

Novel Surfactants

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Synthesis and characterisation of carboxy amide-bonded pyridinium Gemini surfactants: influence of the nature of the spacer group and counterions on the aggregation behaviour

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Abstract: A series of novel dimeric pyridinium surfactants has been synthesised and the effects of a semi-flexible *p*-xylyl spacer and flexible, polyethylene glycol spacers have been studied. The nature of the spacer determines solubility and aggregation behaviour in two- and three-dimensional systems. Some of these insoluble compounds form two-dimensional, rigid-condensed structures at the air–water interface, while others form liquid-analogue monolayers. Whereas the latter compounds become soluble after exchange of the counterions, the former remain insoluble. The aggregation behaviour of Langmuir layers was, inter alia, investigated by Brewster angle microscopy. The micellisation behaviour of diluted aqueous solutions of soluble surfactants was primarily investigated by conductometric measurements and thermodynamic parameters of aggregation have been deduced with respect to the spacer length.

Keywords: cationic Gemini surfactant; counterion effects; spacer effects; surfactant solubility.

1 Introduction

Cationic pyridinium surfactants consisting of amide functionalities linked to the charged head group represent a barely researched field in surfactant science. These types of surfactants are of special interest in terms of structure performance experiments, as their self-assembly is

influenced by the ability to form hydrogen bond networks [1–3]. The rigid amide group, linked to the charged aromatic ring affects the orientation, which enhances the intermolecular interaction [4]. In polymer science, this effect explains the special properties of aramid polymers compared to aliphatic polyamides [5]. Monomeric chlorides of this type of surfactant are known to form hydrogels as result of these complex intermolecular forces [1]. Dimerisation of surfactants leads to a major enhancement of the surface-active properties [6–12]. Gemini surfactants of amide bonded pyridinium surfactants combine the amplification of hydrophobic interaction resulting from dimerisation with the orienting effects of hydrogen bonding [2]. The spacer group, which connects the surfactant groups, significantly affects the aggregation behaviour [13–17]. Its nature in terms of length, polarity, rigidity and functionalisation shape the microstructures of the aggregates in bulk solutions [18–20] as well as in Langmuir layers [7]. Flexible polyoxyethylene-spacers, which do not significantly contribute to the hydrophobic interactions of cationic Gemini surfactants, influence aggregation depending on their length [21–23]. This allows to tune the micellisation properties and has been utilised for polymerisation in microemulsion in order to control the size of the polymer particles [23]. Packing parameters [24, 25] of micelles of Gemini surfactants depend on the spacer and the distance of the ionic groups as well as conformational isomerism [26] and affect the ionic head group interactions [20, 27], which contribute to the shape and stability of aggregates [28]. Ionisation parameters of micelles strongly depend on length and nature of the spacer [22, 29, 30]. Rigid *p*-xylyl spacers were found to decrease the solubility of cationic surfactants and lead to higher critical micelle concentrations (CMC) [20], whereas hydroxyl groups, which have a strong influence on the surrounding water molecules, promote the micellisation processes [22]. As we found in our own studies, Gemini surfactants, consisting of two amide groups attached to the cationic

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heterocycle often led to insoluble compounds. Halides of this type are usually insoluble in water and most organic solvents, formates in contrast show a far better solubility [2]. This allows to investigate the aggregation behaviour in two-dimensional systems as well as in three-dimensional systems. In both cases the nature of the spacer has been proven to be a crucial factor (Schemes 1 and 2).

2 Experimental procedure

2.1 Synthesis

All organic solvents were distilled before usage, high-purity water (Elga PURELAB flex) was always used. Glassware was treated by pyrolysis at 450 °C and rinsed with high-purity water. Formic acid was distilled under reduced pressure.

The precursor, *N*-(pyridin-3-yl)stearamide (P1) was synthesised as described by Brahmachari et al. [1]. Polyoxyethylene-dibromides were synthesised by treatment of the corresponding polyethylene glycols with phosphorus tribromide in dry dichloromethane and subsequent filtration and extraction of the dibromide with dichloromethane. The residue was at first washed with water, then with sodium carbonate solution and again with water for three times. Quarternisation of P1 with the polyoxyethylene-dibromides was performed by refluxing in acetonitrile over longer durations. The solvent was removed on a rotary evaporator to yield the stearamidopyridinium bromide Gemini surfactants $\text{Py}_2\text{EO}_m\text{Br}$. The reaction progress was monitored by TLC using a mixture of 94 wt% methanol, 3.5 wt% *N,N*-dimethylformamide and 0.5 wt% formic acid as eluent. After the reaction was finished, the solution was cooled to 10 °C and the raw product was washed with cold methanol. The product was recrystallised several times in methanol to yield the bromide forms as a white powder. The mother liquors of every step were collected and poured on a flash chromatography column with silica gel as adsorbent. The column was then washed with methanol until no spots of the eluate were detectable on a fluorescent marked TLC plate. Formic acid was used as eluent to rinse off the quarternary Gemini surfactant and the solvent was removed on a rotary evaporator afterwards. Ion exchange was performed by the usage of a strongly basic ion exchange resin to receive the pure formates, as described before [2]. The quarternisation of P1 with α,α' -dibromo-*p*-xylene was performed by heating to 70 °C in dry *N,N*-dimethylformamide for two

days. The residue was washed with methanol in an ultrasonic bath and filtrated several times. Ion exchange was performed in the same manner as for the polyoxyethylene surfactants.

