at higher detergent concentration a transformation into rod-like structures is observed. Such detergent systems with two or more *cmc*'s were denoted as 'multi-*cmc* systems' [38], and are characterised by a stepwise aggregation of monomers with a discontinuous transformation of the different aggregate structures.

Based on the pseudo phase separation model, the colloids are considered as a separate phase (Fig. 2b) and $\Delta G_{\mathrm{demic}}$ as well as $\Delta S_{\mathrm{demic}}$ can be calculated as described previously. These data are represented in Fig. 5.

Due to the fact, that two *cmc*' are found for NaO, two data sets are obtained for $\Delta G_{\mathrm{demic}}$ [36]. A strong temperature dependence is observed for the change in entropy and enthalpy, whereas the change in Gibbs free energy is nearly not affected by temperature changes (Fig. 5). $\Delta G_{\mathrm{demic}}$ are positive over the whole investigated temperature range. As can be seen, the total $\Delta H_{\mathrm{demic}}$ is negative below room temperature and becomes positive above 25°C. This is the case for most detergents. At a temperature where $\Delta H_{\mathrm{demic}}=0$, the formation of micelles is completely entropy driven, which usually happens for ionic detergents at room temperature. At this temperature, the *cmc* shows a minimum in its temperature dependence (Fig. 3). At higher temperatures, the driving force for the aggregation becomes more and more of enthalpic nature. The $T\Delta S_{\mathrm{demic}}$ values become usually positive at extremely high temperatures. $\Delta H_{\mathrm{demic}}$ increases linearly for NaC, whereas for NaO $\Delta H_{\mathrm{demic}}$ does not increase linearly with temperature. As a result of this behaviour, the temperature dependence of the entropy term $T\Delta S_{\mathrm{demic}}$ of NaO is also curved and it is not clear whether $T\Delta S_{\mathrm{demic}}$ of NaO will ever become zero. The observed behaviour for the different thermodynamic functions is caused by the hydrophobic effect, which describes an enthalpy-entropy compensational effect during the self-association of detergent monomers [36].

During the demicellisation process changes concerning exposed hydrophobic surface area are induced. This information can be obtained by analysing the change in heat capacity $\Delta C_{\mathrm{p\ demic}}$ [39], which is defined as $\Delta C_{\mathrm{p\ demic}}=(\partial \Delta H_{\mathrm{demic}}/\partial T)_{\mathrm{p}}$. $\Delta H_{\mathrm{demic}}$ as a function of temperature (Fig. 5) can be fitted by a second order polynomial and as a consequence, $\Delta C_{\mathrm{p\ demic}}$ shows a linear temperature dependence. At 25°C, $\Delta C_{\mathrm{p\ demic}}$ of NaO in water at pH 7.5 is +780 J mol^{-1} K^{-1}, but $\Delta C_{\mathrm{p\ demic}}$ of NaC in water at pH 7.5 is smaller with +240 J mol^{-1} K^{-1}. Compared to the $\Delta C_{\mathrm{p\ demic}}$ values of bile salts, the $\Delta C_{\mathrm{p\ demic}}$ of NaO is much larger as can be explained by the different chemical nature of the amphiphiles. Positive $\Delta C_{\mathrm{p\ demic}}$ values indicate a transfer of hydrophobic surfaces into the surrounding water phase [40]. We have shown previously [39], that the contribution of the hydration of the hydrophilic surface areas, and the counter ions dissociating during the demicellisation has to be considered, however the latter is very small (~3% of the total contribution of $\Delta C_{\mathrm{p\ demic}}$ of NaO).

