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SAXS and SANS Techniques for Surfactant Characterization: Application in Corrosion Science

Deepak Dwivedi and Kateřina Lepková

Additional information is available at the end of the chapter

Abstract

This chapter presents advances in the characterization of surfactants and detergents using small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) techniques. Surfactant molecules have been extensively used for corrosion prevention as part of commercial corrosion-inhibitor formulations. It is generally established that the interactions between surfactant molecule and metallic substrate play a key role in the formation of a corrosion-protective film. It is therefore essential to develop understanding about the nature of surfactant and detergent molecules in bulk solutions prior to formation of a surface film, as well as the mechanisms of their interactions with metallic substrates. These properties and interactions determine the properties of the surface film, including its persistency, and in turn define its protectiveness against corrosion. X-ray and neutron reflectivity methods are important investigating tools that could be used to characterize surfactant interactions with metallic substrates. These techniques have recently been utilized to investigate adsorption energies and contact angles between molecules or particles and variable substrates. This chapter addresses basic principles of these techniques and discusses their application for surfactant and detergent studies in corrosion science. Several case studies are presented and provide outlook for future prospects in this field of science.

Keywords: corrosion inhibitor, corrosion, surfactant, small angle neutron scattering, small angle X-ray scattering, aggregation, surface film formation, critical micelle concentration

1. Introduction

Corrosion of metals or alloys is a prime concern for various industries, such as oil and gas, steel and chemical to name few. To mitigate corrosion, application of corrosion inhibitors is a common and effective practice.

Adsorption of inhibitor molecules on substrate depends on various factors such as inhibitor concentration, pH and temperature of the corrosion media, etc. It is known that properties of metallic substrates, such as for example carbon steel, influence adsorption of organic surfactants. These properties have been recently reviewed [1]. It is very important for corrosion scientists to understand mechanistic insights and fundamentals associated with adsorption of surfactants on metallic substrates.

Film-forming surfactant molecules have many advantages, such as low cost, easy production, and high inhibition efficiency [2]. Surfactant molecules consist of hydrophilic head group and hydrophobic tail group, but the mechanism by which they adsorb to the substrate and form protective films has not been fully understood to date. Surfactant molecules tend to aggregate and interact with other molecules available in system, for example other components in commercial corrosion inhibitor formulations.

Film formation of organic surfactants has been largely characterized using for example scanning electron microscopy, X-ray photoelectron spectroscopy and atomic force microscopy. Some methods only provide information about fully formed film, but do not allow for analysis of possible interactions of the surfactant molecules with other components present in the corrosive media. Small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) could potentially characterize surfactant molecules in solution even in the precursor state (if it is available with other molecules in solution) and provide information about the surface film properties. This chapter provides background technical information on the two emerging characterization methods, SAXS and SANS, as well as discusses prospects of their use to characterize organic surfactants in corrosion science.

2. Principles of small angle neutron scattering (SANS) and small angle X-ray scattering (SAXS)

2.1. Small angle neutron scattering (SANS)

Phenomenon such as reflection or diffraction can be observed with neutron. Neutron behaves as a wave (same as electron) and is accepted in quantum mechanics. The interaction of neutron with nucleus is one way of its interaction with matter. Alternately, unpaired electrons also interact with neutron (specifically momentum of neutron). The scattering of neutron depends on the interaction potential between nucleus and neutron. Wavelength of neutron falls in the order of $1A°$ and it is worth to note that interaction potential, which is represented by $V(r)$, falls in the order of 10^{-15} m. Therefore, nucleus incites scattering.

Let us discuss few important terms that are encountered in neutron scattering. Scattering length can be defined as a complex number, but it should be noted that imaginary component of a complex number can only be considered if the atom is a heavy nuclei, such as boron, and shows high absorption coefficient. One should also be aware that nuclear scattering length is different from magnetic scattering length. Magnetic scattering length needs to be considered in magnetization studies because neutron momentum interacts with unpaired electrons. This fundamental phenomenon was responsible for the developments of SANS technique, which is widely used to characterize magnetic materials.

Interaction of neutron beam with matter is possible through two ways: (a) interaction between neutron beam and nucleus and (b) momentum of neutron with unpaired electron (magnetic interaction). Therefore, magnetic information about a surface film and a substrate can be obtained through SANS. It is particularly important for corrosion applications, where SANS could be used for determination of various iron oxide phases (i.e. corrosion products) owing to the magnetic nature of iron. Corrosion of iron usually promotes formation of these phases, often characterized with X-ray diffraction spectroscopy (XRD). It is important to point out, with regards to analysis of XRD and SANS data, that SANS analysis is more complex compared to a conventional XRD.

Elastic scattering describes a phenomenon of no change of neutron during scattering. The opposite phenomenon is known as inelastic scattering where the energy of neutron changes during scattering. Total scattering cross section is another technical parameter, particularly important to corrosion scientists performing experiments with SANS. Total scattering cross section is a ratio of total number of neutrons scattered per second to the number of neutron incident per second. The scattering data quality depends on this parameter as it suggests how strong the neutron scattering signal will be.

Let us discuss briefly small angle neutron scattering (SANS) technique. SANS is an instrument that uses neutron for sample characterization, and a monochromator is used to obtain mono-chromatized neutron beam. The velocity of neutron beam is controlled through rotating velocity selector made from an absorbing blade. Neutron beam passes through velocity selector and is controlled in terms of velocity along with monochromatization (order of 10%). Neutron beam divergence is limited by collimator, diameter of which is changed according to an application. The collimation length varies between 1 and 10 m. Flat samples must be used and mounted perpendicular to the beam direction so that the entire sample thickness is available to neutron scattering. In corrosion applications, thin and flat samples are suitable for SANS analysis. Using thin metallic foil (1–1.5 mm) is advisable in order to avoid multiple scattering and absorption of neutron beam. A position-sensitive detector (PSD) is usually used to determine incident neutron position, and the length can be changed as per the experiment requirement (5–20 m). PSD is typically positioned into an evacuated tank to avoid additional scattering occurring due to air (nitrogen). Schematic of SANS experimental setup is shown in **Figure 1** [3].