2.2 Chemical characterisation

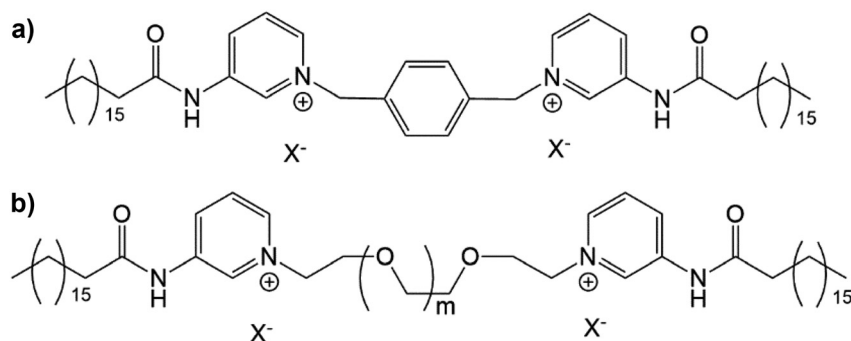
NMR measurements of the ionic compounds were performed in solvent mixtures containing deuterated formic acid, chloroform and *N,N*-dimethylformamide. This was necessary because of the strong aggregation properties of the compounds and resulting broaden of the signals, which was predominant in pure solvents. Coupling constants of ^1H NMR measurements could not be obtained due to the quality of the spectra. However, coupling was proved by 2D-NMR. The average spacer length of $\text{Py}_2\text{EO}_3\text{HCOO}$ and $\text{Py}_2\text{EO}_7\text{HCOO}$, which were synthesised from polyethylene glycols, was proven by integration of the ^1H signals. Liquid chromatography–mass spectrometry measurements were performed on a Bruker compact QTOF including ESI ion-source, coupled to an Agilent 1260 HPLC-system.

$\text{Py}_2\text{EO}_1\text{HCOO-1,1'-}((\text{ethane-1,2-diylbis(oxy)})\text{bis(ethane-2,1-diyl)})\text{bis(3-stearamidopyridine-1-ium)}\text{ dimethanoate}$: ^1H NMR (CDCl_3 , DCOOD , DMF-d_7 , 25 °C, 400 MHz) δ [ppm]: 0.66–0.74 (6H) 1.06–1.17 (56H), 1.44–1.56 (4H), 2.25–2.39 (4H), 3.34–3.50 (4H), 3.73–3.87 (4H), 4.51–4.72 (4H), 7.71–7.48 (2H), 8.29–8.53 (4H), 9.35–9.50 (2H); ^{13}C NMR (CDCl_3 , DCOOD , DMF-d_7 , 25 °C, 100.64 MHz) δ [ppm]: 13.64, 22.21, 24.63, 29.23, 31.44, 36.42, 61.77, 68.67, 70.03, 127.62, 134.23, 134.50, 138.67, 139.45, 173.86.

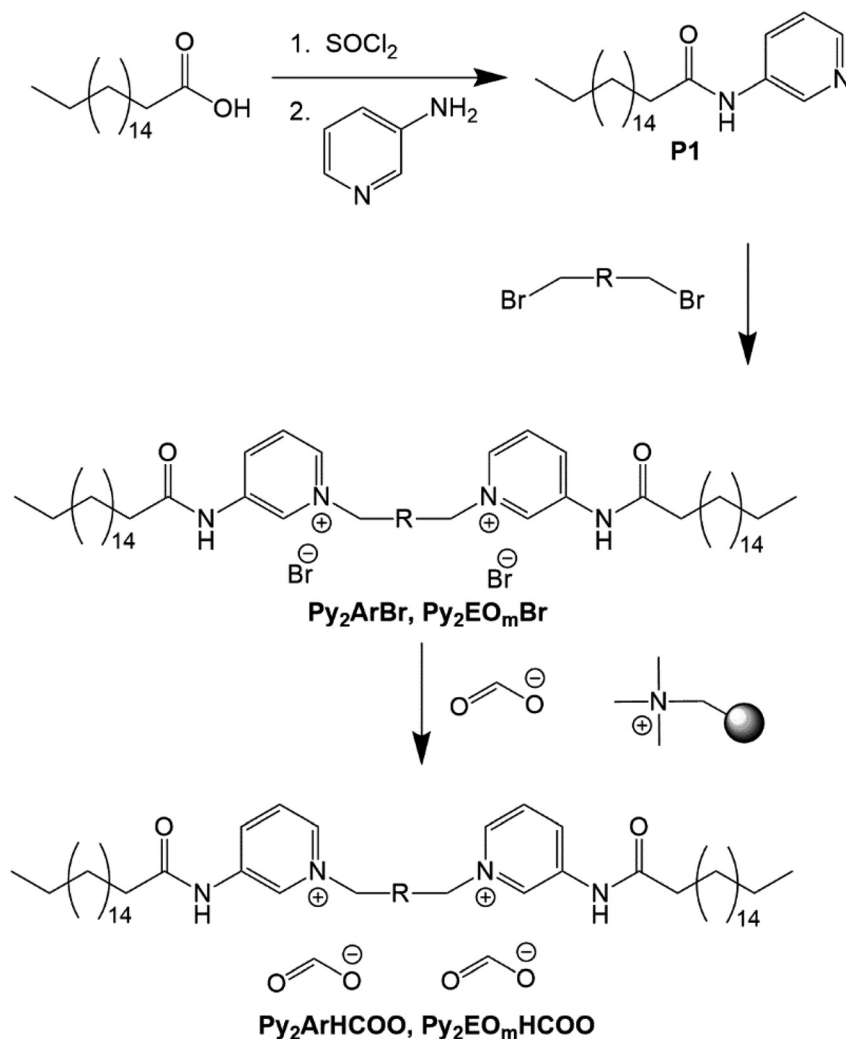
$\text{Py}_2\text{EO}_2\text{HCOO-1,1'-}(((\text{oxybis(ethane-2,1-diyl)})\text{bis(oxy)})\text{bis(ethane-2,1-diyl)})\text{bis(3-stearamidopyridine-1-ium)}\text{ dimethanoate}$: ^1H NMR (CDCl_3 , DCOOD , DMF-d_7 , 25 °C, 400 MHz) δ [ppm]: 0.72–0.78 (6H), 1.12–1.26 (56H), 1.52–1.61 (4H), 2.34–2.41 (4H), 3.41–3.43 (8H), 3.82–3.89 (4H), 4.60–4.68 (4H), 7.79–7.85 (2H), 8.39–8.45 (4H), 9.41–9.48 (2H); ^{13}C NMR (CDCl_3 , DCOOD , DMF-d_7 , 25 °C, 100.64 MHz) δ [ppm]: 13.78, 22.36, 24.79, 29.39, 31.60, 36.63, 61.87, 68.62, 69.77, 70.00, 127.75, 134.58, 134.69, 139.05, 139.42, 174.43; LC/MS: Base Peak: 440.6, Molecular Ion Peak: 880.0.