A general observed trend is that increasing the ionic strength induces a decrease of the *cmc*, which implicates a micelle formation at lower total detergent concentration, when the ionic strength is increased. The reason for this behaviour is due to the fact, that the higher ionic strength decreases the surface charge of the detergent micelles by shielding the charges as a re-

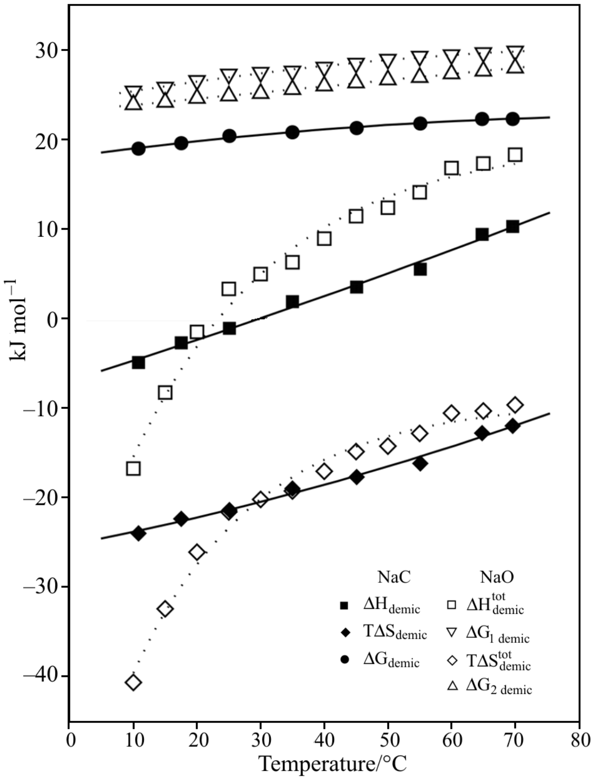

Fig. 5 Thermodynamic parameters of the demicellisation of sodium cholate (NaC) and sodium oleate (NaO) in water at pH 7.5 as a function of temperature

sult of counterion adsorption, and as a consequence, it becomes energetically more favourable for the monomers to self-associate into larger aggregates [26, 28].

The number of molecules associated in the self-organisation of a micelle can be derived from ITC data, by the simulation of the titration curve. The simulation model for the titration curves is based on the mass action model, by additionally taking counter ion binding to the aggregates into account [28].

The formation of a micelle M_n with n monomers D^- and γn bound counterions B^+ is given by:

$$n\mathrm{D}^- + \gamma n\mathrm{B}^+ \leftrightarrows \mathrm{M}_\mathrm{n}^{-(1-\gamma)\mathrm{n}} \qquad (1)$$

The concentrations $[\mathrm{M}_\mathrm{n}^{-(1-\gamma)\mathrm{n}}]$, $[\mathrm{D}^-]$, $[\mathrm{B}^+]$, the total detergent concentration c_t^D and the total counter-ion concentration c_t^B, with $c_\mathrm{t}^\mathrm{D}=c_\mathrm{t}^\mathrm{B}=c_\mathrm{t}$, are related by:

$$c_\mathrm{t}=[\mathrm{D}^-]+n[\mathrm{M}_\mathrm{n}^{-(1-\gamma)\mathrm{n}}]=[\mathrm{B}^+]+\gamma n[\mathrm{M}_\mathrm{n}^{-(1-\gamma)\mathrm{n}}] \qquad (2)$$

With the equilibrium constant K

$$K=[\mathrm{M}_\mathrm{n}^{-(1-\gamma)\mathrm{n}}]/([\mathrm{D}^-]^\mathrm{n}[\mathrm{B}^+]^{\gamma\mathrm{n}}) \qquad (3)$$

one obtains the following equation

$$[\mathrm{M}_\mathrm{n}^{-(1-\gamma)\mathrm{n}}]=[\mathrm{D}^-]^\mathrm{n}\{c_\mathrm{t}(1-\gamma)+\gamma[\mathrm{D}^-]\}^{\gamma\mathrm{n}}K \qquad (4)$$

The relation between K and ΔG is

$$\Delta G=-RT\ln K=n\Delta G_0 \qquad (5)$$

with ΔG_0 being the Gibbs energy change of the transfer of a monomer from water into the aggregate. Equations (2) and (4) are the basis for the simulations of the titration curves [28], using five adjustable parameters, namely the aggregation number n, ΔG_0, the enthalpy ΔH_demic, the dilution enthalpy of monomers $\Delta H_\mathrm{mon,\ dil}$, and the dilution enthalpy of micelles $\Delta H_\mathrm{mic,\ dil}$. The degree of counterion binding γ was introduced as a fixed parameter and values for γ were taken from the literature [41, 42].