In SANS, coherent elastic neutron beam interacts with a sample and scattering vector, which is also known as a wave vector or a momentum vector, and is an important factor in a SANS experiment. The scattering vector is denoted by q and can be defined as:
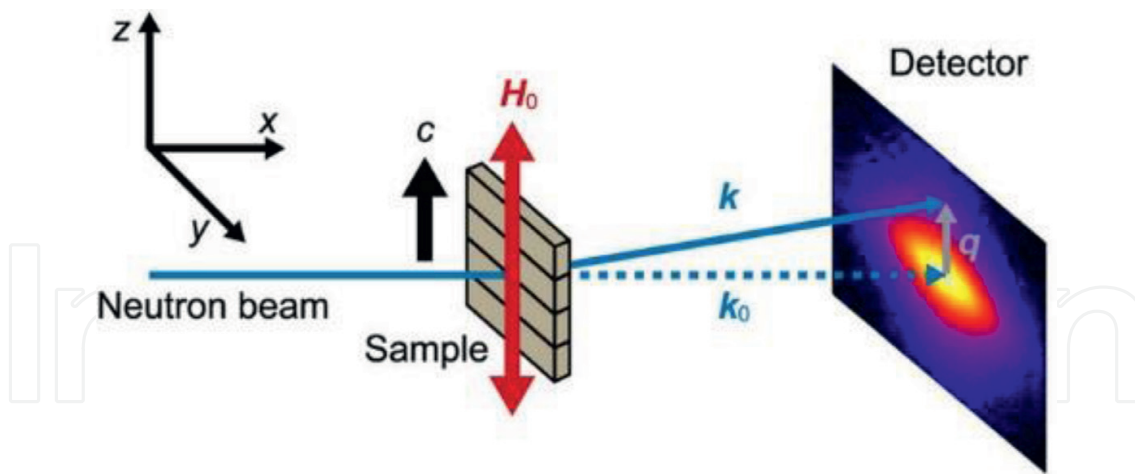
$$q = K_s - K_i \tag{1}$$

Figure 1. Schematic of SANS experimental setup [3]. Reprinted with permission. Copyright 2016 Nature Publishing Group.

where K_s is the scatter wave vector and K_i is the incident wave vector.

Mathematically, q can be represented as:

$$q = \frac{4\pi}{\lambda} \sin\theta \qquad (2)$$

where 2θ is the angle between K_s and K_i. The unit of q is $A^{\circ -1}$ or nm^{-1} and λ is the wavelength of neutron.

In direct space, q can be represented as:

$$q = \frac{2\pi}{d} \qquad (3)$$

where d is the interplanar spacing in the crystal.

It is recommended to the reader to refer to a specialized literature for detailed information [4].

Time of flight (ToF) SANS is an advanced technique that requires special detector for detecting large dynamic range in q (scattering vector). It is worth to mention that for different λ of neutron, different q is depicted even at the same scattering angle, and this phenomenon describes the range of q. It is possible to cover large q range through the ToF instrument. It is feasible to change a steady state instrument into ToF SANS by introducing a ToF detector. SANS data analysis has been reported by Brulet et al. [5] and provides fundamental insight into the process.

Neutron-based technique such as SANS is considered a non-destructive technique that does not introduce any changes to the sample. It is therefore recognized as an important characterization technique in corrosion science where in situ monitoring of the corrosion and corrosion-inhibition processes is required in mechanistic studies. SANS can also be useful for various corrosion-related scientific fields, such as analysis of surfactants, nanoparticles, microparticles, polymers, corrosion inhibitors and thin films.

2.2. Small angle X-ray scattering (SAXS)

Small deviation of radiation from its incident direction occurs due to interaction between radiation and a homogeneous matter. This small deviation from the incident direction is known as small angle scattering. This scattering can also be explained as a wave or an object. Background information for this phenomenon can be obtained from other sources [6, 7].

It is fundamentally established that scattering power depends on electron density. This means that electron density is directly proportional to the scattering phenomenon. SAXS analysis is suitable for a range of samples and is most often used to analyse two-phase systems. An application of SAXS in a multiphase system requires assumption of a two-phase system only. In such case, one phase consists of much higher electron density than the other phases (considered as one combined phase) [8]. This methodology of a two-phase assumption results in a rare application of SAXS for multiphase systems [9, 10].

SAXS has been utilized for the analysis of precipitation phenomenon in metals and alloys, crystal growth, particles' behaviour in solution, and so on. For example, Wang et al. [11] studied biocorrosion of artificial hip implant. Orthopaedic prostheses were lubricated by pseudosynovial fluid that contains protein, which results in corrosion and wear of the hip (implant). It was observed that a nanocrystalline layer formed on Co-Cr-Mo alloy surface. Particle size distribution of this layer was measured through SAXS. The application of SAXS has not been limited to stainless steel or carbon steel, but was used also for corrosion of Mg alloys [12–15].

It should be highlighted here that coupling SAXS and SANS data could provide valuable information about complex systems, such as corrosion. Combination of SAXS with transmission electron microscopy (TEM) was successfully applied in the analysis of gold nanoparticles [16] and also for metals/alloys with the objective to identify rod-shaped precipitates [17]. In summary, one can even use SAXS to obtain useful information about morphological features that usually belong in the region of micro- to subnanometer. SAXS may require combinatory data from TEM analysis for a multiphase system and thus appears less favourable. SAXS however allows for obtaining data in situ, which is not possible from TEM analysis alone.