$\text{Py}_2\text{EO}_3\text{HCOO-1,1'-[poly(oxyethylene)]bis(3-stearamidopyridine-1-ium)}\text{ dimethanoate}$ ($n \approx 3$): ^1H NMR (CDCl_3 , DCOOD , DMF-d_7 , 25 °C, 400 MHz) δ [ppm]: 0.69–0.77 (6H), 1.09–1.25 (56H), 1.48–1.57 (4H), 2.29–2.38 (4H), 3.35–3.55 (12H), 3.81–3.91 (4H), 4.63–4.75 (4H), 7.82–7.88 (2H), 8.36–8.44 (2H), 8.46–8.54 (2H), 9.40–9.55 (2H); ^{13}C NMR (CDCl_3 , DCOOD , DMF-d_7 , 25 °C, 100.64 MHz) δ [ppm]: 12.97, 21.57, 24.03, 28.08–28.59, 30.82, 35.73, 61.02, 68.11, 69.20, 69.40, 126.99, 133.30–138.34, 138.94, 172.68.

$\text{Py}_2\text{EO}_7\text{HCOO-1,1'-[poly(oxyethylene)]bis(3-stearamidopyridine-1-ium)}\text{ dimethanoate}$ ($n \approx 7$): ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ [ppm]:



Scheme 1: Scheme of the structure of the surfactants. The counterions (X^-) are bromide (Br^-) or formate (HCOO^-), the spacer group consists of **a**) a semi-flexible aromatic group referred to as Py_2ArX or **b**) a flexible polyoxyethylene group with varying length ($m = 1, 2, \approx 3, \approx 7$) referred to as $\text{Py}_2\text{EO}_m\text{X}$.



Scheme 2: Synthesis process of the surfactants, including ion exchange and designation of the compounds.

0.82–0.87 (6H), 1.20–1.36 (56H), 1.63–1.72 (4H), 2.82–2.59 (4H), 3.40–3.77 (28H), 3.90–4.04 (4H), 4.64–4.77 (4H), 7.68–7.79 (2H), 8.31–8.60 (2H), 8.73–8.85 (2H), 9.09–9.40 (2H), 9.90–10.60 (2H); ^{13}C NMR (CDCl_3 , 25 °C, 127.71 MHz) δ [ppm]: 14.08, 22.65, 25.13, 29.20–29.67, 31.89, 36.92, 61.55, 69.08, 69.22, 69.35, 70.30, 70.48, 70.61, 127.29, 134.26, 134.10, 139.69, 139.01, 169.02, 175.11.

$\text{Py}_2\text{ArHCOO-1,1'-(1,4-phenylenebis(methylene))bis(3-stearamidopyridin-1-ium) dimethanoate}$: ^1H NMR (CDCl_3 , DCOOD, DMF-d_7 , 25 °C, 500 MHz) δ [ppm]: 0.65–0.71 (6H), 1.05–1.19 (56H), 1.44–1.53 (4H), 2.30–2.37 (4H), 5.63–5.70 (4H), 7.37–7.41 (4H), 7.82–7.87 (2H), 8.29–8.35 (2H), 8.46–8.52 (2H), 9.43–9.47 (2H); ^{13}C NMR (CDCl_3 , DCOOD, DMF-d_7 , 25 °C, 100.64 MHz) δ [ppm]: 13.39, 22.05, 24.58, 28.52–29.09, 31.35, 36.69, 64.30, 128.42, 129.87, 134.39, 135.00, 138.87, 139.16, 175.16.

2.3 Physicochemical characterisation

Brewster angle microscopy (wavelength of the incident LASER beam 690 nm) and interfacial characterisation were performed on an Accurion Nanofilm Ultra BAM equipped with a Langmuir Blodgett

trough, including a Wilhelmy plate and Kelvin probe (Kelvin probe KP1). Stock solutions of the samples were prepared by dissolving the amides in a 1/9 methanol/chloroform (v/v) mixture and spread via gastight glass syringe. Before starting the measurements, 20 min passed to allow the solvent to evaporate. All measurements were performed at 22 °C. Tensiometric measurements were performed on a DCAT 11 tensiometer (Dataphysics) equipped with a platinum–iridium Du Noüy ring at 22 °C. The ring was cleaned before each measurement by annealing on a Bunsen burner. Diluted solutions were stored over two days in the covered sample vessel and carefully placed into the tensiometer without concussions. The measurements were performed until no significant change of the surface tension over time was observed and the average plateau value was used. All measurements were performed twice to ensure reproducibility. Conductivity measurements were performed in a sealed vessel using a WTW Cond 7310 probe. High-purity water with a conductance of 18.2 M Ω cm was always used. Measurements of solutions of less than 1 mM surfactant were flushed with argon before sealing. The probe was cleaned in hot water by ultrasonic treatment. All samples were stirred during the measurement. Reproducibility was verified on a random basis. Dynamic light scattering experiments were performed on a Malvern

Zetasizer ZS nano instrument. Samples of micellar solutions were filtered through 0.2 μm filters (VWR) to avoid interference with dust particles. These supplementary measurements were performed to confirm the micellisation data.

