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abstract

Determining the surface tension of surfactant solutions sounds simple, and the state of the art for decades has been Pendant Drop Tensiometry (Drop Shape Analysis). According to DIN/EN/ISO standards and OECD guidelines, the only legally existing methods in the field of surfactants are the ring/plate methods, basically from the pre-computer era. For many technical surfactants and especially for surface-active polymers, these vintage methods have serious technical shortcomings caused by an inherently uncontrolled surface age. This will be demonstrated by discussing the surface tension results of two associative thickeners. Normalization activities have been initiated to „legalize" the current state of the art, Pendant Drop Tensiometry, also in the field of surfactants.

Introduction

The determination of surface tension of aqueous solutions is one of the most fundamental physicochemical characterizations of any surfactant molecule. Different methods are used depending on the time scale of surface tension reduction relevant for the specific application: Wilhelmy plate [1], du Noüy ring [2,3] or Drop Shape Analysis (Pendant Drop Tensiometry) [4,5] for slow processes or equilibrium values, or the Maximum Bubble Pressure method [6] for dynamic surface tensions, which is more relevant for fast wetting processes such as printing. For regulatory purposes, the (static) surface tension of a 0.5% aqueous solution/mixture is required for both the Customs Tariff Regulation [7] and the EU Detergent Regulation [8,9]; in addition, the Critical Micelle Concentration (CMC; derived from the determination of surface tension as a function of concentration) [10] is often used to calculate the octanol/water partition coefficient log K_{ow} [11]. None of these regulations specify which method should be used to measure surface tension. The only "official" methods, according to OECD Technical Guideline 115 [12], are the "vintage" (>100 years old) ring/plate methods as described in ISO [13] and EN [14] standards, which basically date from the pre-computer era. During the discussions on the upcoming regulation on Polymers&REACh, it was recognized by several parties [15] that guidance is needed on how to identify surface active polymers, as surface activity will most likely be one of the grouping criteria of Polymers Requiring Registration (PRR) [16]. Obviously, any classification of polymers as being surface-active should be based on their properties and not on shortcomings of the analytical methods. Unfortunately, the ring/plate methods (i.e. the only "legally existing" ones) have a serious technical deficiency, especially for technical surfactants and surface-active polymers.

History – Wilhelmy and du Noüy

A general feature of the ring/plate method is that the surface age of the air/water interface of the surfactant solutions is poorly defined. This may not be a problem for hydrophilic, well water-soluble, high purity, low molecular weight surfactants, as they are mostly used in academic studies. In the case of "normal" (to avoid the term "technical") surfactants with alkyl chain distributions (e.g. coco = C8 – C18), the presence of the more hydrophobic components can be quite problematic for performing surface tension measurements; the same is true for solutions of surface-active polymers. Once a more hydrophobic fraction of the sample material or an impurity (e.g. processing aid, educt, residual fatty acid in an ester-based product) has found its way to the air/water interface, it will dominate the measurement and prevents the determination of the surface activity of the substance intended to be analyzed.

One fairly obvious example of this general shortcoming of these two methods is the "reverse" method for determining CMC [10]. Here, the determination of the surface tension as a function of concentration starts with a concentrated surfactant solution that is gradually diluted. The practical advantage is that the titration equipment only needs to be filled with water, which eliminates the need to clean the equipment. However, this ease of handling comes at the expense of data quality: Any small fraction of a more hydrophobic component that has found its way to the surface at high concentrations will not leave the surface upon dilution below CMC – there is no real equilibrium between the molecules at the air/water interface and those dispersed in the subphase. Therefore, the measured surface tension is much lower than the "real" value of the corresponding pure surfactant.

State of the art: Drop Shape Analysis

Advances in image processing and computing power over the past three decades have made Drop Shape Analysis a well-established method; corresponding Pendant Drop Tensiometers are commercially available from several companies. Since a new drop is formed for each measurement, the surface age is well defined and it is even possible to follow the kinetics of surface tension reduction. This is one of the reasons why Drop Shape Analysis (Pendant Drop Tensiometry) has been the state of the art in surface tension measurement for decades in both academic and industrial laboratories. Unfortunately, this progress has not yet found its way into surfactant-related standardization; the current activities of the relevant standardization groups are outlined below.