Experimental setup for SAXS measurements is technically very similar to that used for SANS (**Figure 1**). It is advisable for the reader to recall few technical parameter definitions discussed earlier in the SANS section. SAXS intensity [18, 19] is a function of scattering vector q, which is presented as a function of θ and wavelength of photon that scattered from the sample, and is mathematically described by Eq. (2). It is, however, important to note that the λ used in neutron (SANS) and X-ray (SAXS) are different. Some other factors, such as electron density, particle size and collimation of beam resolution [20], are important for corrosion science and for application of surfactant molecules in corrosive media. Let us, for example, consider particle size in the analysis of SAXS data. It was mentioned earlier in this chapter that scattering is a function of electron density. Amplitude of scattering intensity

A(q) usually depends on radial electron density of particle $\rho(r)$, besides being influenced by volume of the particle. When particles are in solution, buffer solution scattering must be separated (subtracted) from scattering that originates from the system of study, that is the analysed samples. This method is known as contrast method and utilizes the difference of average electron density $\rho(r)$ of particles from the electron density of solvent in which particles are dispersed. It is therefore necessary to acquire SAXS profile from blank buffer solution apart from measurements conducted with particles in solvent. One should keep in mind that dialyzing a sample for macromolecules is highly desirable. Corrosion scientists should note that the presence of salts results in increased background response. For example, a signal recorded from a brine solution (sodium chloride-containing medium) with a corrosion inhibitor will combine responses from both the brine solution and the inhibitor molecules.

In corrosion inhibition, aggregation of molecules is a common phenomenon that affects scattering results. Using diluted solutions of corrosion inhibitor is expected to reduce the aggregation, but could result in insufficient scattering signal as large clusters of particles or agglomerates will give a stronger scattering signal.

Data obtained from SAXS measurements can provide information on size, shape and surface of agglomerates or particles. A schematic representing the type of information that is available from SANS data, through various data-processing methods, is presented in **Figure 2** [21]. Discussion on the data analysis, specific for corrosion scientists is provided later in this chapter, in application section. Readers who are interested in obtaining additional details may refer to the review published by Pauw et al. [22] which addresses in detail SAXS profile collection and processing.
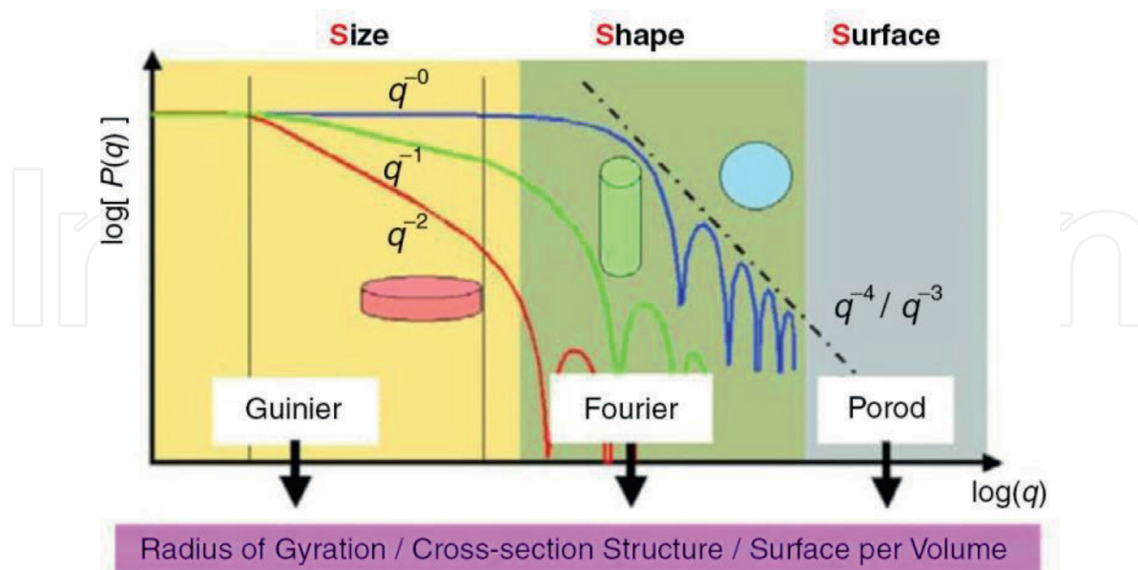

Figure 2. Schematic of the information which is possible to extract through various data-processing techniques in SAXS. Copyright 2015, Lauren Boldon et al. [21].

3. Application of SANS and SAXS techniques for analysis of surfactants in corrosion science

3.1. Application of SANS technique

SANS can provide significant mechanistic insights into the corrosion phenomenon specifically related to applications of corrosion inhibitors. In particular, SANS can be applied to determine the interaction between various components used in commercial corrosion-inhibitor formulations. It is known, for example, that organic surfactants used in the corrosion-inhibitor formulations form micelles in the solution that are believed to adsorb to metallic substrate and protect against corrosion. It is however not known whether any interactions between these organic surfactants and other compounds in the corrosion inhibitor formulations take place in the corrosive media. Such interactions could potentially influence their adsorption to the steel surface and their efficiency to inhibit corrosion. Additionally, SANS could provide information about the precursor state of inhibitor molecules including nucleation of these molecules at steel, which depends on the degree of super saturation. The super saturation level and consequently nucleation are expected to be affected by different chemical compounds present in corrosion inhibitor formulations. It is therefore desirable for corrosion scientists to evaluate behaviour of inhibitor molecules both before and after their adsorption to a metallic substrate in order to develop mechanistic understanding of the corrosion-inhibition process.

