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Application of mass spectrometry for study of the adsorption of multicomponent surfactant mixtures at the solid/solution interface

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Abstract The selective adsorption of the components of a polydisperse gemini surfactant blend (alkylbenzenesulfonate-Jeffamine salt, ABSJ) in aqueous solution onto Berea sandstone, a reference material in enhanced oil recovery (EOR), was investigated. The individual adsorption isotherms of the four, benzene-ring containing ABSJ components with different alkyl chain lengths (ranging from decyl to tridecyl of the alkyl chain length) were simultaneously determined by using a four-channel electrospay ionization mass spectrometer (ESI-MS) for concentration analysis. This analytical device provided selective information (based on the differences in the mass to charge ratio) on the adsorption of each component in the mixed surfactant system. The overall isotherm obtained from the superposition of the individual isotherms determined by ESI-MS agreed well with the isotherm determined by UV spectrometry; the UV equipment is benzene-ring sensitive, irrespective of the alkyl chain length. The S-shaped isotherms reached a plateau at the critical micelle concentration. Longer-chain surfactants adsorbed preferentially over the short chain homologs, independently of solution concentration. This analytical device provided the net adsorption isotherm. Most analytical methods are not component selective, and thus they are not able to measure the individual isotherms in multicomponent solutions. Here, we report on a novel method which describes the selective determination of the individual adsorption isotherms of surfactants in a multicomponent mixture. The theoretical background of the method is described in detail.

Keywords Gemini surfactants · Multicomponent solutions · Adsorption · Berea sandstone · Mass spectrometry · Enhanced oil recovery

1 Introduction

Adsorption at the solid/solution interface is of great interest both academically and as concerns practical applications. For multi-component solutions or for solutions of polydisperse samples, determination of either the individual adsorption isotherms or the overall isotherm (the superposition of the individual isotherms) is a challenging task, because of the technical difficulties involved in quantitative analysis. For the individual isotherms, the analytical device must be selective for the individual components. For the overall isotherm, the analytical device must be equally sensitive for each component. Surfactant mixtures and polydisperse surfactants are widely used in practice (e.g. wetting, detergency, flotation, dispersion stabilization, soil remediation and oil recovery) (Myers 1988; Rosen 1989; Karsa 1999; Zhang and Somasundaran 2006). The subject of the present study is an investigation of the adsorption of a polydisperse surfactant sample on sandstone in relation to enhanced oil recovery (EOR). Berea sandstone has been used in the petroleum industry as a standard material in core analysis research and in laboratory core flooding experiments (Iglauer et al. 2010; Øren and Bakke 2003). Surfactants help reduce

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oil trapping and improve sweep efficiency, and hence increase oil production. As oil prices increase, EOR can revitalize exhausted fields and generate substantial profit. One of the major problems in surfactant flooding is surfactant adsorption on the surface of the rock or the sandstone. If adsorption is excessive, surfactants are depleted rapidly from the slug as it moves through the reservoir. Thus, adsorption directly affects, and may well dictate, the economics of an oil recovery process.

A variety of petroleum sulfonates originating from refinery feedstocks, and also synthetic alkyl or alkylarylsulfonates are in use in surfactant flooding EOR processes (Curbelo et al. 2007; Lawson et al. 1978; Rouquerol and Partyka 1981; van Os and Haandrikman 1987; Grigg and Bai 2004). We recently reported on the synthesis, the micellar behavior and the adsorption properties of a polydisperse, counter-ion-coupled gemini (cocogem Menger and Keiper 2000) surfactant, bis(4-(2-alkyl)benzenesulfonate)-Jeffamine salt (ABSJ) (Páhi et al. 2008). Because of their highly effective performance (low critical micelle concentration, cmc; high interfacial activity), gemini surfactants are of potential use in the chemical industry, among others for EOR (Zana and Xia 2004; Weifeng et al. 2011). The limitations of the large-scale application of geminis mainly originate from the high cost of their synthesis. Although ABSJ is polydisperse, it is a cost-effective gemini. The present point of interest was the competitive adsorption of the constitutive homolog components of ABSJ on Berea sandstone. Two methods were used for the concentration analysis: UV spectrometry (sensitive only to the benzene ring, and thus providing the overall isotherm directly), and electrospray ionization mass spectrometry, ESI-MS, (selective for the individual components in terms of mass per charge, m/z, and hence providing the individual isotherms; in addition, the superposition of these isotherms provides the overall isotherm also). The good agreement between the overall isotherms obtained from the application of the two analytical devices indicates that ESI-MS is a versatile tool for the determination of both the individual and the overall adsorption isotherms on solid surfaces in solutions containing multi-component or polydisperse solutes. This is the first report of the application of ESI-MS on the determination of the individual adsorption isotherms in a multi-component system.

