

Summary of Ph.D. Thesis

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**Characterization of the self-assembly of functional and gemini surfactants  
in the bulk phase and on the solid/liquid interface**

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## Introduction and objectives

Research relating to surface-active materials has been being carried out for almost three decades in the Colloid Chemistry Department at the University of Szeged. These investigations include the organophilization of cation-exchanger clay minerals with cationic surfactants, the organophilization of anion-exchanger layered-structure double hydroxides with anionic surfactants, the stabilization of emulsions, microemulsions and catalytically active noble metal nanoparticles with anionic surfactants, and the preparation of mesoporous materials based on the self-assembly of surfactants by the template method.

The properties of classic surfactants (e.g. alkyltrimethylammonium halides, alkali metal salts of alkylsulfates and alkylsulfonates, and alkylated or arylated polyethylene glycol derivatives) have been exhaustively examined during recent decades, and the possibilities of the widespread utilization of these surfactants have therefore become more or less known. Investigations connected with the synthesis of new types of surfactants (e.g. twin-structural gemini surfactants and functional surfactants) are currently emphasized, and extensive studies are performed on their properties and possible applications.

The utilization of surfactants exploits their capability of forming nanostructures and, due to the molecular structure, their spontaneous self-assembly in solution and on interfaces. The driving force of micelle formation and their adsorption on solid/liquid (S/L) interface is based on thermodynamic causes. The direct and most important experimental method via which to study the thermodynamic driving force is microcalorimetry. One of my objectives was to examine the micelle formation of a functional, chiral cationic surfactant, (1*R*,2*S*)-(–)-*N*-dodecyl-*N*-methylephedrinium bromide (DMEB) by conductometric titration and titration microcalorimetry. One of my tasks was to organophilize montmorillonite with the surfactant and to prepare organic phase suspensions to decide whether the DMEB is suitable for the hydrophilization of montmorillonite of a required degree, which promotes the swelling of the organocomplex in appropriately chosen organic media. An immobilized ephedrine derivative is regarded as a heterogenated homogeneous catalyst which provides a possibility for the execution of enantioselective catalytic reactions.

Investigation of the micelle formation of a further two new types of gemini surfactant obtained from MOL Hungarian Oil and Gas Company Ltd. was among my tasks:  $\alpha,\alpha'$ -[2,4,7,9-tetramethyl-5-decyne-4,7-diyl]bis[ $\omega$ -hydroxylpoly(oxyethylene)] (Surfynol 465, S465), a non-ionic, and bis(4-(2-dodecyl)benzenesulfonate)-Jeffamine salt (DBSJ), an anionic

gemini surfactant; this preselection was designed to decide whether these compounds could be applied for the improved efficiency of enhanced oil recovery (EOR) processes.

One important parameter in terms of EOR is the extent of adsorption on the reservoir rocks. One of my aims was to determine the adsorption isotherm and the amounts adsorbed, considered as the adsorption loss, of the two surfactants by a dynamic method on an Algyó sandstone surface. For this, it was necessary to elaborate a real process-simulating dynamic adsorption measurement technique, and to construct an automated flow frontal column chromatography measurement system and the procedure for evaluation of the measurement results.

Mass spectrometry is an appropriate method with which to determine the molecular weight distribution of tested surfactants. The setting-up and optimization of liquid chromatography apparatus combined by a mass spectrometry detector (HPLC-MS) for surfactant studies was also my assignment. My aim was the investigation of component-selective adsorption and desorption of surfactants acceptable for EOR processes, followed by determination of the molecular weight distribution of polydisperse surfactants. I had to adapt the HPLC-MS measurement system to the execution of these kinds of measurements. One of my further research work objectives was to elaborate the method of evaluation of the results determined with the above-mentioned novel apparatus.

Accordingly my work not only involved basic science; the planned measurements were additionally motivated by practical utility.

## **Experimental**

### *Materials*

During my doctoral work, I examined various physical chemical properties of aqueous solutions of (1*R*,2*S*)-(-)-*N*-dodecyl-*N*-methylephedrinium bromide (DMEB), a cationic chiral surfactant,  $\alpha,\alpha'$ -[2,4,7,9-tetramethyl-5-decyne-4,7-diyl]bis[ $\omega$ -hydroxypoly(oxyethylene)] (Surfynol 465 or S465), a nonionic gemini surfactant, and bis(4-(2-dodecyl)benzenesulfonate)-Jeffamine Salt (DBSJ), an anionic gemini surfactant, synthesized in University of Pannonia laboratories ordered by MOL.