Processing and analysis of SANS spectra is graphically described in **Figure 2**. Inverse Fourier Transform (IFT) is one of the methods used to analyse scattering data, including describing the pair distribution function p(r). It is important to mention here that if there are any oscillations in the curve between p(r) vs. r (inter atomic radius), then it is mandatory to consider intermicellar interactions as part of the data analysis. This is best demonstrated with the help of data reported by Hassan et al. [23]. In this work, the X_{PTHC}(molar ratio between salt and surfactant) was varied from 0 to 0.6 (**Figure 3**). In the case of X_{PTHC}= 0.5 and 0.6, no negative oscillations were observed at the spectra, meaning the interparticle interactions do not have to be included in this analysis. On contrary, in the case of X_{PTHC}= 0, 0.3 and 0.4, negative oscillations appear at the spectra and confirm the presence of intermicellar interactions. Another feature in **Figure 3** is the intensity of oscillations, especially the negative ones. Larger negative oscillation can be easily observed for X_{PTHC}= 0.3 compared to X_{PTHC}= 0.4 and indicates larger sized aggregates. It is worth noting that anisotropic micelles can be examined directly using IFT spectra with high scattering vector (q).

Following the IFT analysis, generalized indirect Fourier transform (GIFT) can be employed to provide information about growth of micelles, particularly the growth mechanism. GIFT usually separates two scattering phenomenon known as intraparticle scattering (form factor) and interparticle scattering (structure factor). The GIFT analysis could be combined with a mathematical approximation model, such as Ornstein-Zornike equation that is used for evaluating structure factor and for describing resultant waves (phase and amplitude) from atoms in unit cell. The most common model is rescaled mean spherical approximation (RMSA). RMSA
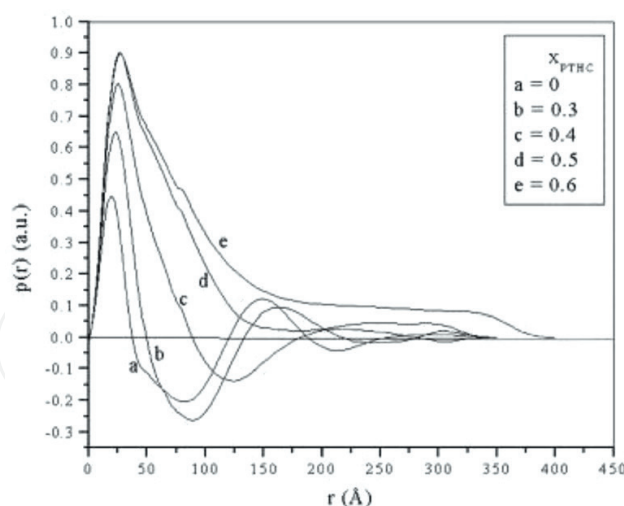
Figure 3. Pair distance distribution functions, p(r), through IFT analysis of SANS spectra for 50 mM SDS at different values of X_{PTHC} [23]. Reprinted with permission. Copyright 2003 Elsevier Science (USA).

provides significant advantage in reducing computational complexities. Alternatively, one can use Rogers and Yong (RY) closure. Readers should keep in mind that results derived from different closure applications will vary as they are dependent on the method of analysis used. Details of these approximation models can be found in a SANS tool box [24].

Guinier analysis is a common terminology in scattering analysis. Since Porod approximation takes high scattering vector to analyse low q limit of scattering spectra, Guinier analysis becomes useful. There are different formulas available for particles of different shapes. For example, radius of gyration of sphere would be $R_g^2 = 3/5\ R^2$ and R_g can be extracted slope of ln I (Q) vs. Q^2 curve. But one should note that $R_g \ll 1$. We recommend a book by A. J. Jackson for further details on the data analysis [25].

Apart from the examination of interaction among surfactant molecules, SANS can also be used to extract information about electrostatic interactions and type of growth, for example uniaxial growth of surfactant assemblies. Shape of the micelles could also be identified with SANS and correlated with for example TEM analysis., while combined application of SANS and zeta potential measurements could help to relate particle charge with aggregation number. Application of Yukawa potential with RMSA closure provides similar information to the latter. Determining particle properties would be helpful in mechanistic investigations as defining the effect of surface charge on particle growth could reveal whether any specific charge promotes the growth of a surfactant assembly.

Let us discuss the application of SANS using case studies involving surfactant molecules in corrosion applications. Hassan et al. [23] studied a surfactant molecule, namely sodium dodecyl sulphate (SDS) and its interaction with cationic hydrophobic salt known as P-toluidine hydrochloride (PTHC). This experiment depicted the interaction among these molecules. Repulsive intermicellar interactions were observed and confirmed through the appearance of a well-pronounced peak in SANS spectra at low salt concentration. The experiment was conducted with neutron wavelength 6 $A^{\circ-1}$, path length 2 mm with scattering vector range

(q) 0.005–0.6 A$^{\circ-1}$. As mentioned in the principle section on SANS technique, background correction is necessary before final data analysis. In this study, the authors recorded spectra of empty test cell (quartz). Background could also be determined through Porod correction [25]. To avoid aggregation of inhibitor molecules during the experiment, the molar ratio of PTHC to SDS was kept below 0.6 or the solution became turbid. In general, molar ratio of inhibitor to surfactant will depend on the type of corrosion inhibitor, and turbidity will vary for solutions with a cationic or an anionic surfactant. These solution properties need to be considered by corrosion scientists when designing their experiments.

Mobin et al. [26] investigated SDS and cetyltrimethyl ammonium bromide (CTAB) for their synergistic effect with L-methionine to inhibit corrosion of mild steel. Through potentiodynamic polarization measurements, the authors concluded that the efficiency of L-methionine as a corrosion inhibitor was higher in the presence of SDS compared to CTAB. L-methionine was more effective with CTAB than with SDS. As both compounds, CTAB and SDS, can be analysed with SANS, it can be envisaged that the application of SANS would provide additional information on the mechanisms of the interactions of L-methionine with CTAB and SDS.