2 Experimental section

2.1 Materials

Berea sandstone was purchased from Temco. The core was ground and sieved. The sieve fraction of 100–250 µm was used in the adsorption study. The BET surface area of the grains proved to be 0.868 m^2/g as determined by N_2 adsorption measurement at 77 K with a Micromeritics Gemini 2375 sorptometer. The mineral composition was determined by using a Philips 1820 X-ray diffractometer (Cu-$K_{\alpha 1}$ radiation; $2° \leq 2\theta \leq 70°$; 40 kV; 30 mA) to be quartz (SiO_2) 83 %; microcline ($KAlSi_3O_8$) 4 %; albite ($NaAlSi_3O_8$) 4 %; ancerite ($Ca(Fe, Mg)(CO_3)_2$) 3 %; kaolinite ($Al_2[Si_2O_5(OH)_4]$) 3 %; and siderite ($FeCO_3$) 3 %. This composition is slightly different from that provided by the supplier.

ABSJ was synthesized via the 2:1 coupling reaction between Lutensite A-LBS and Jeffamine D230 as described earlier (Páhi et al. 2008). The mean molar mass of the surfactant was determined by ESI-MS to be 884 Da. The cmc of ABSJ was determined with a Krüss K100 MK2 Tensiometer to be 0.048 g/L (0.054 mM). The structure and the chemical composition of ABSJ are given in Fig. 1.

Ultrapure water was produced with a Milli-Q purification system (Millipore). Surfactant solutions were made up volumetrically.

2.2 Methods

The molar mass distribution (the percentage composition) of ABSJ was determined by ESI-MS (Agilent Technologies LC/MS; 6120 Single Quad; 1200 series LC pump) in the SCAN (scanning) mode at both positive and negative polarization. The methodology and the experimental conditions were described in detail (Páhi et al. 2008) and are therefore not repeated here. Analysis of the concentration of the supernatant solution was performed by two

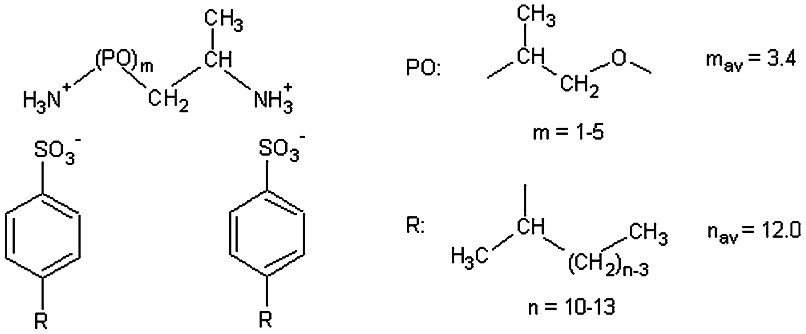

Fig. 1 The structure and the chemical composition of bis(4-(2-alkyl)benzenesulfonate)-Jeffamine salt (abbreviated as ABSJ), synthesized via the 2:1 coupling reaction between Lutensite A-LBS and Jeffamine D230. The polydispersity index (1.04) and the mean molar mass (884 Da) of the surfactant were determined by ESI-MS (Páhi et al. 2008)

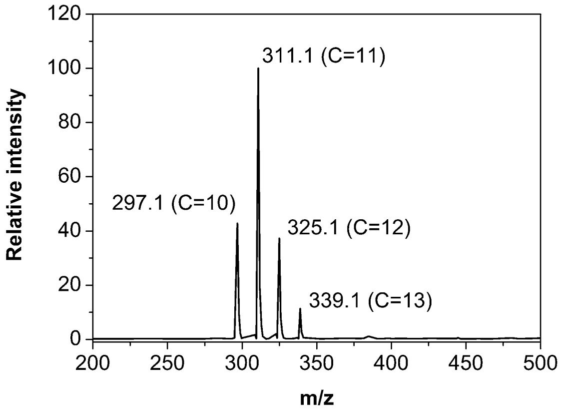

Fig. 2 ESI-MS spectrum of ABSJ: $z = -1$ charge states for the surfactant tail homologs