The experimental data and simulated curves are reported in [28]. For NaC, the aggregation number at low temperature is n=4–5 and increases only slightly to n=6 with temperature. The influence of the ionic strength is negligible. For NaDC (sodium dihydroxy cholate), however, the influence of temperature and ionic strength is more pronounced. Aggregation numbers between 5 and 13 are found, depending on the temperature and ionic strength [28]. The calculated values for n are in agreement with previous observations by other groups, thus showing that ITC is a valuable method for the determination of the aggregation number of colloidal systems [28].

The monomer and micellar concentrations as a function of the total concentration are also obtained from the simulations. In contrast to the curves shown in Fig. 2b, monomer and micelle curves for e.g. NaC show that the monomer concentration still increases well above the *cmc*, particularly when no additional salt is present. This shows that the pseudo phase separation model, in which a constant monomer concentration above the *cmc* is assumed (Fig. 2b), is not always appropriate.

The physical properties of association colloids composed of two components depend, in addition to environmental conditions (e.g. salt concentration), also on the intermolecular interactions in the colloidal aggregate. The properties of such binary association colloids can be derived from ITC data. This will be demonstrated for the system NaC/NaO with a molar ratio of 5:2 [36].

The ITC demicellisation experiments show a characteristic temperature dependence of the *cmc* of the mixed micellar systems, with its minimum at room temperature. In general, it is observed that the presence of NaO induces a decrease of the *cmc* compared to the pure bile salt micelles [36]. In contrast to pure NaO, only one *cmc* is observed for the binary system NaC/NaO.

Assuming ideal mixing behaviour of two components forming association colloids, a cmc_mix can be calculated using the *cmc* data of the pure components. These data are then compared to the *cmc* data as obtained from the experiment to check the validity of the model, and thus, allowing more insights into the formation of these colloids.

Lange and Beck [43] as well as Clint [44] proposed a model for the calculation of cmc_{mix} value for ideal mixing according to:

$$\frac{1}{cmc_{\text{mix}}} = \frac{\alpha}{cmc_{\text{BS}}} + \frac{1-\alpha}{cmc_{\text{NaO}}} \tag{6}$$

with α being the total mole fraction of the bile salt (BS).

Rubingh [45] adapted this relation for non-ideal mixing behaviour of the components using a model based on regular solution theory, by introducing a non-ideal interaction parameter β_{I} which takes into account all deviations from an ideal mixing behaviour. β_{I} is thus defined as:

$$\beta_{\text{I}} = \frac{\ln\left(\dfrac{\alpha cmc_{\text{mix}}}{x_{\text{BS}} cmc_{\text{BS}}}\right)}{(1-x_{\text{BS}})^2} \tag{7}$$

with x_{BS} being the mole fraction of the bile salt in the colloid. x_{BS} is obtained by solving the following numerical equation:

$$\begin{aligned} x_{\text{BS}}^2 \ln\left(\frac{\alpha cmc_{\text{mix}}}{x_{\text{BS}} cmc_{\text{BS}}}\right) &= \\ = (1-x_{\text{BS}})^2 \ln\left[\frac{(1-\alpha) cmc_{\text{mix}}}{(1-x_{\text{BS}}) cmc_{\text{NaO}}}\right] \end{aligned} \tag{8}$$

A non-ideal mixing behaviour of both detergents is given by $\beta_{\text{I}} \neq 0$. Knowing β_{I} and x_{BS} the activity coefficients for both components f_{BS} and f_{NaO} can now be calculated:

$$f_{\text{BS}} = \exp[\beta_{\text{I}}(1-x_{\text{BS}})^2] \tag{9}$$

$$f_{\text{NaO}} = \exp(\beta_{\text{I}} x_{\text{BS}}^2) \tag{10}$$

The model presented by Rubingh [45] corrects the *cmc* values of both detergents by these activity coefficients and the cmc_{mix} is calculated as:

$$\frac{1}{cmc_{\text{mix}}} = \frac{\alpha}{f_{\text{BS}} cmc_{\text{BS}}} + \frac{1-\alpha}{f_{\text{NaO}} cmc_{\text{NaO}}} \tag{11}$$

The calorimetric data analysis of BS/NaO association colloids reveal that the experimental cmc_{mix} lies between the *cmc* data of the pure components, with the calculated cmc_{mix} values assuming ideal behaviour being larger than the experimental ones. The difference between the experimental cmc_{mix} and the calculated cmc_{mix} is smaller when the model of non-ideal mixing [45] is used compared to the simple model assuming ideal [44] mixing behaviour.