Surfactants can also be combined with protein to protect against corrosion [27]. Sodium dodecyl sulphate (SDS) was used as an anionic surfactant with zein, which is a corn protein and is insoluble in water. It was observed that SDS was less effective in inhibiting corrosion when used as a sole molecule, compared to its combined use, that is SDS-protein and zein-SDS. It was suggested that the enhanced zein-SDS efficiency resulted from the formation of zein-SDS complex. The interactions between zein and SDS are yet to be described. SANS could be a suitable technique to evaluate this phenomenon where the approach by Khan et al. [28] can be adopted. The authors applied SANS technique to study the interaction between protein, nanoparticles and surfactants. Nanoparticle used in this study was silica with sodium dodecyl sulphate surfactant along with the bovine serum albumin protein. Each system was studied separately. In the nanoparticle-protein system, protein did not adsorb on nanoparticle and formed aggregates. No physical interaction was observed in the nanoparticle-surfactant system, but surfactant interacted with protein and formed necklace-like structure probably due to the formation of a protein-surfactant complex as elucidated by Roy and Sukul [27]. It is worth to note that the test solution was D$_2$O instead of H$_2$O as D$_2$O provides better contrast than H$_2$O.

Figure 4 shows a complex SANS spectra for a three-component system [29]. The three-component system contained 1 wt% BSA protein with 50 mM SDS and 1 wt% silica nanoparticles in 0.2 M NaCl in D$_2$O.SANS was applied with neutron wavelength 6 A$^{\circ}$, $\Delta\lambda/\lambda$= 9% (fwhm) with q ranges between 0.007 and 0.30 A$^{\circ-1}$. Quartz cell was used with 1–2 mm path length, and a non-linear least square fitting was applied. **Figure 4** clearly depicts that the combined system behaved differently than each individual system (see insets of **Figure 4**). In the mixed system, low q region contained a lot of scattering intensity whereas this was not the case for individual components, such as nanoparticle, protein and surfactant. Interestingly, high Q region was almost the same for the individual and combined systems. Aggregation of nanoparticles was observed in the nanoparticle-protein system. This is caused by the lack of
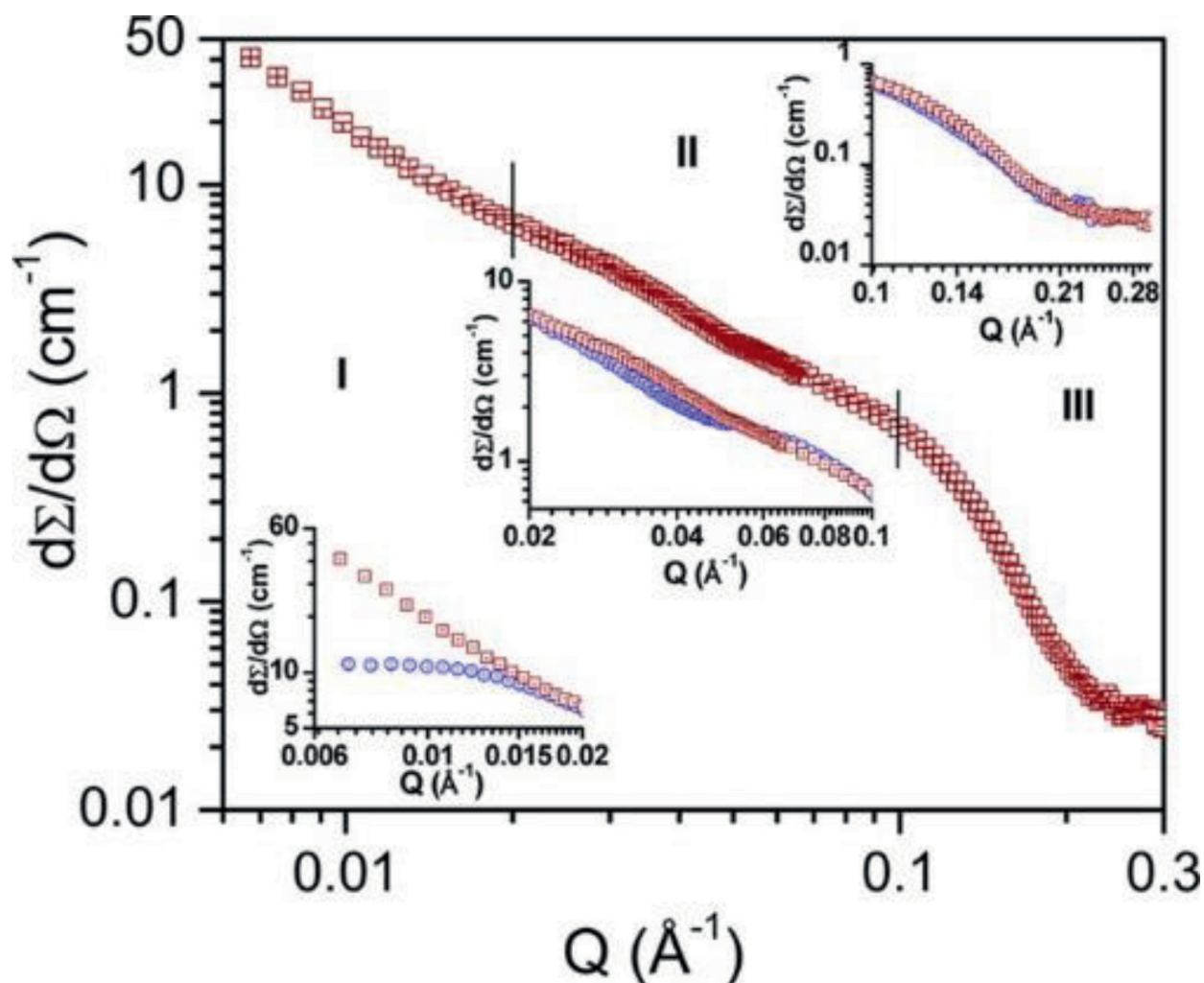
Figure 4. SANS data from a three-component system. Reprinted with permission from [29]. Copyright 2013 American Chemical Society.

adsorption of protein in nanoparticle due to depletion of forces. In other words, there was not enough driving force to govern the process of adsorption. Similarly, no physical interaction between nanoparticle and SDS was observed whereas interaction between SDS and protein was noted.