Organic suspensions were prepared by using organophilic montmorillonite with the precipitation of DMEB. *n*-Hexane, ethanol, tetrahydrofuran and toluene were applied as swelling media.

Ethanol, *n*-propanol, *n*-butanol, *n*-pentanol, *n*-hexanol and urea were employed as additives to influence Surfynol 465 micelle formation.

Jeffamine Salt D230, NP-10 (nonylphenylpolyglycol ether containing 10 ethylene oxide functional groups), or cocoDEA (coco acid diethanolamide) additives, and as main component DBSJ gemini surfactant containing surfactant mixtures were synthesized in the University of Pannonia laboratories ordered by MOL. An attempt was made to decrease the adsorption loss of DBSJ by applying PEG 20,000 (average molecular weight of polyethylene glycol: 20,000) and PVA 20,000 (average molecular weight of polyvinyl alcohol: 20,000).

The 100-250  $\mu\text{m}$  grain size fraction of powdered rock from the oil field in Algyó was used for the liquid chromatography and mass spectrometry. The dead volume of the column load was determined with deuterium oxide.

### *Methods*

The critical micelle concentrations of the surfactants and the accompanying changes in enthalpy were studied with a VP-ITC (Microcal, USA) titration microcalorimeter.

A Radelkis OK-0907P platinum bell electrode and a TitroLine 96 automatic burette were used for the conductometric determination of cmc values and dissociation constants of ionic surfactants.

The dynamic adsorption and desorption of DBSJ gemini surfactant and several surfactant mixtures were examined by a frontal adsorption column chromatography (high-pressure liquid chromatography HPLC) method involving UV and refractive index detectors that I assembled.

The molecular weight distributions of the surfactants were determined by an ESI-MS (electrospray ionization mass spectrometry) method.

I reconstructed LC-MS (liquid chromatography combined with a mass spectrometric detector) equipment appropriate for the research objectives of specific detection of the flow fronts of DBSJ, in four channels simultaneously at positive and negative ionization.

The specific surface area of adsorbent sandstone from Algyó was determined by a BET method under standard circumstances (nitrogen vapor adsorption at 77 K) in a Micromeritics Gemini 2375 automatic sorptometer.

The basal spacings of EMX-826 montmorillonite suspended in DMEB solution (DME-M), and of that swollen in ethanol, *n*-hexane, tetrahydrofuran or toluene as solvent, were identified with a Philips X-Ray diffractometer.

## Research topics and findings

**T1.** The temperature dependence of the solubility and critical micelle concentration (cmc) of (1*R*,2*S*)-(-)-*N*-dodecyl-*N*-methylephedrinium bromide (DMEB) was determined by conductometry and titration microcalorimetry. The Krafft temperature of the surfactant, taken from the point of intersection of the two functions, is 280 K.

Study of the temperature dependence of the apparent dissociation constants ( $\alpha_{\text{app}}$ ) investigated by conductometry in the range 288–328 K led to the conclusion that the micelle-composing surfactants dissociate entirely to surfactant cation and bromide counterion. The charge of the micelle is determined by the structure of its diffuse double layer. The enthalpies determined directly by titration microcalorimetry ( $\Delta_{\text{mic}}H_{\text{cal}}$ ) in the temperature range 288–348 K are in fine agreement with the van't Hoff enthalpies ( $\Delta_{\text{mic}}H_{\text{vH}}$ ) calculated from the temperature dependence of the cmc, if the temperature dependence of  $\alpha_{\text{app}}$  is not taken into account. My results corroborate the theory of Gilányi [T. Gilányi, *J. Colloid Interface Sci.*, 78 (1988) 641].

With increasing temperature, the micelle formation of DMEB changes from exothermic to endothermic at 292 K, where the process becomes athermal and purely entropy-controlled. Below this temperature, the unfavorable enthalpy term (positive) is overcompensated by the favorable entropy term (positive). The Gibbs free energy term (negative) barely changes in a wide temperature range, due to the enthalpy-entropy compensation attributable to the temperature dependence of the hydrophobic effect.