3 Results and discussion

3.1 Langmuir layers

The bromides of all compounds were found to be able to form stable Langmuir layers. Brewster angle micrographs of the film structures are shown in Figure 1. The textures of Langmuir films in the low compression range (at film pressures π of the film well below 1 mN/m) were found to be dependent on the nature of the spacer. Two-phase regions were observed: In case of $\text{Py}_2\text{EO}_m\text{Br}$ two-dimensional foam analogue aggregates were found for all surfactants (see Figure 1b), which was interpreted as a two-phase region which involved a liquid analogue phase. In contrast, the Py_2ArBr surfactant formed two-dimensional fractal-type aggregates, which indicates the formation of solid-analogue structures (Figure 1a). Further insights into lateral interactions of the surfactants were gained by pressure–area and surface potential–area isotherms and hysteresis experiments (see Figure 2). Although the *p*-xylyl spacer is the shortest, the film pressure increases at higher areas per molecule, which can be explained by the resistance of rigid, two-dimensional networks against compression, which leads to an increase of the film pressure as loosely packed films. The areas of increase of the film pressures of

polyoxyethylene-linked surfactants correspond to their spacer length. Noticeable hysteresis effects were observed for the Py_2ArBr surfactant even without preceding film collapse, while only minor hysteresis effects were observed for the $\text{Py}_2\text{EO}_m\text{Br}$ surfactants (see Figure 2b). For Py_2ArBr , the surface potential increases noticeably with compression even before formation of a packed Langmuir film, while for $\text{Py}_2\text{EO}_m\text{Br}$ a sudden increase was observed when a condensed film evolved. This increase might be the area, at which the two-phase foam analogue area is compressed into one homogenous layer. Consequently, the lateral interactions are considerably influenced by the nature of the spacer.

In order to find out more about the effects of the backbone structure without ionic contributions, we studied insoluble films of the precursor P1 of the surfactants. Although the structure is similar to that of long chain fatty acids or alcohols it was found that the formation of two-dimensional crystalline aggregates is favoured and already occurs at very low film pressures of less than 5 mN/m (see Figures 1c and 2). The absence of ionic repulsion explains the stronger tendency to form two-dimensional crystalline structures. This can be explained by the nature of the amide functionality. In contrast to ester bonds, which are structural similar to amides, hydrogen donors and acceptors are present. As a result, the cohesive forces are much stronger in case of an amide. A simple example is the difference in the boiling temperature of ethyl acetate and *N*-ethylacetamide: Although the structure is similar and the molecular mass of the ester and the amide is nearly the

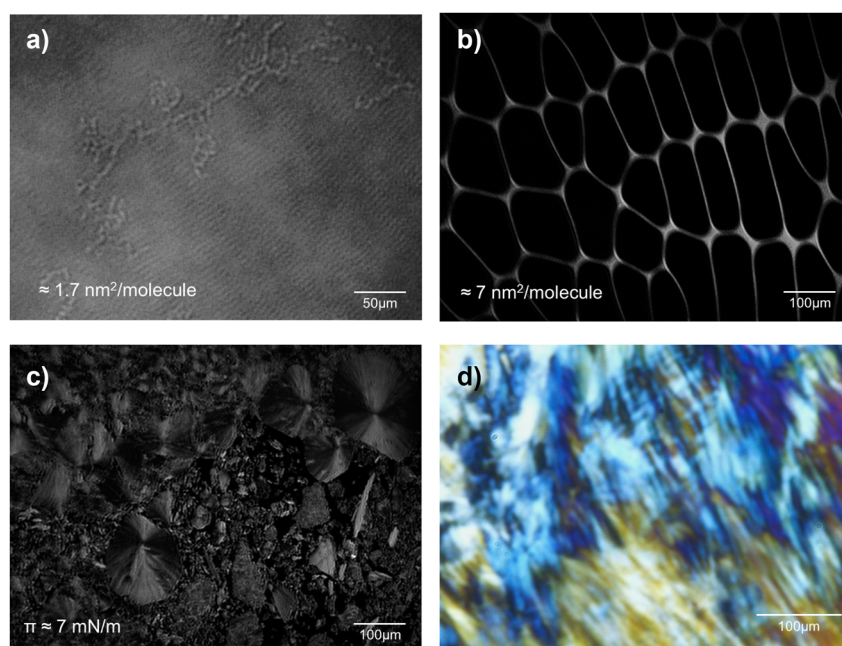


Figure 1: Brewster angle micrographs of two-dimensional aggregates: a) Py_2ArBr and b) $\text{Py}_2\text{EO}_7\text{Br}$, expanded films before compression; c) P1 at moderate film compression. d) Photomicrograph of textures of aqueous 80 wt% $\text{Py}_2\text{EO}_7\text{HCOO}$ obtained in cross-polarised light.