analytical methods. UV spectrometry (UVIKON 930 spectrophotometer, KONTRON Instruments) at a wavelength of 225 nm was applied for the direct determination of the net isotherm. The calibration curve for the UV analysis was prepared in the usual way. The four channels of the ESI-MS instrument enabled us to determine the individual adsorption isotherms simultaneously. Calibration curves for the decyl-, undecyl-, dodecyl- and tridecylbenzenesulfonate moieties (Fig. 2) were recorded in the SIM (selective ion monitoring) mode at negative polarization at $m/z = 297.1$, 311.1, 325.1 and 339.1 Da, corresponding to the four alkylbenzenesulfonate homologs. Adsorption measurements were performed by the batch method. 2 g of sandstone was suspended in a series of 20 mL surfactant solutions with different concentrations in glass sample vials. End-to-end stirring was applied overnight. The suspensions were next centrifuged (60 min; 11000 rpm), placed in a water bath at 298 K and left for thermal equilibration for another day. Samples were then taken for analysis of concentrations by UV spectrometry and ESI-MS.

2.3 Material balance of adsorption from multicomponent solutions on solid surfaces

For dilute solutions containing only one solute and the solvent, the amount of solute adsorbed on the solid can be determined (Király et al. 1996) as:

$$n^s = \frac{V^0}{m}\left(c^0 - c\right) \qquad (1)$$

where m is the mass of the solid, V^0 is the volume of the solution, c^0 and c is the concentration of the solute before and after adsorption, respectively. For polydisperse or multicomponent solutes, there are several (i) species in the solution:

$$c^0 = \sum_i c_i^0 \quad \text{and} \quad c_i^0 = f_i c^0 \qquad (2)$$

$$c = \sum_i c_i \quad \text{and} \quad c_i = f_i c \qquad (3)$$

where c^0 is the initial and c is the equilibrium total concentration of all the dissolved materials, while f_i is the weighting factor of the i-th solute component, which describes in what proportion this component is distributed in the mixed solute sample:

$$0 \le f_i \le 1 \quad \text{and} \quad \sum_i f_i = 1 \qquad (4)$$

The individual adsorption of the i-th sample can be calculated in a manner similar to Eq. (1):

$$n_i^s = \frac{V^0}{m}\left(c_i^0 - c_i\right) \qquad (5)$$

The total amount of solutes adsorbed is the sum of the amounts of the individual components adsorbed:

$$n^s = \sum_i n_i^s \quad \text{and} \quad n_i^s = f_i n^s \qquad (6)$$

The normalized amount adsorbed, $\langle n_i^s \rangle$, may be defined as the real amount adsorbed normalized with respect to the percentage composition of the i-th species. This assumes that the constitutive components in the sample are distributed in equal proportion:

$$\langle n_i^s \rangle = \frac{n_i^s}{f_i} \times \frac{1}{i_{\max}} \quad \text{and} \quad \sum_i \frac{1}{i_{\max}} = 1 \qquad (7)$$

where $i_{\max}$ is the maximum number of different components in the multicomponent sample. (For instance, for $i = 1, 2, 3, 4$, as in the present study, $i_{\max} = 4$.) Alternatively, the relative magnitude of adsorption can be expressed as a dimensionless quantity:

$$F_i(\%) = \frac{\langle n_i^s \rangle}{\sum_i \langle n_i^s \rangle} \times 100 \quad \text{and} \quad \sum_i F_i(\%) = 100 \qquad (8)$$

F_i is a good measure of the adsorption affinity of the i-th component for the solid surface in a multicomponent solution.

For multicomponent solutions, the determination of either the individual isotherms or the overall isotherm is a challenging task, due to difficulties with concentration analysis. For the individual isotherms, the analytical device must be selective for the individual components. For the overall isotherm, the analytical device must be equally sensitive for each component. In a favorable case, the overall isotherm obtained from the superposition of the individual isotherms will agree with the directly determined isotherm (and with the total amount adsorbed).

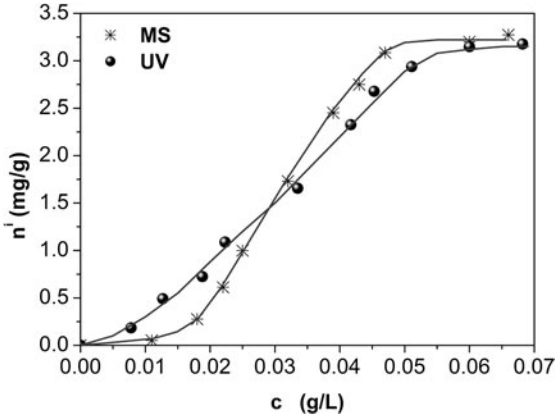

Fig. 3 Adsorption of ABSJ from aqueous solution onto Berea sandstone, as determined by UV spectrometry and ESI-MS (Eqs. (5) and (6))

3 Results and discussion

The molar mass distribution obtained by ESI-MS in the SIM mode provided the abundance (f_i) of the individual alkylbenzenesulfonate moieties in the polydisperse ABSJ surfactant sample (Fig. 2). The following values were obtained for the homolog members: $C_{10} : C_{11} : C_{12} : C_{13} = 0.289 : 0.418 : 0.218 : 0.075$. This knowledge of the molar composition plays a very important role in the interpretation of the material balance of the adsorption of the four components.