A comparison of the temperature dependence (molar heat capacity) of the micelle formation of DMEB with that of the prototype of the corresponding anionic and cationic surfactants (sodium dodecyl sulfate, NaDS, and dodecyl trimethylammonium bromide, DTAB, respectively) demonstrates that the structure and composition of the ionic head groups influence the energy of micelle formation to a significantly lesser extent than does the alkyl chain length of the surfactant.

**T2.** The organophilization of sodium montmorillonite (S-M) by ion exchange of the ephedrine-based chiral cationic surfactant (DMEB) resulted in a heterogenated homogenous catalyst (DME-M), which proved to be an effective and enantioselective catalyst in the alkylation of aldehydes by diethylzinc [Á. Mastalir, Z. Király, *Catal. Commun.* 9 (2008) 1404].

X-Ray diffraction (XRD) experiments demonstrated that the layered-structure catalyst can be swollen in organic media (toluene, ethanol, tetrahydrofuran and *n*-hexane). The interlamellar spacing can be controlled by varying the nature and composition of the organic medium.

**T3.** The molar weight distribution of  $\alpha,\alpha'$ -[2,4,7,9-tetramethyl-5-decyne-4,7-diyl]bis[ $\omega$ -hydroxypoly(oxyethylene)] (Surfynol-465, S465) nonionic gemini surfactant, was determined by an ESI-MS method through  $\text{Na}^+$  and  $\text{K}^+$  cationization. The number-average molecular weight ( $M_N$ ) proved to be 698 Da and 702 Da, respectively, and the polydispersity index of the surfactant was  $\text{PD}=1.04$ . S465 was found to contain an average of  $11.4 = (702 - 202) / 44$  ethylene oxide segments.

**T4.** Titration microcalorimetry measurements indicated that the cmc of S465 decreases with increasing temperature in the range 288-348 K in distilled water. Of the structure-maker alcohols, *n*-pentanol and *n*-hexanol are incorporated into the structure of the surfactant micelles and reduce the cmc. The cmc decreases with increasing chain length at a given concentration, and with increasing alcohol concentration at a given chain length. The structure-breaker urea increases the cmc even at a concentration of 0.1 M, with further increases at higher concentrations (0.1 M-5 M).

S465 micelle formation is endothermic in distilled water, in the presence of urea in the range 298–348 K and in the presence of 40 mM *n*-pentanol or 20 mM *n*-hexanol in the interval 298-328 K. The process is entropy-controlled and  $\Delta_{\text{mic}}H_{\text{cal}}$  decreases slightly with increasing temperature. Only a slight difference can be observed in the temperature dependence of the Gibbs free energy, due to the enthalpy-entropy compensation.

The enthalpies determined by titration microcalorimetry and the van't Hoff enthalpy values calculated from the temperature dependence of cmc display good agreement in the cases of distilled water and urea, which confirms the theory that urea is not built into the micelles. Urea breaks the hydrogen-bond structure of the water surrounding the surfactant molecules, thereby energetically favoring the situation of single surfactant molecules, and micelle forming therefore takes place at higher concentration. The difference between the microcalorimetric and van't Hoff enthalpy values is significant for *n*-pentanol and *n*-hexanol. The reason for the difference is that the incorporation of alcohol molecules into the micelles promotes the individual surfactant molecules to organize into micelles. The extent of

incorporation of the additives continually increases the difference between the measured and calculated enthalpy values.

**T5.** The molar mass distribution and polydispersity of the anionic gemini surfactant bis(4-(2-dodecyl)benzenesulfonate)-Jeffamin Salt (DBSJ), synthesized in the University of Pannonia laboratories ordered by MOL Ltd., were determined by an ESI-MS method. I proved that the surfactant with a number-average molar mass of 883 Da consists of decyl-tridecyl alkyl chains with a weighted average of 12.0. The number of polypropylene oxide (PPO) segments binding surfactant monomers is 1-5, with a weighted average of 2.7.

**T6.** The cmc values of DBSJ determined by conductometry and titration microcalorimetry are in excellent agreement. In the temperature range 288-348 K, the cmc changes in the range 0.060-0.118 mM. The tendency to association of the surfactant decreases with increasing temperature. This behavior is characteristic of ionic surfactants.

