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Influence of bulk concentration on the organisation of molecules at a membrane surface and flux decline during reverse osmosis of an anionic surfactant

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ABSTRACT

Surfactants are extensively used in household and industrial products. Several processes exist to treat industrial wastewaters, including membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis (RO). We studied fouling of RO membranes during filtration of aqueous anionic surfactant solutions under different conditions. The aim was to describe the local organisation of the surfactant at the membrane interface. To this end, the typical surfactant sodium dodecyl sulfate (SDS) and a polyamide membrane (SG, GE Water & Process Technologies) were selected. A marked surfactant mass loss was experimentally quantified and attributed to the accumulation of surfactants on the membrane surface and adsorption on the non-membrane materials in the filtration system. The concentration of surfactant in the polarisation layer compared with the SDS phase diagram, combined with contact angle measurements and flux decline analysis, enabled us to deduce a structure for the fouling. The fouling layer presented different structures according to the surfactant concentration: from a dense hydrophobic layer at very low concentration to a lamellar hexagonal phase in the gel layer at concentrations above 35 wt% in water.

1. Introduction

Surfactants are amphiphilic molecules are extensively used in household products, detergents, industrial processes and pesticide formulations for their fundamental properties, such as micellisation in solutions and adsorption on interfaces/surfaces [1,2]. Owing to their frequent use, they may also persist in wastewater treatment systems at relatively high concentrations. To avert serious health and environmental problems resulting from direct and indirect release of surfactants, effective clean and sustainable methods are needed to remove surfactants from industrial wastewater to prevent their release into the environment.

Various approaches have shown that membrane filtration, such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), is an effective technique to remove surfactants from effluents [3,4]. Membrane technology stands out as being environment-friendly and easy to operate, and requiring no added chemicals. The best retention of surfactants has been achieved by the RO process [4,5], although surfactant adsorption on the active layer of the membranes led to folding and thus penetration (i.e. partitions) inside the membrane of this, as other trace organics, and some weak leakage [6]. However, accumulation of matter may occur during membrane filtration of surfactants, resulting in severe flux decline [4,7–12]. Classic modelling of RO membrane fouling can take into account the following phenomena: adsorption (accumulation of solutes on the external and internal surfaces, changing membrane hydrophobicity), cake formation (accumulation of particles on the membrane forming a second porous media) and concentration polarisation (rise of solute concentration in the layer near the membrane surface). Understanding the behaviour of surfactants at the RO membrane interface in filtration requires deeper investigation. In an earlier study, a theoretical approach was taken to investigate the interaction between the surfactant molecules [13].

The aim of this work was to describe the local organisation of an anionic surfactant at the membrane interface during RO filtration of synthetic solutions. This work is based on the

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quantification of accumulated matter compared with the surfactant phase diagram, linked to flux decline and hydrophobicity modification.

1.1. Surfactants in solution

A surfactant molecule bears at least one hydrophilic group comprising an ionised or polar assembly, and a hydrophobic moiety made up of carbonated chains. Owing to their amphiphilic nature, surfactants adsorb preferentially at interfaces, and form aggregates called micelles when they reach their critical micelle concentration (CMC). For sufficiently low monomer concentrations, most of the molecules in the solution are isolated. Once the concentration reaches the CMC, addition of surfactant molecules results in the formation of micelles, leaving monomer concentrations largely unchanged at the CMC value [4]. The CMC values are influenced by the nature of the hydrophobic tail and hydrophilic head, pH, ionic strength, temperature, etc.

When the mass fraction of surfactants in water rises, the molecules can form more complex aggregates as described in phase diagrams by Kekicheff and co-workers [14–16]. The binary phase diagram of SDS in D_2O is presented in Fig. 1. The organisation of SDS in water (H_2O) is considered to be similar. The structures of many liquid and semi-liquid phases have been identified, and classified structurally. The most common structures are the micellar phase (mic), the liquid crystal phase (*C*), where local organisation in lamellar fragments occurs, the lamellar phase (*L*) where bilayers of amphiphilic molecules are separated by water layers, and the hexagonal or reversed hexagonal phases (*H*), where cylinders of amphiphile (or water) are arranged in a two-dimensional hexagonal lattice. Four intermediate phases have also been identified between the hexagonal and the lamellar phases: a two-dimensional monoclinic phase (*M*), a rhombohedral phase (*R*), a cubic phase (*Q*) and a tetragonal phase (*T*). In the cubic phase, the primary units are short rodlike aggregates, connected at each end to form two interwoven, but otherwise independent three-dimensional networks. In what follows, the generic word “gel” will be used to describe the accumulation of surfactants organised in three-dimensional structures in the aqueous phase; no polymerisation occurs here. Since the experiments with the RO process in this work were carried out at 25 °C, the phase diagram of SDS at this temperature is discussed. At 25 °C, the SDS is in a micellar phase below 37 wt%, and then forms a hexagonal phase, in equilibrium with micelles between 37% and 40 wt%. In the range of 40–86 wt%, the hexagonal and liquid crystal phases co-occur. There is only a liquid crystal phase above 86 wt%.