Solubility in water as prerequisite

Any determination of surface tension, including Drop Shape Analysis, only makes sense for water-soluble products – unless the substances are liquid themselves and the surface tension of the bulk material is of interest. Therefore, dissolution tests have to be carried out before a surface tension measurement can be started. It is also necessary to decide which concentration to use for the measurement. According to OECD TG 115 [12] on the determination of surface tension, the concentration to be used should be 90% of the saturation solubility, but not more than 1 g/L. For most surfactants, this is above the Critical Micelle Concentration (CMC), but there is no such thing as a saturation limit for surfactants – the only exception: Ionic surfactants below the Krafft temperature [17]. Ideally, some guidance on solubility should be found in the relevant OECD technical guidelines. The guidelines 105 and 120 [18,19] are, however, not helpful when it comes to surfactants and surface-active polymers; this topic is being discussed in a separate paper in this volume [20].

The best option, and most probably the only one that provides clear guidance, would be to perform the surface tension measurements for grouping purposes at a defined concentration; whether this should be 1 g/L (as in the current OECD TG 115 [12]) or 5 g/L (as in the Customs Tariff [7] as well as the Detergent Regulation [8,9]) could still be debated. Ideally, the sample should be completely homogeneous and dissolved in order to avoid artifacts which do not allow conclusions to be drawn about the substance (e.g. polymer) under investigation. Complete solubility, however, is not required for the Customs Tariff classification, where it is accepted that the material may form an emulsion, as long as there is no separation of insoluble matter. This is conceptually difficult, as an emulsion is inherently unstable; moreover, there is no guidance given in the regulation on how to experimentally assess the absence of "separation of insoluble matter" in an emulsion.

Determination of Critical Micelle Concentration (CMC)

For regulatory purposes, the CMC is often considered a valuable parameter of a surfactant, e.g. to calculate log K_{ow} [11]. However, from an application perspective, the relevance of CMC values for the formulator is rather limited; they are only useful for people working with single surfactants in distilled water. There are also some challenges when taking the only existing standard for determining CMCs (ISO 4311:1979 [21]) seriously. A determination of CMCs by measuring surface tension as a function of concentration is straightforward for super-pure surfactants used in academia, but as soon as there are alkyl chain distributions or a distribution of homologues e.g. in the case of ethoxylates with different degrees of ethoxylation, the surface tension vs. concentration plots do not show the characteristic kink as in case of the super-pure surfactants, but a more or less smooth curve[10]. An example of the effect of an alkyl chain distribution in alkylamidopropyl betaines is shown in **Figure 1**: Pure C12 (■) vs. Coco (□). The ISO norm 4311 explicitly states that if a CMC curve looks like the one for CAPB (□), "experimentally no value for the range of c.m.c. can be defined". This part of the standard is usually completely ignored, as there is no other option.

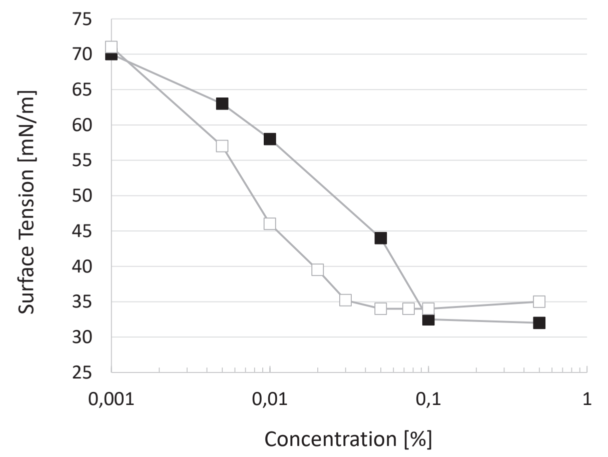

Fig. 1 Surface tension of Cocamidopropyl betaine (□) and Lauramidopropyl betaine (■) as a function of concentration (DataPhysics OCA 25, static values at 600s)