The micellization of DBSJ at 288.5 K is athermic; the process is simply entropy-controlled. The process is endothermic ( $\Delta_{\text{mic}}H > 0$ ) below this characteristic temperature, and exothermic above ( $\Delta_{\text{mic}}H < 0$ ), and the aggregation is favored by both the entropy and the enthalpy. The Gibbs free energy term (negative) barely changes in a wide temperature range, due to the enthalpy-entropy compensation attributable to the temperature dependence of the hydrophobic effect.

The enthalpies determined directly by microcalorimetry ( $\Delta_{\text{mic}}H_{\text{cal}}$ ) and the van't Hoff datas ( $\Delta_{\text{mic}}H_{\text{vH}}$ ) calculated from the temperature dependence of cmc agree very well with each other.

**T7.** I have constructed a flow frontal adsorption column chromatography measurement system (high-pressure liquid chromatography, HPLC) equipped with UV and refractive index measuring detectors. The adsorption, retention, dynamic desorption and elution with water of surfactants were studied on the solid/liquid interface by a novel method in continuous operating mode in a flow system on an Algyó sandstone column filler adsorbent, which is important as concerns the EOR in the neighborhood of Szeged. The EOR process was modeled by the applied new method under laboratory circumstances.

The plateau of the adsorption isotherm of DBSJ is at 3.43 mg/g, which corresponds to the adsorption capacity of appropriate surfactant homologs (sodium decyl benzene sulfonate,

NaDBS, and sodium dodecyl benzene sulfonate, NaDDBS), measured on Bentheim [N.M. van Os, G. Haandrikman, Langmuir 3 (1987) 1051] and Fontainebleau [J. Rouquerol, S. Partyka, J. Chem. Tech. Biotechnol. 31 (1981) 584.] sandstone, respectively. The adsorption capacity of DBSJ is less because of its higher molar size.

The adsorption of DBSJ on sandstone from Algyó decreases in the presence of Jeffamine D230 salt, NP-10 (nonylphenyl-polyglycol ether, which contains 10 ethyleneoxide groups) and cocoDEA (coco acid-diethanolamide) agent; PEG 20,000 (polyethyleneglycol with a molecular weight of 20,000) and PVA 20,000 (polyvinyl alcohol with a molecular weight of 20,000) polymers. The values of the plateau are 1.83, 1.87 and 2.36; 1.73 and 1.76 mg/g.

**T8.** A fractional rapid sampling adsorption column chromatography measurement system with a mass spectrometer (LC-MS) was constructed, which is capable of detecting flow fronts at four channels and of specific detection for the components even in the case of polydisperse samples at either positive or negative ionization.

The adsorption of DBSJ containing decyl and undecyl homologs proved to be relatively small/negligible and nearly reversible. The adsorption affinity decreases in the following sequence C13>C12>C11>C10. The longer the carbon chain of the surface-active alkylbenzenesulfonate groups, the higher the adsorption of the DBSJ polydisperse cocogem surfactant components. The desorption of C10 and C11 benzenesulfonate homologs confirms normal behavior, while the C12 and C13 homologs are retained. The concentrations of these components on the column filler increase during pressing and they can be eluted later by water. Examination of break-through fronts based on a  $-(\text{PO})_n-$  polypropylene oxide spacer (bridge group) indicated that the adsorption of surfactant components or the adsorption amount is not or only slightly influenced by the length of the spacer group.

**T9.** For utilization in the EOR process, I have presented quantitative data regarding the adsorption loss of DBSJ on the surface of sandstone from Algyó. This loss can be ascribed to oil recovery through elution by water if the adsorption is reversible, which results in enhanced oil recovery. A pore size volume of 5 g/L surfactant solution of at least  $V_p=2.5$  is necessary to reach monomolecular coverage on the surface of sandstone from Algyó in the DBSJ practice.



