

**Investigation of inclusion complex formation of surfactants
in liquid phase and the study of surfactant adsorption at
the solid/liquid interface**

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1. Introduction and objectives

The association colloids are perhaps the most well-known molecules in colloid chemistry and surfactants belong to these types of molecules. Surfactants have an amphiphilic (molecules made of polar and apolar units) characteristic which makes them very appealing for every day use and for research as well.

Because of their amphoteric nature they tend to self-assemble and this is why they were chosen as model material for phospholipids. Due to their self-assembly characteristics they tend to accumulate in the interface. They have a wide range of application, like preparing various dispersions (foams, aerodispersions, emulsions) and through surface functionalization organophilized clay minerals can be synthesized. Nowadays surfactants are used as stabilizing agents for various kind of nanoparticles. Furthermore they are essential components in pharmaceutical products, because they help the absorption in the body and they play the main role in the membrane transport.

Their application in the oil production technology is also significant, because during surfactant and polymer-surfactant flooding processes enormous amounts are used in order to increase the extrusion efficiency.

Surfactants can interact with numerous molecules, for example with cyclodextrin which is constructed of the cyclization of α -D- glucopyranose units. In this type of reaction so called inclusion complexes are formed. Through secondary bonds the hydrophobic part of the surfactant interacts with the hydrophobic cavity of the cyclodextrin. This way the cyclodextrin is able to alter the properties of the surfactant. Due to complex formation, badly soluble parts of the molecule can become soluble. As the complex formation processes are reversible the obtained complexes can pose as drug-carriers as well as drug release systems which nowadays are essential in the pharmaceutical industry.

In the first part of my work I examined the temperature dependent complex formation of β -cyclodextrin (β CD) with the homologous series of the surfactants which contained different alkyl chain length and head groups. The complex formation was investigated with isotherm titration microcalorimeter. The objective of these experiments was to understand the thermodynamical nature of the reactions.

During my work I got involved with a project from the MOL Co. (Hungarian Oil and Gas Company) which revolved around the research of the tertiary oil extraction technology. In this project I examined the surface adsorption of a gemini structured surfactant called as bis-alkyl benzene sulfonate Jeffamine salt (ABSJ) at solid/ liquid interfaces.

For these measurements I assembled a fully automatized measurement technique and for the evaluation of the results I developed a new evaluation method.

2. Experimental

Materials

In the first part of this work, in order to study β -cyclodextrin inclusion complexes homologous series of four surfactants were used. The homologous series were made of the following surfactants: sodium alkane sulfate (SC_xS ; $x = 6; 8; 10; 12$), sodium alkane sulfonate (SC_xSN ; $x = 6; 8; 10; 12$), alkyltrimethylammonium bromide (C_xTAB ; $x = 6; 8; 10; 12; 14; 16$), dimethyl alkyl amine oxide (DC_xAO ; $x = 8; 10; 12$) and a polydisperse gemini surfactant known as bis-alkyl benzene sulfonate Jeffamine salt (ABSJ).

In the second part of the experimental work the surface adsorption of polydisperse gemini ABSJ was investigated with different medium (ultrapure water, synthetic ground water and Algyó ground water), and adsorbents (quartz, Berea sandstone, Algyó sandstone, the sieve fraction of the adsorbents were: 100-250 μm) at 298 K.

Methods

Isotherm titration microcalorimetry (ITC) was used to investigate the inclusion complex formation of the β CD. During the experiments the concentration of the surfactants were kept under the critical micelle concentration (cmc). The reason for this was that when the surfactant is diluted the superposition property of the demicellization enthalpy can influence the investigations of inclusion complexes. In those cases where this was not possible, the measured enthalpy change of the complex formation process was corrected with the previously obtained demicellization enthalpy which occurred during the dilution of the surfactant.

With ITC and surface tension (SFT) measurements the cmc of the ABSJ gemini surfactant and the formation of inclusion complexes were characterized.