Figure 3 depicts the adsorption isotherms of ABSJ, on Berea sandstone at 298 K, determined by UV spectrometry and ESI-MS (overall isotherm, Eq. (1)). The agreement is satisfactory if it is considered that, while UV spectrometry is sensitive to the benzene ring, regardless of the difference in the alkyl chain length in the four homologs, ESI-MS is sensitive to m/z, and selective for the alkyl chain length of the individual components. The isotherms are S-shaped, which is characteristic of the adsorption of surfactants on hydrophilic surfaces (Király and Findenegg 2000). Along the rising section of the isotherm, surface aggregation takes place via a co-operative adsorption mechanism. Flattened globular surface aggregates or a surfactant bilayer are formed until the adsorption levels off at the plateau as the cmc is reached (Király and Findenegg 2000). The adsorbed amounts of the four components are plotted against their individual concentrations in Fig. 4. The corresponding plots on the total concentration scale are given in Fig. 5. Each isotherm is S-shaped and the extent of adsorption (plateau value) increases in the sequence $C_{10} < C_{13} < C_{11} < C_{12}$.

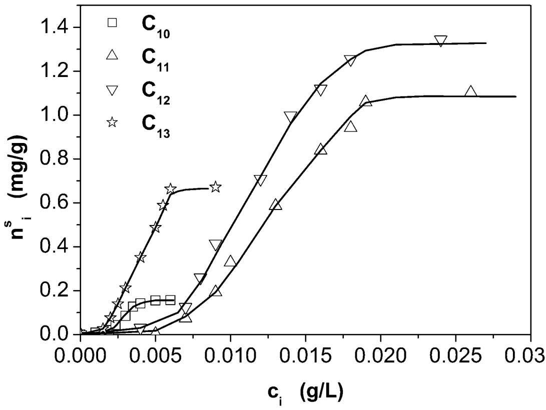

Fig. 4 Individual adsorption of the ABSJ homologs from aqueous solution onto Berea sandstone, plotted against the individual concentrations of the components

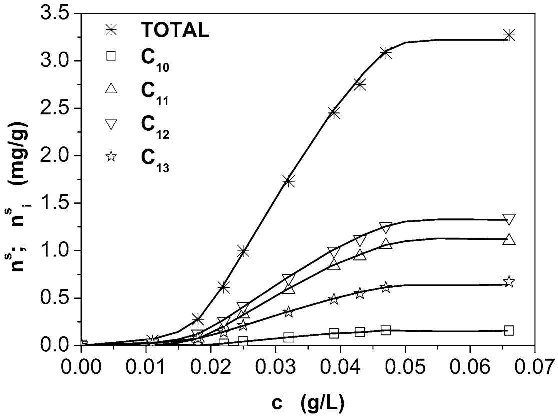

Fig. 5 Individual adsorption of the ABSJ homologs from aqueous solution onto Berea sandstone, plotted against the total concentration

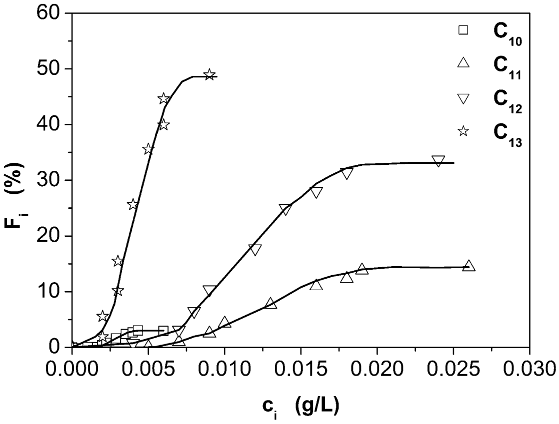

Fig. 6 Normalized individual adsorption of the ABSJ homologs on Berea sandstone (Eqs. (7) and (8)), plotted against the individual concentrations of the components