## Scientific publications

### Publications related to the scientific topic of the dissertation

1. **Annamária B. Páhi**, Dénes Varga, Zoltán Király, Ágnes Mastalir  
*Thermodynamics of micelle formation of the ephedrine-based chiral cationic surfactant DMEB in water, and the intercalation of DMEB in montmorillonite*  
Colloids and Surfaces A: Physicochemical and Engineering Aspects, 319( 2008) 77-83  
**IF<sub>2008</sub>: 1.926**
2. **Annamária B. Páhi**, Zoltán Király, Ágnes Mastalir, József Dudás, Sándor Puskás, Árpád Vágó  
*Thermodynamics of Micelle Formation of the Counterion Coupled Gemini Surfactant Bis(4-(2-dodecyl)benzenesulfonate)-Jeffamine Salt and Its Dynamic Adsorption on Sandstone*  
Journal of Physical Chemistry B, 112 (2008) 15320–15326  
**IF<sub>2008</sub>: 4.189**
3. **Annamária B. Páhi**, Zoltán Király, Sándor Puskás  
*Mass spectrometric characterization of the non-ionic gemini surfactant Surfynol 465 and a microcalorimetric study of its micelle formation in water*  
Colloids and Surfaces A: Physicochemical and Engineering Aspects, 345( 2009) 13-17  
**IF<sub>2008</sub>: 1.926**

### Other publications

4. Attila Keresztes, Mária Szűcs, Attila Borics, Katalin Kövér, Enikő Forró, Ferenc Fülöp, Csaba Tömböly, Antal Péter, **Annamária Páhi**, Gabriella Fábián, Mariann Murányi, Géza Tóth  
*New Endomorphin Analogues Containing Alicyclic beta-Amino Acids: Influence on Bioactive Conformation and Pharmacological Profile*  
Journal of Medicinal Chemistry, 51 (2008) 4270-4279  
**IF<sub>2008</sub>: 4.898**  
**ΣIF: 12.939**

### Lectures and posters in international conferences

1. **A. B. Páhi**, Z. Király:  
*A Thermometric Titration Study on the Effect of Temperature and Various Cosolutes on the Micellization of a Novel Gemini Surfactant.*  
Russian International Conference on Chemical Thermodynamics, Moscow, 27 June - 2 July 2005, Book of Abstracts Vol. II., PV-75.
2. **A. B. Páhi**, D. Varga, Z. Király  
*Thermodynamics of Micellization of the Ephedrine-Based Chiral Cationic Surfactant DMEB*  
12<sup>th</sup> IACIS International Conference on Surface and Colloid Science, October 15-20, 2006 Beijing, China, Book of Abstracts p. 88.

3. **A. B. Páhi**, Z. Király  
*Microcalorimetric Study of the Micelle Formation of a Nonionic Gemini Surfactant*  
12<sup>th</sup> IACIS International Conference on Surface and Colloid Science, October 15-20, 2006  
Beijing, China; Book of Abstracts p. 88.
4. **A. B. Páhi**, Z. Király  
*Thermodynamics of the Micelle Formation of a Nonionic Gemini Surfactant Surfynol-465*  
The VIII<sup>th</sup> International Symposium „Young people and multidisciplinary research”, May 11-12, 2006 Timisoara, Romania; Book of Abstracts p. 57.
5. **A. B. Páhi**, D. Varga, Z. Király  
*Thermometric and Conductometric Titration Studies on the Micelle Formation of (-)-N-Dodecyl-N-Methylephedrinium Bromide*  
The VIII<sup>th</sup> International Symposium „Young people and multidisciplinary research”, May 11-12, 2006 Timisoara, Romania; Book of Abstracts p. 56.
6. **A. B. Páhi**, Z. Király  
*Microcalorimetric Study of the Micellization of a Novel Gemini Surfactant in Aqueous Solution in the Presence of Structure-maker and Structure-breaker Additives*  
3<sup>rd</sup> Zsigmondy Colloquium, April 6-7, 2006 Berlin, Germany; Book of Abstracts p. 84.
7. **A. B. Páhi**, D. Varga, Z. Király, Á. Mastalir, I. Dékány  
*Characterization of a Cationic Chiral Surfactant by Conductometric Titration, Surface Tension Measurements, Titration Microcalorimetry and X-ray Diffraction Measurements*  
3<sup>rd</sup> Zsigmondy Colloquium, April 6-7, 2006 Berlin, Germany; Book of Abstracts p. 83.
8. D. Varga, **A. B. Páhi**, Z. Király, Á. Császár, Á. Mastalir  
*Thermodynamics the Micelle Formation of the Chiral Surfactant Dodecylmethylephedrinium Bromide*  
20<sup>th</sup> Conference of the European Colloid and Interface Society and 18<sup>th</sup> European Chemistry at Interfaces Conference September 17-22, 2006 Budapest, Hungary; Book of Abstracts p 262.
9. **A. B. Páhi**, Z. Király  
*Titration Microcalorimetric Study on the Effect of Micelle Builder and Micelle Breaker Agents on the Aggregation of a Nonionic Gemini Surfactant*  
20<sup>th</sup> Conference of the European Colloid and Interface Society and 18<sup>th</sup> European Chemistry at Interfaces Conference, September 17-22, 2006 Budapest, Hungary; Book of Abstracts p 261.
10. **A. B. Páhi**, T. Aradi, Z. Király, J. Dudás, S. Puskás, Á. Vágó  
*Micelle Formation of a Cocogem Surfactant Studied by Electromotive Force Measurements, Conductometry and Titration Microcalorimetry.*  
9<sup>th</sup> Conference on Colloid Chemistry; Colloids for Nano- and Biotechnology, 3-5 October 2007 Siófok, Hungary; Book of Abstracts p.118.