1.2. Surfactant at liquid–solid interface

The adsorption of surfactants at a liquid–solid interface is governed by a number of forces such as electrostatic interactions, hydrogen bonding, lateral interactions between the adsorbed species, hydrophobic/hydrophilic interactions between the substrate and the surfactants, and solvation and desolvation of the surfactants, as described elsewhere [17–21]. Classical model surfaces are either positively or negatively charged in the aqueous medium by ionisation/dissociation of surface groups or by the adsorption of ions from solution on a previously uncharged surface [20]. Based on previous approaches, several models of surfactant adsorption on solids and corresponding structures have been proposed.

A typical isotherm of ionic surfactant adsorption on an oppositely charged solid surface can be split into four regions when plotted on a log–log scale, as shown in Fig. 2. According to Paria et al. [20], in region I, the concentration of surfactant is low and surfactant molecules are electrostatically adsorbed on the solid surface. At this stage, the adsorption obeys Henry's law: the adsorption amount increases linearly with surfactant concentration. In region II, due to lateral interaction between hydrophobic chains of the adsorbed monomers, surface aggregation of surfactants develops continuously, with a sudden increase in the curve. These surfactant aggregates, termed admicelles or hemimicelles by various investigators, are assumed to be largely flat. Region III shows a slower rate of adsorption than region II. At this stage, the solid surface is electrically neutralised by the adsorbed surfactant ions; with no electrostatic interaction between the surfactants and the surface, the adsorption takes place due only to lateral attraction, with a reduced slope. Region IV is the plateau region above the CMC. Sometimes region IV shows a maximum, due to the presence of trace surface-active impurities [20,21].

The adsorption of surfactants on a solid phase with the same charge occurs through hydrophobic adsorption to limit the contact

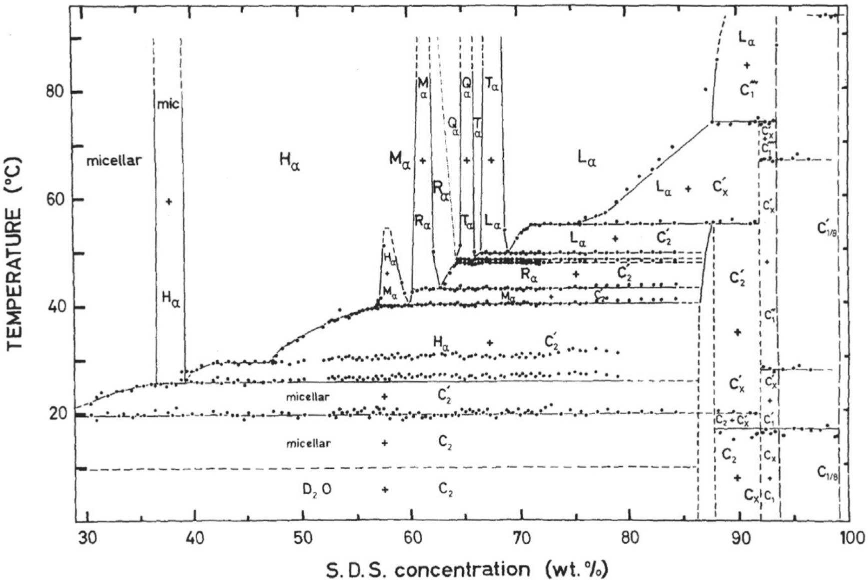

Fig. 1. Schematic SDS–D_2O phase diagram suggested by Kekicheff et al. [14]. Compositions are expressed as SDS weight percentage. Different structures are labelled according to the symmetry of their lattice: mic: micellar phase; Hα: hexagonal phase; Mα: two-dimensional monoclinic phase; Rα: rhombohedral phase; Qα: cubic phase; Tα: tetragonal phase; Lα: lamellar phase; *C*: crystal phase.