With increasing temperature the difference between calculated and observed cmc_{mix} values increases slightly. In the temperature range between 20–70°C, negative β_{I} are obtained. Negative values for β_{I} are characteristic for a deviation from ideal mixing behaviour with attractive interactions between the two components. For the system NaC/NaO, it was found that with increasing temperature, the mole fraction x_{NaC} in the mixed micelle increases, i.e. more NaC is transferred into the mixed micelle. Small deviations from ideal mixing behaviour are observed at low and high temperatures as is derived from the slightly negative β_{I}. The attractive interaction parameter is attributed to favourable changes in the packing behaviour in the binary association colloids and an induced reduction of particle surface charge [46].

Conclusions

Various calorimetric studies were summarised linked to the thermodynamic properties of association colloids. As presented in this paper, isothermal titration calorimetry (ITC) is a highly potent experimental technique for studying the self-aggregation of association colloids. From one and the same ITC demicellisation experiment, data are obtained, respectively derived and calculated, which are related to the formation and stability of colloidal systems. These data include the critical micellisation/aggregation concentration (*cmc*), the change in demicellisation enthalpy (ΔH_{demic}), the change in demicellisation entropy (ΔS_{demic}), the change in demicellisation Gibbs energy (ΔG_{demic}), the change in heat capacity ($\Delta C_{\text{p demic}}$), and the aggregation number (*n*), representing the number of monomers forming the colloids.

Additionally, using models describing ideal or non-ideal mixing behaviour, information concerning the interaction and self-association of different detergents in association colloids are obtained.

Acknowledgements

We thank Bettina Fölting for her excellent technical assistance. This work was supported by grants from the Max-Planck-Gesellschaft zur Förderung der Wissenschaften (P.G.).

References

1 B. Jirgensons and M. E. Straumanis, Kurzes Lehrbuch der Kolloidchemie. Bergman und Springer. Berlin, Heidelberg, New York 1949.
2 H. Staudinger, Organische Kolloidchemie, 3. Ausgabe, Vieweg Verlag, Braunschweig 1950.
3 G. Wedler, Lehrbuch der Physikalischen Chemie, Verlag Chemie VCH, Weinheim 1987.
4 J. J. Galán, A. González-Pérez, J. L. Del Castillo and J. R. Rodríguez, J. Therm. Anal. Cal., 70 (2002) 229.
5 A. González-Pérez, J. J. Galán and J. R. Rodríguez, J. Therm. Anal. Cal., 72 (2003) 471.