Bergstroem and Garamus [30] studied cationic surfactants, hexadecyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB) and didodecyldimethyl-ammonium bromide (DDAB) with variable chain lengths. The authors observed significant differences in the growth behaviour in various surfactant mixtures. It was noticed that DTAB formed oblate spheroidal micelle with [NaBr]=0.1 M. On contrary, addition of CTAB resulted in a transformation into prolate spheroidal micelles. Similar growth rate of CTAB/DTAB mixture was observed in all directions, whereas DDAB/DTAB mixture grew only in the length direction of micelle. The DDAB/DTAB micelles later transformed to form a bilayer structure. Another interesting outcome was the effect of salt addition on

the transition point of micelle to bilayer. Furthermore, an addition of [NaBr] salt in DDAB/DTAB mixture resulted in aggregation of DTAB. This is relevant to corrosion science as corrosive media often contain various salts, such as NaCl in sea-salt simulations. The presence of salts could affect the behaviour of a surfactant in the solution and vary the micelle aggregation.

Singh et al. [31] used SANS to study interaction of CTAB surfactant with Pluronic F 88, a compound used as a corrosion inhibitor for Zn in alkaline battery in suspension form. It was found that Pluronic formed super molecular assembly with CTAB. Pluronic's micelle hydrophobic core was occupied with CTAB (hydrophobic chain). Interestingly, an increment in the CTAB concentration affected the electrostatic interaction, which was found to increase due to the change in the rotational correlational time of anionic probe. The pluronic-CTAB interaction led to formation of super molecular assembly with hydrophobic chain of CTAB placed at the hydrophobic core of pluronic micelle. Pluronic was established as a useful corrosion inhibitor for Zn and therefore further analysis of pluronic acid with DTAB, TTAB and other surfactants could be explored as it holds potential for corrosion inhibition applications.

Similarly, micelles of cationic octadecyltrimethylammonium chloride (OTAC) and anionic ammonium dodecyl sulphate (ADS) surfactants were investigated through SANS for their structural transitions [32]. It was observed that 100 mM ADS exhibited spherical shape with core shell, whereas oblate ellipsoid shapes were observed at concentrations above 100 mM. SANS was also employed to elucidate interaction of non-ionic surfactant with silica nanoparticle and decaethylene glycol monododecyl ether. The experiment was conducted using 1 wt.% nanoparticles and 0–1 wt.% surfactant. The non-ionic surfactant was found to adsorb on nanoparticles in the absence of electrolyte (NaCl), whereas in the presence of electrolyte it was not adsorbed, leading to the aggregation of nanoparticles [33]. This study could be useful for corrosion scientists as nanoparticle interactions with non-ionic surfactants are relevant to applications of corrosion-protective coatings containing nanoparticles. Nanoparticles are typically synthesized with the help of various capping agents and there is an opportunity to select a surfactant as a capping agent suitable for corrosion-protective coatings.

SDS surfactant was also used in combination with Al^{3+} ($Al(NO_3)_3.9H_2O$) and D_2O as a solvent. SANS analysis confirmed the formation of clusters as shown in **Figure 5** [34]. Including other modern characterization techniques into the study could provide mechanistic insights into the formation (e.g. shape) and composition of the formed clusters. Transmission electron microscopy with energy dispersive spectroscopy and electron energy loss spectroscopy and secondary ion mass spectrometry could be the possible options.

In this section, we have discussed the possibility of SANS application for surfactants that have been used as corrosion inhibitors and outlined future experiments concerning the use of SANS. Despite most studies being conducted in solutions (electrolytes), it should be noted that SANS can also be useful for investigating atmospheric corrosion studies, such as wet-dry oxidation [35].
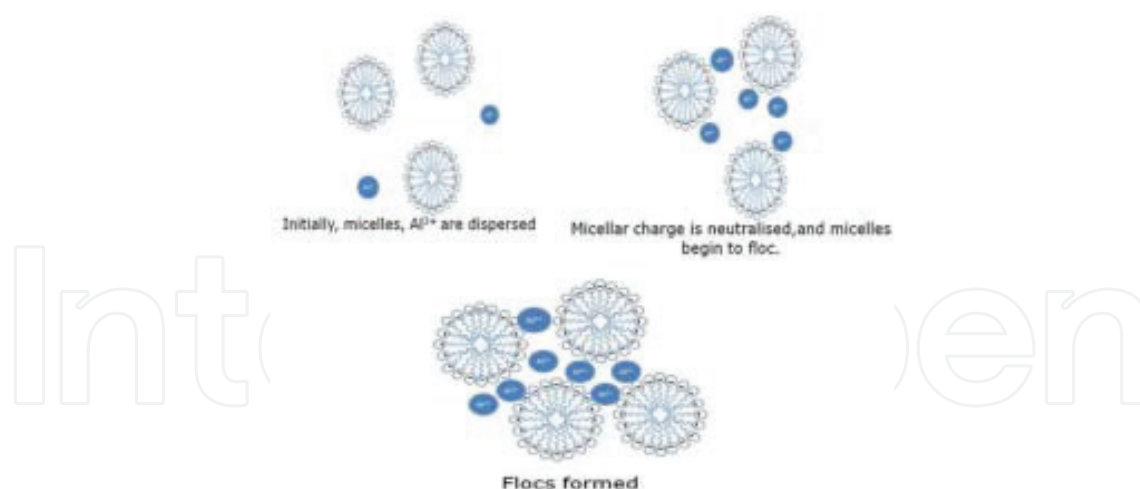
Figure 5. Cluster formation process [34]. Reprinted with permission. Copyright 2015 American Institute of Physics.