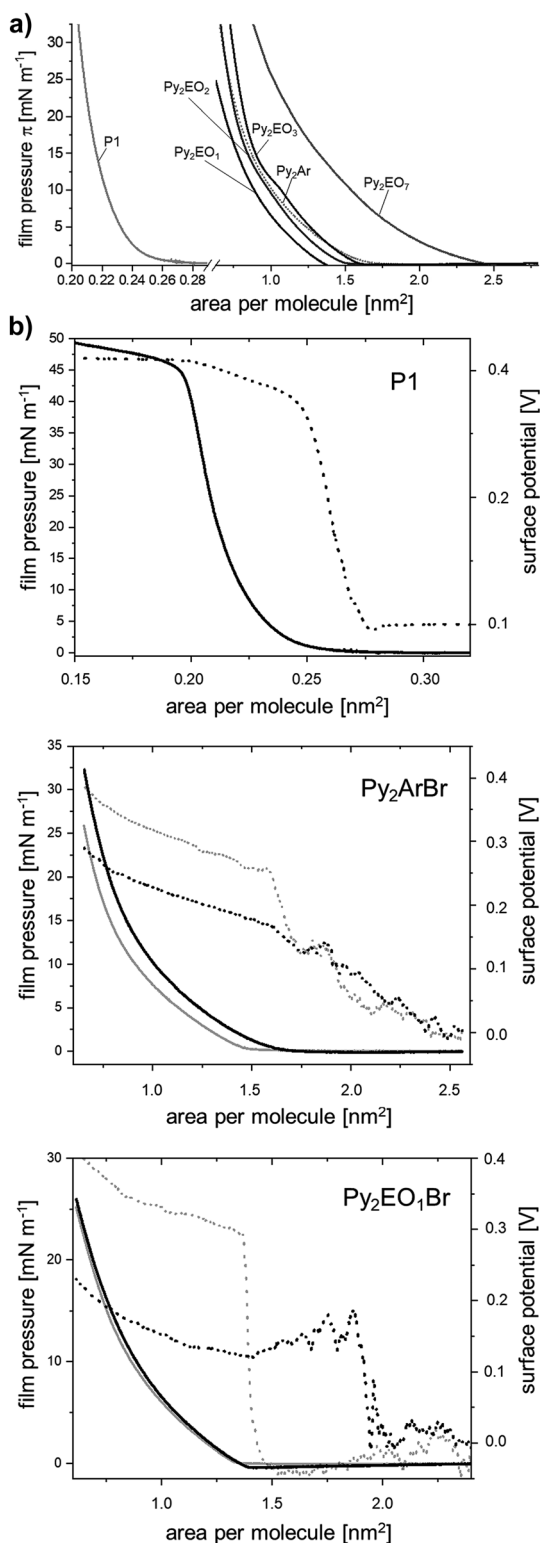


Figure 2: Langmuir layers: a) Comparative plot of the surface pressure versus area isotherms of the Gemini surfactants and the precursor on water, b) Surface pressure versus area (solid) and surface potential versus area (dashed) isotherms of the surfactant bromides (Py₂EO₁Br representing the polyoxyethylene-linked surfactants) and the precursor on water. The grey lines indicate the hysteresis measurement after 45 min of film regeneration time at maximal expansion. Temperature of measurements: 22 °C.

same, the boiling temperature of the amide is about 150 K higher. This effect can also be present in case of monolayers, if the structural geometry of the molecules enables hydrogen bonding, in addition to the lateral van der Waals forces.

3.2 Solubility and counterion

The counterion has a significant influence on the solubility of the surfactants. As the long-time stability of the Langmuir layers proves, bromides are insoluble compounds for both types of spacers. The exchange of the counterion into formates leads to a significant improvement of the solubility: The Py₂ArHCOO surfactant becomes soluble in methanol but remains insoluble in water at room temperature. The Krafft point, which was not further investigated, was found to be over 80 °C. However, the Py₂EO_mHCOO surfactants become water-soluble, even at high concentrations. The formation of textures, typical for liquid crystals could be obtained under polarised light at high concentrations. Figure 1d shows a structure, which may be regarded as hexagonal liquid crystal phase. LC-phases were found for all Py₂EO_mHCOO surfactants. It is therefore conceivable that the formate counterion, which is a charged hydrogen bond acceptor, interacts with the hydrogen bond network of the amide bonds and leads to an amelioration of solvation.

3.3 Effect of the spacer on the aggregation in aqueous solution

Detailed investigation of the micellisation properties was conducted for the Py₂EO_mHCOO series by tensiometry and conductivity measurements. The results were confirmed by dynamic light scattering as a complementary method. Because of the high Krafft temperatures, the aggregation properties of Py₂ArHCOO in aqueous solution were not further investigated.

3.3.1 Tensiometry

The length of the polyoxyethylene spacer has a significant effect on the adsorption at the air–water interface (see Figure 3). Shorter spacers lead to a higher charge density, which enforces electrostatic repulsion [31]. It was found that the lowering of the surface tension of the surfactants with longer spacers is greater and that short-spacer surfactants reduce the surface tension of water even at very low concentrations. However, the adsorption process was ongoing for many hours, especially at lower concentrations. This

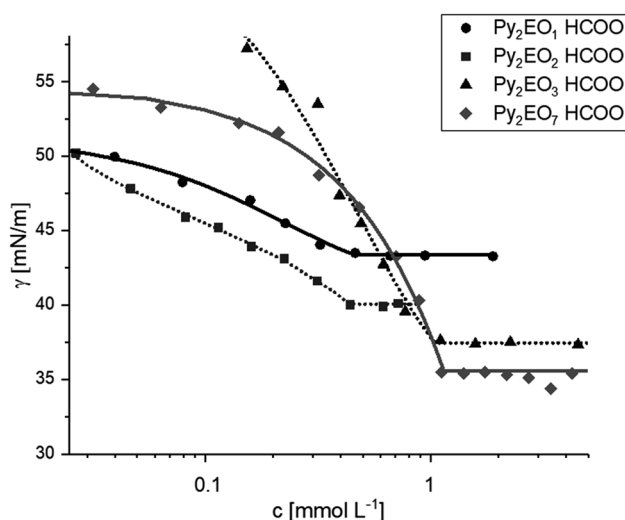


Figure 3: Surface tension γ against concentration of aqueous solutions of the $\text{Py}_2\text{EO}_m\text{HCOO}$ at 22 °C.

behaviour has been often found for cationic surfactants [7] and impedes the conduction of tensiometric experiments. The basicity of the formate counterion is many orders of magnitude larger than those of commonly used counterions as halides, therefore the association–dissociation equilibrium complicates the analysis of the Gibbs adsorption layer [31]. We found that the linear range of the Gibbs isotherms in the semi-logarithmic plot is rather narrow. The spacer length determines the maximal lowering of the surface tension γ_{CMC} and also the slope of the Gibbs isotherm in the γ versus $\log(c)$ plot. Because of the uncertainty of dissociation in the Gibbs adsorption layers of the pyridinium amide formats, the surface excess could not be determined with sufficient reliability. However, if the slopes of the linear ranges of the Gibbs isotherms in the semi-logarithmic plot are compared, a clear trend can be found: the shorter $\text{Py}_2\text{EO}_2\text{HCOO}$ has a maximal slope, which is in absolute values about 10% higher than that of $\text{Py}_2\text{EO}_1\text{HCOO}$, in case of $\text{Py}_2\text{EO}_3\text{HCOO}$ it is about twice as high and for $\text{Py}_2\text{EO}_7\text{HCOO}$ it is four times higher. The shorter spacers of $\text{Py}_2\text{EO}_1\text{HCOO}$ and $\text{Py}_2\text{EO}_2\text{HCOO}$ are consequently stronger hindered in the formation of a Gibbs adsorption layer by electrostatic repulsion, have a lower surface excess and a minor lowering of the surface tension at the CMC.