During the adsorption experiments the concentrations of the surfactants were determined with double-beam UV-VIS spectrophotometer and an altered version of HPLC-MS.

The adsorbents were characterized by their surface area (BET), and to determine the composition of the adsorbents X-ray diffraction (XRD) measurements were made.

In a few cases thermoanalytical investigations were necessary; these were obtained with thermogravimetric (TG) measurements.

3. Summary of the novel scientific results

T1. The investigation of temperature dependent inclusion complex formation of β CD and surfactants with dodecyl (C_{12}) alkyl chain

It was proven that the head group of the surfactant does not have any effect on the formation of the inclusion complexes. The stoichiometry of the complexes is β CD : surfactant = 1 : 1. During the complex formation the association equilibrium constant linearly decreased at higher temperatures. It was found that hydrophobic effect is a main driving force in the complex formation, due to the amphipathic character of the surfactant.

There are two more driving forces which influence the reaction. The first is the detachment of the water molecules from the cavity of the cyclodextrin and the second is the binding of the surfactants inside the cavity of the cyclodextrin.

During the process the enthalpy-entropy compensation was ensured.

The complex formation is an exothermic reaction and the change of the Gibbs free enthalpy is negative which means the complex formation occurs spontaneously.

The calculated and measured van't Hoff reaction enthalpies are in the same order of magnitude, but some diversion was observed in the enthalpy change – temperature functions.

T2. The investigation of the inclusion complex formation with β CD and homologous series of the surfactants at 298 K

The stoichiometry of the formed complexes was proved to be 1 : 1. The critical alkyl chain length which is the smallest chain length that allows complex formation was different depending on the head group of the homologous series. The evidences indicate that at small chain length (C_x , where $x < 10$) the head group influences the complex formation. Although this effect decreases and ceases to exist at longer alkyl chain lengths. This is indicated by the exponential increasing of the equilibrium constant with the increasing number of carbon atoms.

T3. Temperature dependent (288-338 K) complex formation between gemini surfactant and β CD

In the first part I examined the ABSJ gemini surfactant's ultra low cmc value through a temperature dependent (283-343 K) experiment. This experiment was used as base for comparison between the applied methods Isotherm Titration microcalorimeter (ITC) and surface tension measurements (SFT)).

Afterwards the temperature dependent (288-338 K) complex formation experiment with β CD was investigated with both techniques.

It was found that in the presence of CD the SFT results only showed the shifting of the cmc values. This promoted the development of a new evaluation method for these results.

Therefore it became possible to gain thermodynamical information from SFT measurements for the temperature dependent inclusion complex formation. The results from different measurement techniques correlated well which indicates that thermodynamic information can be obtained from a non-thermoanalytical instrument.

The determined stoichiometry for β CD : ABSJ system is 2 : 1. This is not surprising because the ABSJ gemini surfactant contains two alkyl chains which can independently form an inclusion complex with β CD.

T4. Determining the isotherms of the individual components in the polydisperse ABSJ surfactant

At the beginning it was a big problem, that there was no fully operational instrument. Only the main sub-units were accessible. This measurement method had to be appropriately developed (HPLC-MS). Comparing measurements with UV spectrophotometer proved that this method is functional and exact.

The Berea sandstone is a standard adsorbent in the oil industry for depression experiments. The comparative experiment was adsorption of the ABSJ on Berea sandstone in ultra pure water. The following results show the specifically adsorbed amounts: $n^s(\text{MS}) = 3.27 \text{ mg} \cdot \text{g}^{-1}$, $n^s(\text{UV}) = 3.16 \text{ mg} \cdot \text{g}^{-1}$.

Beside the determination of the isotherm of the surfactant mixture, the isotherms of the individual components were also obtained. This was possible because the registration of the individual components in the MS instrument was done in several channels. From the examination of the individual isotherms it can be concluded that the individual components contribute to the overall isotherm in a weighted ratio, due to their percent composition.

With the normalization of the composition – as if the components were present in the same amount in the mixture – the specifically adsorbed amounts correlated well with the Traube's rule: $C_{13} > C_{12} > C_{11} > C_{10}$.