3.2. Application of SAXS technique

As discussed earlier in this chapter, SAXS is a powerful technique which allows for measuring particles in the size range of 1–100 nm. Particles must be presented in a dispersed form. Usually, amphiphilic molecules exhibit aggregation through self-assembly or organization. SAXS is an ideal technique to analyse the phenomenon of aggregation/self-assembly of these molecules. In this section, we discuss various research studies that were performed with SAXS and are relevant for corrosion science.

Jensen et al. [36] studied the formation of surfactant micelles under non-isothermal condition using synchrotron SAXS. The system was equipped with stop-flow mixing technique for kinetic investigations. The studied surfactant was dodecyl maltoside (DDM) in dimethyl formamide (DMF). Time-resolved SAXS was used with X-ray wavelength 0.995 A° and sample detector distance 1 m. Scattering vector was measured in the range of 0.01–0.6 A°⁻¹. DDM was applied in concentrations of 1.5, 1.8, 2, 2.6 and 3 wt.% in DMF. It was noticed that scattering from hydrocarbon tail caused oscillation in scattering spectrum and generated negative contrast, while maltoside head group offered positive contrast. The ellipsoidal core-corona particles were imagined for micelles and scattering form vector was calculated. SAXS pattern was fitted with a structural model mathematically expressed as:

$$I(q) = \frac{N}{V} [\frac{\psi}{P_{mic}} P_{mic}(q) + (1 - \psi)P_{surf}(q)] \tag{4}$$

where N/V is the total concentration of surfactant molecules, ψ is the fraction of surfactant molecule in micelle, I (q) is the total scattering from solution, $P_{surf}(q)$ is the interference contribution from each point from surfactant and $P_{mic}(q)$ is the interference contribution from micelle (each point). This study revealed new information on the formation mechanism of micelles and suggested that insertion/expulsion of surfactant molecules was responsible for equilibration process of the surfactant [37].

The SAXS technique can be used to determine a critical micelle concentration (CMC) of a surfactant molecule. Surfactants are amphiphilic molecules with hydrophilic and hydrophobic parts (polar or non-polar) that are related to their behavior in solutions. This phenomenon takes place at a specific surfactant concentration known as critical micelle concentration (CMC). CMC depends on the surfactant structure (e.g. hydrocarbon chain length) and on environmental factors, such as pH, temperature and type of solvent.

Lucena et al. [38] studied non-ionic surfactant micelle structure through SAXS and determined critical micellar concentration (CMC), see **Figure 6**. The studied system was nonylphenolpolyethoxylated surfactant mixed with each solvent: octane, decane and dodecane. Ethylene glycol monobutyl ether was used as a polar additive. The authors used SAXS with X-ray wavelength of 0.1542 nm. Samples were analysed in quartz capillary with 1 mm diameter (external) and 10 μm thickness. Sample to detector distance was 700 mm. From the SAXS data, pair distance distribution function (P(r)) was derived using GIFT software. It was observed that at concentrations lower the CMC, surfactant interacts with organic solvent, whereas at the CMC, self-organization takes place through ejection of the ethoxylated part. Ethylene glycol monobutyl, which was used as a polar additive, enhances the micelle formation due to entropic effect. The driving force for the interaction between the polar additive and the polar region of the surfactant are the enthalphic changes that enhance the micelle formation through an increasing cohesion. This study is relevant to corrosion science as CMC reflects important properties (chemical and physical) of a surfactant in its application as a corrosion inhibitor. Interested readers can refer to related literature for broader understanding of the topic and for the development of experimental design [39, 40].

Shrestha et al. [41] studied non-ionic fluorinated micelles to describe the self-organization of perfluoroalkyl sulphonamide ethoxylate in aqueous solution. SAXS experiment was performed with X-ray wavelength of 0.1542 nm with quartz capillary (1 mm diameter (outer) and 10 μm thickness). This conventional SAXS operated at 40 kV and 50 mA. It was observed that rod-like structures form at lower temperature range (10 to 40°C) while planar formations are observed with temperature increase (up to 60°C). P(r) vs. r peak at low r regime exhibited a well-pronounced peak that was nearly flat towards high r regime. Changes in surfactant concentration did not affect the structure of particles. The authors also evaluated the effect of oil on the aggregation and phase transformation of the surfactant. This study is closely related to corrosion science, particularly to oil and gas industry where partitioning between oil and aqueous phase often affects the performance of as corrosion inhibitors.