3.3.2 Conductivity measurements

The specific conductivities with concentration at temperatures between 10 °C and 60 °C are shown in Figure 4. It is particularly noteworthy that at very low concentrations, we found nonlinear behaviour at higher temperatures. This indicates an interaction of the ionic groups that starts even

at very low concentrations. The interaction occurs at lower temperatures and is reduced by an increase of the temperature. This results in a stronger increase of the ion mobility and therefore a non-linear increase of the conductivity with temperature. This behaviour could be found for all $\text{Py}_2\text{EO}_m\text{HCOO}$ surfactants and might be a result of ion pairing at lower temperatures [10]. The amide group of the surfactant ion serves as hydrogen donor and is located in the vicinity of the cationic heterocycle, while the carboxyl group of the counterion is a hydrogen acceptor, therefore a type of localised hydrolysis [32] could explain this behaviour. In order to describe the specific conductivity with concentration, we used a modified Carpena [33] fit function:

$$F(x) = \sigma_0 + (\sigma'_1 \cdot x) + x_1 \cdot (\sigma'_2 - \sigma'_1) \cdot \ln\left(\frac{1}{2} + \frac{1}{2} \exp\left(\frac{x}{\Delta x_1}\right)\right) + (\sigma'_2 \cdot x) + x_2 \cdot (\sigma'_3 - \sigma'_2) \cdot \ln\left(\frac{1 + \exp\left(\frac{x - \text{CMC}}{\Delta x_2}\right)}{1 + \exp\left(\frac{-\text{CMC}}{\Delta x_2}\right)}\right) \quad (1)$$

This function takes the nonlinear behaviour at very low concentrations into account and yielded very good agreement with the experimental points of measurement (coefficient of determination >0.99998). The second derivative of Eq. (1) was used to describe the aggregation behaviour of the surfactants. Figure 5 indicates the deviation from linear behaviour (dark colour) and contains information about the latitude of the transition ranges. The white areas indicate linear behaviour of the specific conductivity with

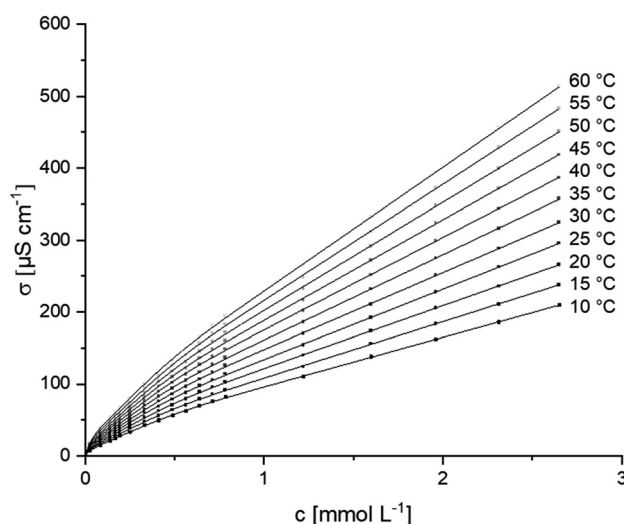


Figure 4: Specific conductivity σ against concentration and temperature of aqueous solutions of $\text{Py}_2\text{EO}_1\text{HCOO}$ (illustrative for all polyoxyethylene-linked surfactants) and fit functions at given temperature (see text).