This apparently irregular behavior can be explained in the knowledge of the molar composition of the polydisperse sample and by the application of Eqs. (6)–(8). Figures 6 and 7 were constructed via normalization of the adsorbed amounts in Figs. 4 and 5 with respect to the relative abundances of the individual components present in the sample (Eqs. (7) and (8)). In Fig. 6, the relative amounts adsorbed are plotted against the concentrations of the individual components (F_i vs. c_i, Eq. (8)) in Fig. 7. The extent of

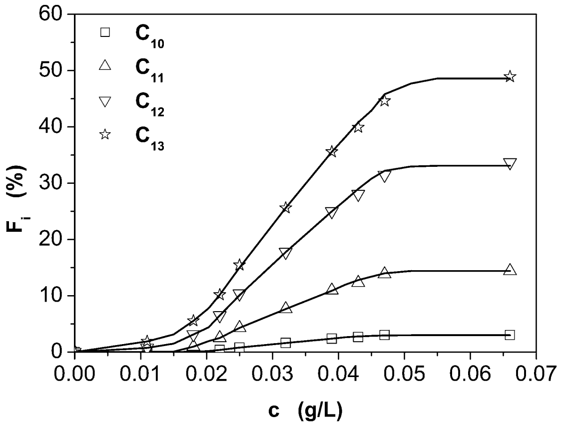

Fig. 7 Normalized individual adsorption of the ABSJ homologs onto Berea sandstone (Eqs. (7) and (8)), plotted against the total concentration

the adsorption is presented on the total concentration scale (F_i vs. c).

It appears that the adsorption affinity increases in the sequence $C_{10} < C_{11} < C_{12} < C_{13}$. This sequence is what might be expected: the longer the alkyl chain of the surfactant, the higher the adsorption affinity, and thus the larger the adsorbed amount. The irregular sequence observed in Figs. 4 and 5 can then be explained as follows. The largest amount adsorbed (40.5 %) relates to C_{12} because the alkyl chain length is the second longest of the four in the surfactant mixture (which implies the second highest adsorption affinity), even though it's relative abundance in the polydisperse sample is moderate (21.8 %). The second in the sequence of the amounts adsorbed is C_{11}. The plateau value is 34.4 % of the total, and the quantity of this homolog in the mixture is the largest: 41.8 %. The amount of C_{13} adsorbed is only 20.5 %. Although this component (the longest alkyl chain homolog) has the highest adsorption affinity, its content in the bulk mixture is only 7.5 %. The extent of adsorption is lowest for C_{10} (4.6 %), even though it's content is the second highest (28.9 %). The reason is that this homolog has the shortest alkyl chain length, and hence the lowest adsorption affinity. By way of summary, a quantitative combination of the bulk composition with the adsorbed amounts of the individual components of the surfactant composite can account for the apparently irregular sequence of the extent of adsorption as depicted by Figs. 4 and 5. The present results have implications as concerns the application of ABSJ in EOR. The cmc of ABSJ is significantly lower than those of individual alkylbenzenesulfonates (e.g. 0.054 mM for ABSJ and 1.72 mM for the monomeric dodecylalkylbenzenesulfonate (van Os et al. 1993)). The adsorption loss upon surfactant flooding can be predicted in the knowledge of the adsorption isotherm. The strength of the adsorption in the polydisperse surfactant sample increases with the alkyl chain length of the surfactant homolog.

4 Conclusions

The adsorption of ABSJ from aqueous solution onto Berea sandstone was investigated by using a four-channel ESI-MS instrument for concentration analysis. The alkyl chain length of components of the polydisperse sample ranged from decyl to tridecyl. The adsorption affinity of the four homologs increased in the sequence $C_{10} < C_{11} < C_{12} < C_{13}$. The individual adsorption isotherms of the multicomponent solution and the overall isotherm (the net isotherm resulting from the summation of the four individual isotherms) were constructed on a theoretical basis. The overall isotherm agreed reasonably well with the isotherm obtained from UV analysis. It is anticipated that multichannel ESI-MS will be a versatile tool for study of the simultaneous adsorption of various solutes from solution at the solid/liquid interface, not only for polydisperse surfactant samples, but also for surfactant mixtures and multicomponent solutions. The individual adsorption isotherms of each of the components in the mixture can be determined simultaneously by using an ESI-MS instrument as the analytical device. As far as we are aware, this is the first report of the application of ESI-MS for the simultaneous determination of the individual adsorption isotherms in a multicomponent solution at the solid/liquid interface. The present method is of interest in EOR applications to predict the adsorption loss when a surfactant mixture is applied for flooding in reservoir rocks.

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