4. Future prospects of SAXS and SANS applications in corrosion science

In situ monitoring of interactions between surfactant and other organic/inorganic compounds, including nanoparticles is highly important for corrosion applications, but only a limited number of techniques is currently available for these characterizations. Therefore, it is desirable to improve small angle scattering resolution and data capturing. There are number
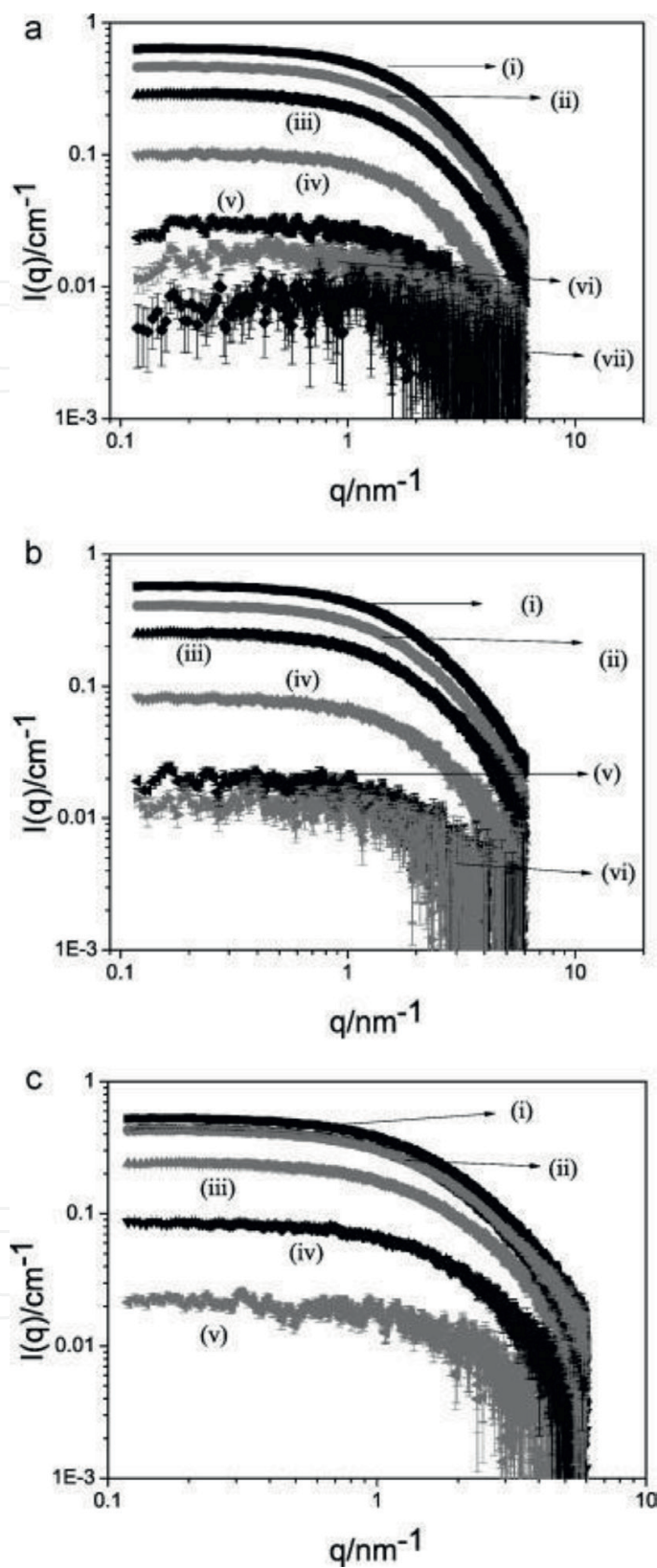
Figure 6. Scattering intensity curve I(q) for the solvents: octane (a), decane (b) and dodecane (c). (i) 0.2 mol/L; (ii) 0.15 mol/L; (iii) 0.1 mol/L; (iv) 0.05 mol/L; (v) 0.02 mol/L; (vi) 0.015 mol/L and (vii) 0.01 mol/L [38]. Reprinted with permission. Copyright 2012 Elsevier B. V.

of suitable applications of these techniques in corrosion investigations and we discuss below the eminent ones that we consider most relevant for investigating surfactants as corrosion inhibitors.

a. Determining critical micelle concentration (CMC): SAXS and SANS can be effectively utilized to determine CMC, which is an important factor in corrosion science as outlined earlier in this chapter. It is evident from earlier studies that CMC largely depends on various factors, such as temperature and pH of the studied system along with the ionic strength of the solution. The applications of the SANS and SAXS techniques to determine CMC for surfactants in corrosive media, such as for example production fluids, could provide mechanistic insights into the performance of the surfactants as corrosion inhibitors under simulated industrial conditions.

b. Surfactant aggregation study: The ability of effective corrosion inhibition by a surfactant compound has been reported to depend strongly on aggregation [42], which is related to properties of the studied system, such as pH and temperature. There are various corrosion inhibitor molecules that have been studied, for example using electrochemical impedance spectroscopy, but no studies applied both the SAXS and SANS techniques, leaving a gap in understanding of their inhibition mechanisms.

c. Monitoring (*in-situ*) of corrosion product formations: Corrosion phases at metal and alloy surfaces evolve in time and can be affected by alloy composition. SAXS and SANS could be used as in situ monitoring techniques of the corrosion-phase evolution. SANS is particularly suitable for such study, as it has the potential to characterize the bulk matrix without altering sample due to the beam exposure. It should be noted however that roughness of the steel substrate and multiple scattering from particles could possibly introduce error to the experiment.

d. Describing surfactant molecules at precursor state: Information at precursor level about interaction of surfactant molecules and other molecules in the corrosive media, such as for example corrosion-inhibitor enhancers or nanoparticles, is not abundantly available. This lack of knowledge presents significant gap in corrosion investigations as nucleation and growth in corrosive media are very important for predicting film formation kinetics and for understanding the dynamics of the corrosion process. Furthermore, the acts of nucleation, growth and interactions among molecules are important aspects of corrosion inhibition and could be elucidated through SAXS and SANS.

5. Conclusions and outlook

In this chapter, we discuss the use of small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) for analysis of organic surfactants that are utilized as effective corrosion inhibitors. We describe various examples of research studies performed with SAXS

and SANS. These methods have emerged as popular techniques in biology, nanoscience and chemical sciences, but have not been extensively explored in the field of corrosion science. We believe that this chapter provides important information for future applications of SAXS and SANS in investigating surfactant molecules as corrosion inhibitors. This chapter includes principles of these techniques, lists available type of measurements, highlights errors that can be Encountered in research studies and briefly discusses data processing steps. This chapter also illustrates the ways for possible future experiments involving surfactants in corrosion science, such as determining critical micelle concentration or the effect of aggregation of the surfactant molecules.

Acknowledgements

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