Interpretation of the surface tension results

The current OECD TG 115 [12] does not provide guidance on how to interpret the surface tension data obtained. According to the REACh regulation [22], substances with a surface tension of <60 mN/m at a concentration of 1 g/L should be considered as surface-active materials. This statement on page 56 (of 739) surprised many physical chemists, because from an application perspective, surface-active substances (= surfactants) typically have surface tensions of about 25-35 mN/m. Accordingly, both the Customs Tariff [7] and the EU Detergent Regulation [9] use a limit of <45 mN/m at a concentration of 0.5%. This value is already quite conservative considering the application performance (i.e. ability to solubilize, wash, clean), but it does make sense from a hazard assessment point of view: It has been shown that surfactants can only interact with lipid membranes if their surface pressure is >25 mN/m, which corresponds to a surface tension of <47 mN/m (surface tension of water (72 mN/m) minus surface pressure of the surfactant solution = surface tension of the surfactant solution) [23]. The reason for proposing a surface tension limit as a grouping criterion for PRR is that surface activity should allow prediction of the (eco)toxicological potential of the polymer, i.e. the possibility of interaction with biological material. This correlation is only given by using the <45 mN/m instead of the <60 mN/m criterion. In fact, it does not take much to reduce the surface tension of water. For example, polyethylene oxide (PEO) is purely water soluble and non-amphiphilic, but nonetheless it reduces the surface tension of water – depending on concentration and molecular weight – down to values even below 50 mN/m [24]. Such a polymer, which does not carry any hydrophobic residues, has no tendency to interact with hydrophobic substances or membranes and therefore should not be included in the category of surface-active materials.

Examples: Associative thickeners

To put this mostly theoretical discussion into practice, we have chosen associative thickeners as an example of amphiphilic polymers: Ethoxylates with a molecular weight of several thousand Daltons, esterified with at least two long chain fatty acids. The structurally simplest associative thickener is PEG-150 Distearate (INCI), which is PEO of MW 6000, esterified at both ends with stearic acid. In order for PEG-150 Distearate to function as an associative thickener, i.e. to bridge surfactant aggregates, it is necessary to ensure that the PEO is esterified at both ends, and therefore – to achieve this during synthesis in a reasonable amount of time – a slight excess of fatty acid is used in the esterification. Consequently, the final product contains some residual stearic acid (salt, depending on the pH of the solution), i.e. soap.

When it comes to determining the surface tension of a solution of such a polymer containing hydrophobic, surface-active impurities (such as residual fatty acid), there is the more or less philosophical question of whether to determine the surface activity of the polymer itself, or that of the product including the impurities. There are two options to determine the surface tension of a solution of the "pure" polymer: Either purify the polymer to remove the low molecular weight surface-active components (if this is possible), or perform the measurement using a method and/or under conditions where the impurities do not dominate the result; in the case of long-chain fatty acids, this means using the Pendant Drop method and choosing a pH value at which the fatty acid is soluble (rather than being protonated, insoluble and with an even stronger tendency to adsorb at the air/water interface).

PEG-150 Distearate presents an additional challenge: since both hydroxyl end groups of PEG-150 are esterified, this model associative thickener lacks sufficient hydrophilicity, and in combination with the readily crystallizable octadecyl chains, PEG-150 Distearate is not clearly soluble in water (without the addition of other surfactants): some "shimmer" (crystalline aggregates) is visible. This presents a challenge when determining the surface tension of aqueous solutions of this amphiphilic polymer. Using the du Noüy ring method, measurements were hardly possible, because the liquid lamella often broke during the measurement – most likely due to the presence of the crystals in the solution. The Wilhelmy plate method gave for both concentrations (0.1 and 0.5%) surface tensions of about 35 mN/m (pH 4) and 31 mN/m (pH 8); it seems like the soluble sodium stearate was more surface-active – at least at higher surface ages – than the protonated stearic acid. The Pendant Drop method provides more insight into the situation, as shown in **Figure 2**.