T5. The adsorption of ABSJ on Algyó sandstone from different medium

The Algyó sandstone is a possible reservoir (adsorbent) for oil industrial field-test.

For the quantitative adsorption of the ABSJ the following medium were used: ultra pure water, synthetic ground water (SZRV) and Algyó ground water (ARV).

During the measurements it was found that the absorption peaks of the synthetic ground water and ground water from Algyó are near the absorption peak of the ABSJ surfactant. For this reason the spectrophotometric measurements in these two medium are impossible. In this case the Mass spectrometry measurements can still provide useful information.

Using this measurement technique smaller specifically adsorbed quantities were measured in synthetic ground water and in ground water from Algyó which possess higher salt concentration: n^s (ultra pure water) = 2.44 mg*g⁻¹, n^s (SZRV) = 0.83 mg*g⁻¹, n^s (ARV) = 1.53 mg*g⁻¹.

T6. Investigation of surfactant adsorption on different adsorbents in the same medium

In the case of three different adsorbent (quartz, Berea sandstone, Algyó sandstone) the specifically adsorbed quantities on mass and surface unit of the adsorbents were measured and compared in ultra pure water.

The results show that the sequences of the beginning of the isotherms are: $m_{\text{Algyó sandstone}} > m_{\text{Berea sandstone}} > m_{\text{Quartz}}$, which shows correlation to the hydrophobic characteristic of the adsorbent and the percent quartz content. There is a significant change in the tendency of the quantitative sequences, when the adsorbed amount of substance is related to mass or surface unit.

T7. The adsorption of ABSJ on oil containing Algyó sandstone

During the mass spectrometry investigation of the oil contained Algyó sandstone an isotherm with three plateau values was obtained.

The value of the first plateau was the same as in the Algyó sandstone without oil. The first plateau was at the critical micelle concentration of the ABSJ. The values of the second and third plateaus were higher. Possibly the surfactant is adsorbed on the surface of the particles after the oil is detached. The surfactant can emulgate (2nd plateau) the oil and because of the amphipathic characteristic of the surfactant, it can dissolve in the oil phase (3rd plateau). This decreased the concentration of the surfactant, due to this loss of the surfactant new plateaus appeared.

T8. New perspectives

The developed HPLC-MS method provides exact quantitative information of the adsorbed amounts, and it is also insensitive to contamination of the sample. The instrument has a high sensitivity for the desired component and it allows us to determine the individual components and their isotherms as well.

Using mass spectrometry technique in surfactant adsorption experiments could lead to major results in understanding the real processes in the adsorption. For example understanding the depression processes in the reservoir.

Scientific Publications

Publications related to the scientific topic of the dissertation

- 1 **M. Benkő**, S. Puskás, Z. Király
Application of Mass Spectrometry for Study of the Adsorption of Multicomponent Surfactant Mixtures at the Solid/Solution Interface
Adsorption, (2012) DOI 10.1007/s10450-012-9419-x
IF₂₀₁₁: 2.000
 - 2 **M. Benkő**, R. Tabajdi, Z. Király
Thermodynamics of Formation of β -Cyclodextrin Inclusion Complexes with Four Series of Surfactant Homologs
J. Therm. Anal. Calorim., (2012) DOI 10.1007/s10973-012-2603-0
IF₂₀₁₁: 1.604
 - 3 **M. Benkő**, Z. Király
Thermodynamics of Inclusion Complex Formation of β -Cyclodextrin with a Variety of Surfactants Differing in the Nature of Headgroup
J. Chem. Thermodyn., 54 (2012) 211–216.
IF₂₀₁₁: 2.422
- Σ IF: 6.026**