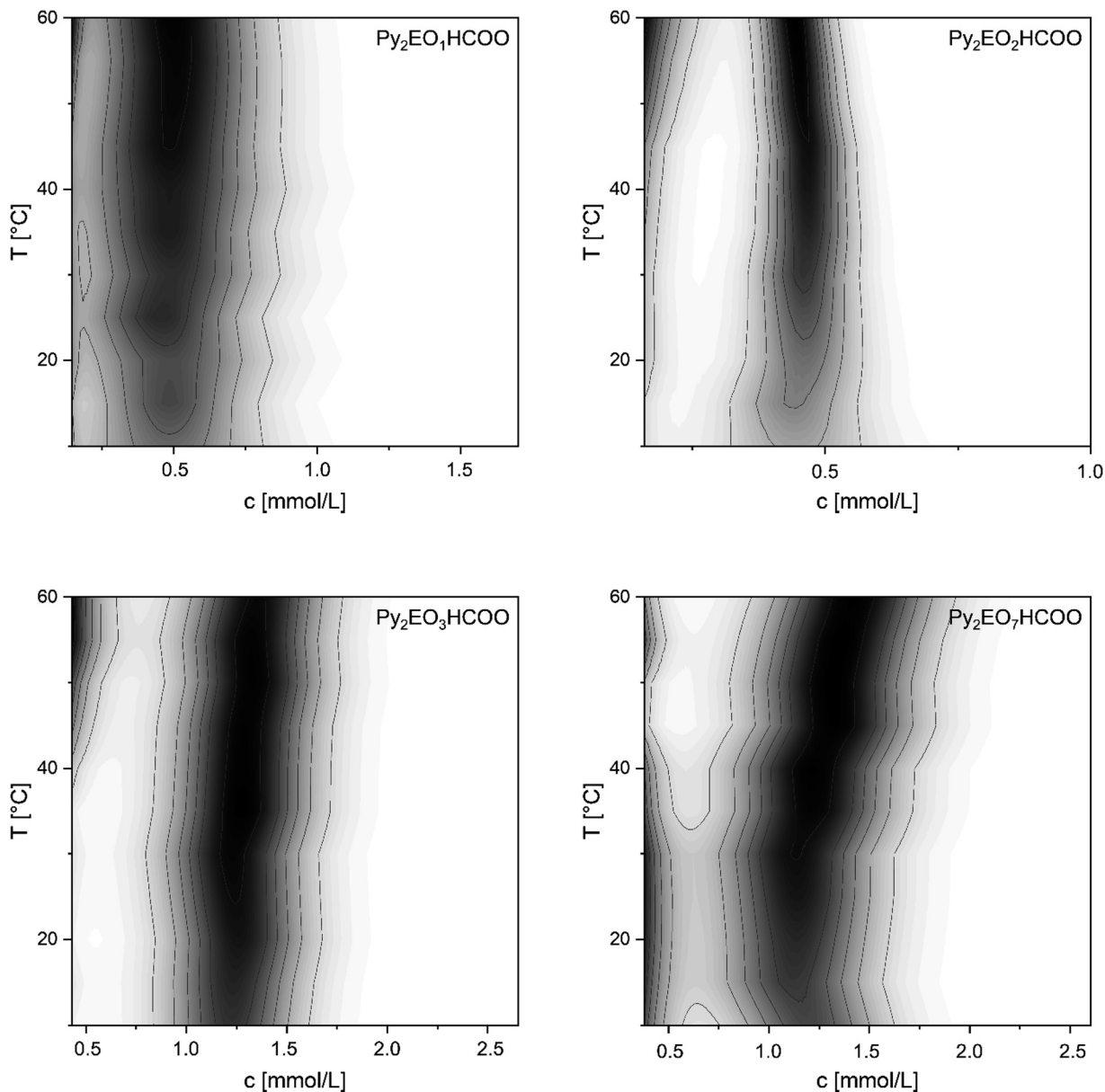


Figure 5: Phase diagrams of the $\text{Py}_2\text{EO}_m\text{HCOO}$ of the low concentration regime, including the transition areas of micellisation, which were determined by Carpena fits. The grey levels indicate the normalised deviation from linear behaviour.

concentration and therefore regions where no phase transition takes place. Figure 6a) compares in addition to Figure 5 the CMC of the surfactants in one plot.

3.3.3 Thermodynamics of micellisation

The data obtained from the Carpena fit functions were utilised to obtain thermodynamic parameters for micellisation. The counterion dissociation of micelles was estimated by

$$\alpha = \frac{\sigma'_2 + \sigma'_3}{2\sigma'_2}. \quad (2)$$

The Gibbs energy of micellisation ΔG_m could be determined by Eq. (3) [34]

$$\Delta G_m = 2RT(1.5 - \alpha)\ln(X_{CMC}), \quad (3)$$

where X_{CMC} denotes the mole fraction of Gemini surfactant at the CMC, R is the gas constant and T the absolute temperature. The enthalpy of micelle formation ΔH_m was derived by the van't Hoff equation (Eq. (4)).