6 J. J. Galán, A. González-Pérez and J. R. Rodríguez, J. Therm. Anal. Cal., 72 (2003) 465.
7 X. Zhang, J. K. Jackson and H. M. Burt, J. Biochem. Biophys. Methods, 31 (1996) 145.
8 K. J. Mysels and L. H. Princen, J. Phys. Chem., 63 (1959) 1696.
9 Y. D. Smet, L. Deriemaeker, E. Parloo and R. Finsy, Langmuir, 15 (1999) 2327.
10 S. Ghosh, A. Krishnan, P. K. Das and S. Ramakrishnan, J. Am. Chem. Soc., 125 (2003) 1602.
11 N. Funasaki, Adv. Colloid Interface Sci., 43 (1995) 87.
12 B. Farhadieh, J. Pharm. Sci., 62 (1973) 1685.
13 K. L. Mittal, J. Pharm. Sci., 61 (1972) 1334.
14 H. Akbaş, T. Sidim and M. Işcan, Turk J. Chem., 27 (2003) 357.
15 A. Dominguez, A. Fernandez, N. Gonzalez, E. Iglesia and L. Montenegro, J. Chem. Education, 74 (1997) 1227.
16 W. Spivak, C. Morrison, C. Devinuto and W. Yyuey, Biochem. J., 252 (1988) 275.
17 A. B. Mandal and B. U. Nair, J. Phys. Chem., 95 (1991) 9008.
18 T. S. Lee and K. W. Woo, J. Colloid Interface Sci., 169 (1995) 34.
19 T. Le Saux, A. Varenne and P. Gareil, J. Chromatography A, 1038 (2004) 275.
20 C. E. Lin, J. Chromatography A, 1037 (2004) 467.
21 E. J. Williams and V. F. Smolen, J. Pharm. Sci., 612 (1972) 639.
22 R. Huttenrauch, S. Fricke and M. Kohler, Pharm. Res., 5 (1988) 726.
23 F. Kopecky, M. Vojtekova, M. Vrana and K. Cizova, Coll. Czechoslovak Chem. Comm., 67 (2002) 245.
24 A. Hildebrand, K. Beyer, R. Neubert, P. Garidel and A. Blume, Colloids Surf. B, 32 (2003) 335 and references therein.
25 H. Heerklotz, G. Lantsch, H. Binder, G. Klose and A. Blume, J. Phys. Chem., 100 (1996) 6764.
26 S. Paula, W. Süs, J. Tuchtenhagen and A. Blume, J. Phys. Chem., 99 (1995) 11742.
27 M. Keller, A. Kerth and A. Blume, Biochim. Biophys. Acta, 1326 (1997) 178.
28 P. Garidel, A. Hildebrand, R. Neubert and A. Blume, Langmuir, 16 (2000) 5267.
29 H. Heerklotz and J. Seelig, Biophys. J., 78 (2000) 2435.
30 P. Garidel, M. Keller, A. Hildebrand and A. Blume, J. Liposome Res., 13 (2003) 62.
31 M. J. Cliff and J. E. Ladbury, J. Molec. Recognition, 16 (2003) 383.
32 P. Garidel and A. Blume, MicroCal Application Note, 2005, in press.
33 A. Blume and P. Garidel, Lipid model membranes and biomembranes. In: P. K. Gallagher (series Ed.), The Handbook of Thermal Analysis and Calorimetry, R. B. Kemp (Ed.), From Macromolecules to Man, 1st Ed., Vol. 4, Elsevier, Amsterdam 1999, pp. 109–173.
34 H. Heerklotz and J. Seelig, Biochim. Biophys. Acta, 1508 (2000) 69.
35 J. J. H. Nusselder and J. B. F. N. Engberts, J. Colloid Interface Sci., 148 (1992) 353.
36 A. Hildebrand, P. Garidel, R. Neubert and A. Blume, Langmuir, 20 (2004) 320.
37 N. Mahieu, D. Canet, J. M. Cases and J. M. Boubel, J. Phys. Chem., 95 (1991) 1844.
38 Y. Zimmels and I. J. Lin, Colloid Polym. Sci., 252 (1974) 594.
39 P. Garidel and A. Blume, Langmuir, 15 (1999) 5526.
40 C. Joliceur and R. R. Philip, Can. J. Chem., 52 (1974) 1834.
41 A. Coello, F. Meijide, E. R. Núñez and J. Vázque Tato, J. Phys. Chem., 97 (1993) 10186.
42 A. Coello, F. Meijide, E. R. Núñez and J. Vázque Tato, J. Pharm. Sci., 85 (1996) 9.
43 H. Lange and K. H. Beck, Kolloid. Z. Polym., 251 (1973) 424.
44 J. H. Clint, J. Chem. Soc. Faraday Trans., 71 (1975) 1327.
45 D. N. Rubingh, Mixed micelle solution. In: Solution chemistry of surfactants, Bd. 1; K. L. Mittal (Ed.) Plenum Press, New York 1979, p. 337.
46 J. Coret, A. Shiloach, P. Berger and D. Blankschtein, J. Surfact. Det., 2 (1999) 51.

DOI: 10.1007/s10973-005-7240-4