11. **A. B. Páhi**, T. Aradi, Z. Király, I. Dékány, J. Dudás, S. Puskás, Á. Vágó  
*Thermodynamics of Micelle Formation of a Novel Cocogem Surfactant, and the Dynamic Adsorption Behaviour of the Cocogem on Sandstone.*  
21<sup>st</sup> Conference of the European Colloid and Interface Society (ECIS 2007), 10-14 September 2007 Geneva, Switzerland; Book of Abstracts p.522.
12. **A. B. Páhi**, Z. Király, I. Dékány  
*Thermodynamics of Micelle Formation of a Gemini Surfactant in the Absence and in the Presence of Micelle Builder and Micelle Breaker Additives.*  
15<sup>th</sup> International Conference on Biological Calorimetry – Pannonia ISBC, 24-30 May, 2008 Pécs, Hungary; Book of Abstracts p 107.
13. **A. B. Páhi**, Z. Király, Á. Mastalir, I. Dékány:  
*Thermodynamics of Micelle Formation of the Chiral Cationic Surfactant DMEB in Water, and the Intercalation of DMEB in Montmorillonite in Relation to Chiral Catalysis.*  
17<sup>th</sup> International Symposium on Surfactants Solution (SIS2008), August 22-27, 2008 Berlin, Germany; Book of Abstracts p.124.
14. S. Puskás, **A. B. Páhi**, Z. Király:  
*Thermodynamics of Micelle Formation of a Gemini Surfactant in the Absence and in the Presence of Micelle Builder and Micelle Breaker Additives.*  
17<sup>th</sup> International Symposium on Surfactants Solution (SIS2008), August 22-27, 2008 Berlin, Germany, Book of Abstracts p. 44.
15. **A. B. Páhi**, Z. Király, J. Dudás, S. Puskás:  
*Thermodynamics of Micellization of a Novel Cocogem Surfactant and the Dynamic Adsorption of the Cocogem on Sandstone.*  
22<sup>nd</sup> Conference of the European Colloid and Interface Society (22<sup>nd</sup> ECIS), 31 August – 5 September 2008 Cracow, Poland; Book of Abstracts, p.362.
16. **Páhi B. A.**, Puskás S., Vágó Á., Dudás J., Király Z.:  
*Thermodynamics of micelle formation of a novel cocogem surfactant, and the dynamic adsorption of the cocogem on sandstone*  
27<sup>th</sup> International Petroleum & Gas Conference and Exhibition, September 16-19, 2008 Siófok, Hungary; Conference Proceedings on CD-ROM, p. 1-18.
17. **A. B. Páhi**, Z. Király, J. Dudás, S. Puskás  
*Thermodynamics of Micelle Formation of a Novel Cocogem Surfactant and the Dynamics Adsorption of the Cocogem on Sandstone*  
13<sup>th</sup> IACIS International Conference on Surface and Colloid Science and the 83<sup>rd</sup> ACS Colloid & Surface Science Symposium, June 14-19, 2009 New York, USA; Book of Abstracts p. 149-150.