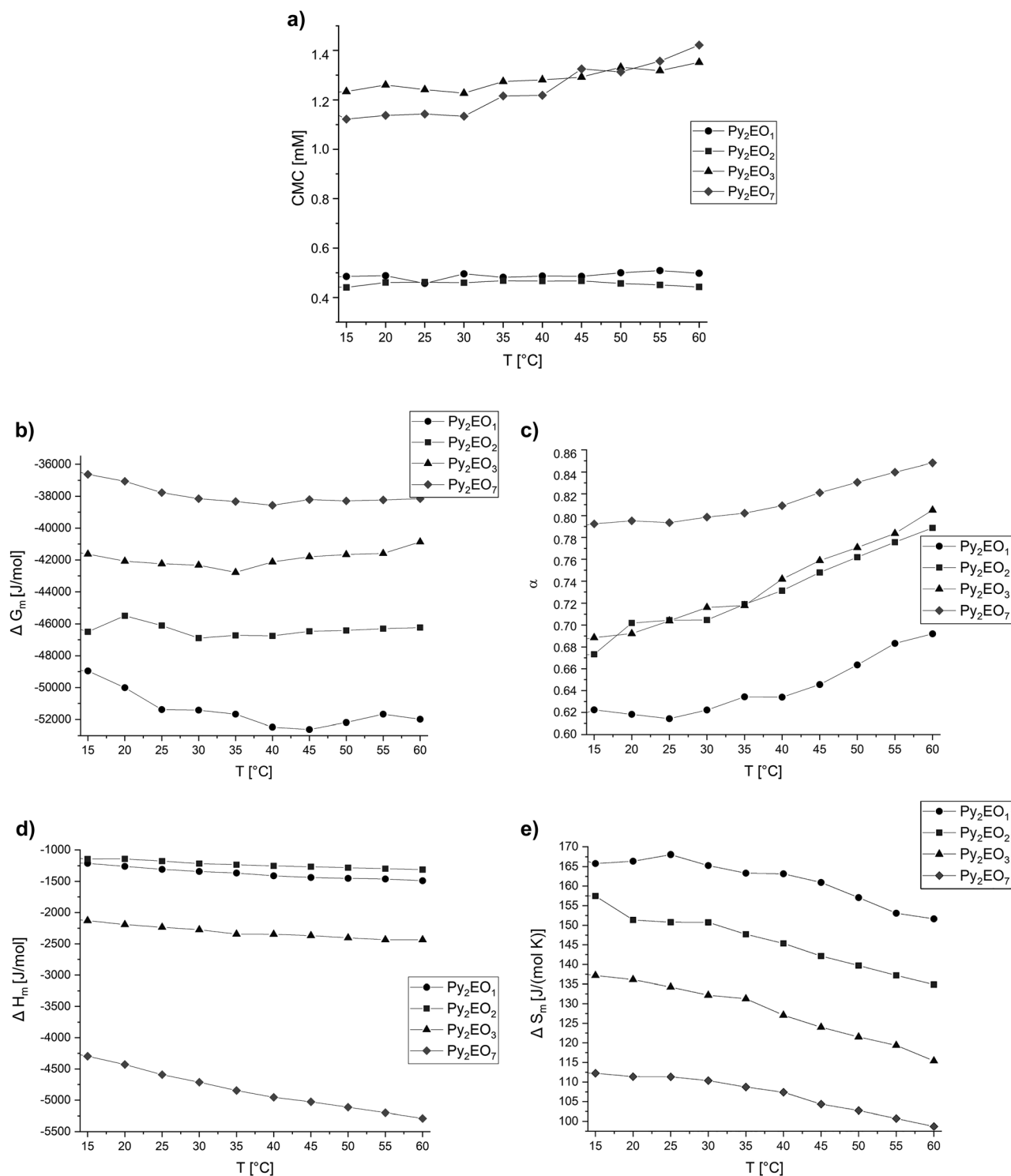


Figure 6: Micellisation data obtained from the conductivity measurements at a temperature range of 15 °C–60 °C.

$$\Delta H_m^0 = -2RT^2(1.5 - \alpha) \left(\frac{\delta \ln(X_{CMC})}{\delta T} \right)_p \quad (4)$$

The term $\frac{\delta \ln(X_{CMC})}{\delta T}$ was received by usage of the fit functions of the CMC curve. The entropy of micellisation ΔS_m^0 was calculated by Eq. (5):

$$\Delta S_m^0 = \frac{\Delta H_m^0 - \Delta G_m^0}{T} \quad (5)$$

The CMC of the $\text{Py}_2\text{EO}_m\text{HCOO}$ varies by a factor of three, depending on the spacer length and tends to increase with the length of the polyoxyethylene spacers. The CMC of the two short-chain surfactants (see Figure 6a) has similar values over the observed temperature range. However, the transition width in relation to the CMC is greater for the short-chain $\text{Py}_2\text{EO}_1\text{HCOO}$ (see Figure 5), which might result from higher charge density. The CMC values of the surfactants with longer spacers ($m \approx 3$ and $m \approx 7$) are considerably higher. The temperature dependence of micellisation is also significantly affected by the spacer length: The CMC of $\text{Py}_2\text{EO}_1\text{HCOO}$ and $\text{Py}_2\text{EO}_2\text{HCOO}$ remains almost constant with temperature, while $\text{Py}_2\text{EO}_3\text{HCOO}$ and $\text{Py}_2\text{EO}_7\text{HCOO}$ increase moderately. The entropy of micellisation ΔS_m^0 decreases with an increasing number of oxyethylene groups (see Figure 6e). The counterion dissociation of micelles α increases with larger spacer length and temperature for all $\text{Py}_2\text{EO}_m\text{HCOO}$ (see Figure 6c). Higher charge density of the short-chain surfactants can explain the order of the α values with spacer length: It leads to stronger electrostatic forces on the surface of the micelle and results in stronger bound counterions. In accordance with this, the ΔH_m values of short-spacer surfactants are considerably lower in absolute values (less exothermic) resulting from higher electrostatic repulsion between surfactant head groups. The entropy of micellisation ΔS_m^0 is higher for surfactants with shorter spacers. This might be an indication of the occurrence of intramolecular alkyl chain condensation, which is more likely, if flexible spacers are long enough to allow contact of the alkyl chains in solution [10]. As result of these effects, the ΔG_m values become more negative with shorter spacers. The CMC values of the $\text{Py}_2\text{EO}_1\text{HCOO}$ and the $\text{Py}_2\text{EO}_2\text{HCOO}$ are more than twice as high than those of comparable dimeric pyridinium amide formates with short hydrophilic spacers and only six linking atoms between the cationic pyridinium heterocycle [2]. The micellar counterion dissociation of $\text{Py}_2\text{EO}_1\text{HCOO}$ with only eight linking atoms, as well as all other surfactants with longer polyoxyethylene spacers, is considerably higher. The micellisation is for the reasons mentioned above less exotherm and the free energy of micellisation is significantly lower on absolute values, as well

as the entropy of micellisation. It can therefore be concluded that the electrostatic effects have a considerable influence on the aggregation, especially for short-spacer surfactants.

4 Conclusions

The effects of the nature of the spacer, as well as counterion effects have been studied. It was found that bromides possess poor solubilities, even with long polyoxyethylene spacers and can form stable Langmuir layers. The behaviour of two-dimensional aggregates is strongly dependent on the nature of the spacer. We found the formation of rigid, branched aggregates at low film pressures of the Gemini surfactant with semi-flexible spacer, while the surfactants with polyoxyethylene spacers form liquid analogue aggregates. The nonionic precursor, which forms stable Langmuir layers, shows the tendency to form two-dimensional solid condensed films at low surface pressures. The formation of two-dimensional solid structures indicates strong lateral cohesive forces which can be explained by the presence of hydrogen donors and acceptors. The solubility behaviour changes dramatically with exchange of the counterion into the formate, which is probably the result of an alteration of the hydrogen bonding network by the hydrogen accepting counterion. The *p*-xylyl-linked surfactant becomes soluble in methanol but remains insoluble in water at room temperature. In contrast, surfactants with polyoxyethylene spacers are well soluble in water and exhibit lyotropic behaviour at high concentrations. Micellisation properties of the polyoxyethylene-linked surfactants as well as the adsorption at the water surface are significantly affected by the length of the polyoxyethylene spacer. The dependence of the micellisation parameters on the spacer length agrees with the results of comparable cationic quaternary ammonium Gemini surfactants [21, 22]. Most effects can be explained by electrostatic considerations: Shorter spacers lead to a higher charge density within a surfactant divalent cation. This leads to stronger binding of counterions and reduces the enthalpy of aggregation. The entropic contribution of micellisation is higher for shorter spacers, as premicellar aggregation and intramolecular alkyl chain condensation are impeded by stronger electrostatic repulsion.

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