Other Publications

- 1 L. Fülöp, I. M. Mándity, G. Juhász, V. Szegedi, A. Hetényi, E. Wéber, Zs. Bozsó, D. Simon, **M. Benkő**, Z. Király
A Foldamer-Dendrimer Conjugate Neutralizes Synaptotoxic β -Amyloid Oligomers
PLoS ONE., 7 (2012) 1-17.
IF₂₀₁₁: 4.092
 - 2 Á. Mastalir, Z. Király, **M. Benkő**, I. Dékány
Graphite Oxide as a Novel Host Material of Catalytically Active Pd Nanoparticle
Catal. Lett., 124 (2008) 34-38.
IF₂₀₀₈: 1.867
- Σ IF: 11.985**

Lectures and Posters in International Conferences

Lectures:

1. **M. Benkő**, Z. Király, É. Frank
Thermodynamics of Host-Guest Inclusion Complexation of Beta-Cyclodextrin with Selected Anionic, Cationic and Nonionic Surfactants
ICPAC International Conference on Pure and Applied Chemistry and Chemistry for Sustainable Development, 26-30. July. 2010.
Mauritius, abstract o. O-48; 62
2. **M. Benkő**, Z. Király
Microcalorimetric Study of Inclusion Complex Formation of Beta-Cyclodextrin with Homologous Series of Anionic, Cationic and Nonionic Surfactants
13th IACIS International Conference on Surface & Colloid Science and the 83rd ACS Colloid & Surface Science Symposium, 14-19. June. 2009.
New York, USA, abstract o. 200-201

Posters:

3. Z. Király, **M. Benkő**, B. László, É. Frank
Binding Studies of Cyclodextrin-Surfactant Complexes
14th Asian Chemical Congress (14ACC), 5-8. Sept. 2011.
Bangkok, Thailand, abstract. o. P0-G7-36a, 1047
4. **M. Benkő**, Z. Király, S. Puskás
Application of Mass Spectrometry for the Selective Determination of the Individual Adsorption Isotherms in Surfactant Mixtures at Solid/Solution Interfaces
ICPAC International Conference on Pure and Applied Chemistry and Chemistry for Sustainable Development, 26-30. July. 2010.
Mauritius, abstract p. P-35; 135
5. **Benkő M.**, Király Z.
Béta-ciklodextrin asszociációs zárványkomplex képződése anionos, kationos és nemionos tenzidekkel
Vegeyészkonferencia és 53. Magyar Spektrokémiai Vándorgyűlés, June. 30 – July. 2. 2010.
Hajdúszoboszló, Hungary, abstract pp. P-7, 97
6. **Benkő M.**, Király Z., Puskás S.
Tenzidkeverékek szilárd/folyadék határfelületi adszorpciójának meghatározása tömegspektrométerrel
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Hajdúszoboszló, Hungary, abstract pp. P-60, 150

7. Á. Mastalír, **M. Benkő**, Z. Király, I. Dékány
Palladium Nanoparticles in Graphite Oxide: Mild and Highly Selective Catalysts for Alkyne Semihydrogenation
13th IACIS International Conference on Surface & Colloid Science and the 83rd ACS Colloid & Surface Science Symposium, 14-19. June. 2009.
New York, USA, abstract p. 241-242
8. Á. Mastalír, Z. Király, **M. Benkő**, I. Dékány
Controlled Colloid Synthesis of Pd Nanoparticles in Graphite Oxide, a Highly Efficient Hydrogenation Catalyst
14th ICC International Congress on Catalysis, 13-18. July. 2008.
COEX, Seoul, Korea, abstract p. PP-12-13, 305
9. Á. Mastalír, Z. Király, **M. Benkő**, I. Dékány
Preparation of Monodispersed Pd Nanoparticles in Graphite Oxide, A Novel Host Material
9th Conference on Colloid Chemistry, 3-5. Oct. 2007.
Siófok, Hungary, abstract p. 128
10. Á. Mastalír, Z. Király, **M. Benkő**, I. Dékány
Graphite Oxide: A Novel Host Material for Transition Metal Nanoparticles
ISHHC XIII International Symposium on Relations between Homogeneous and Heterogeneous Catalysis, 16-20. July. 2007.
Berkeley, USA, abstract p. P-100, 185