The two solutions at the lower concentration (0.1wt%; open symbols) start with higher surface tension values at short drop lifetimes, which is to be expected since less surfactant is available to populate the freshly formed drop surface. However, the plateau values at longer drop ages are somewhat lower at pH 4 (△,▲) than at pH 8 (□), except at the highest concentration (■): The second step (after a drop age of about 100 s) is very atypical and most likely an artifact caused by the presence of the "shimmering" crystals. This shows that the process of sample preparation, including heating to melt and better disperse

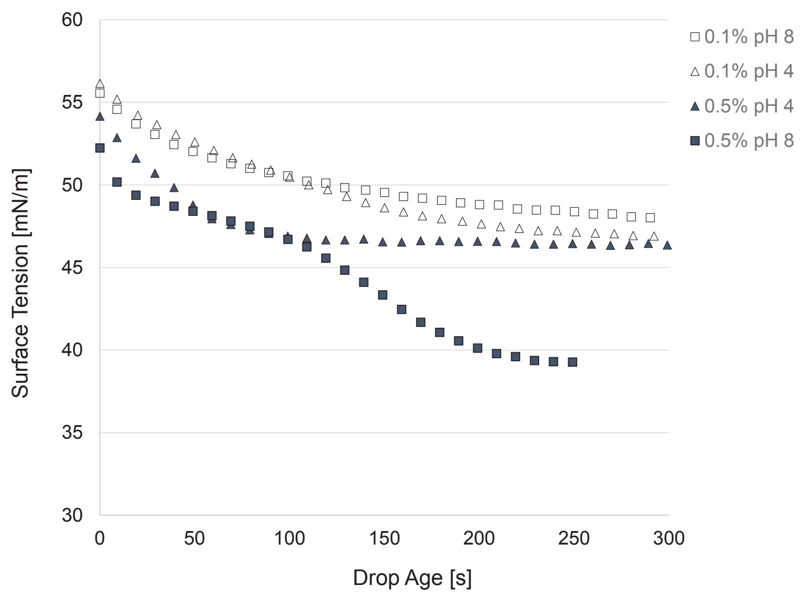

Fig. 2 Surface tension as a function of drop lifetime of 0.1% (open symbols) and 0.5% (closed symbols) aqueous solutions of PEG-150 Distearate using the Pendant Drop Method (DataPhysics OCA 25) at pH 4 (△,▲) and pH 8 (□,■)

the material, followed by stirring during cooling and crystallization, has an influence on the measurement, in case a material does not form a clear solution. However, the aim is to obtain information about the substance itself and not about the effect of the presence of some crystals. It can be concluded that the surface tension of solutions of PEG-150 Distearate is >45 mN/m, and therefore this polymer should not be classified as surface-active. This is not unexpected, since an effective reduction of surface tension requires a more or less close packing of alkyl chains at the air/water interface – which is challenging because (A) each alkyl chain carries (on average) a headgroup of 75 EO and (B) there is also some steric hindrance because the alkyl tails are present as pairs linked by PEG-150.

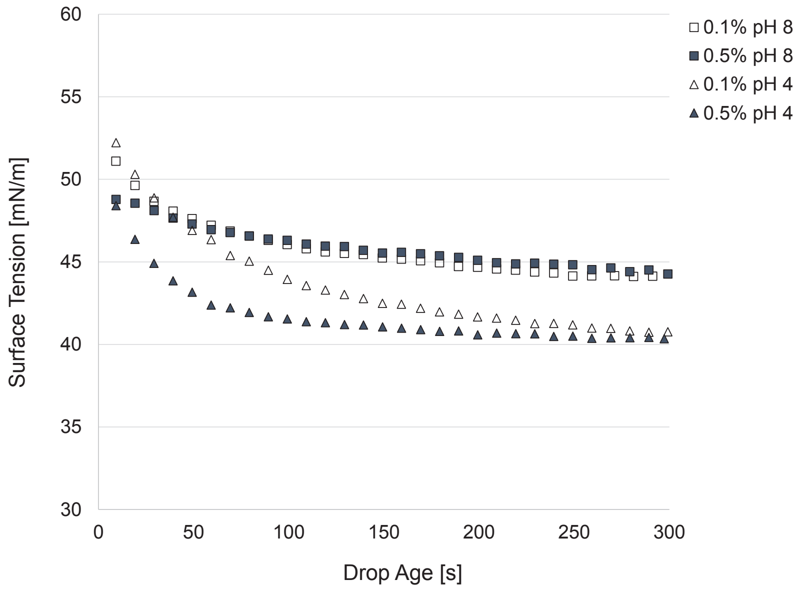

Fig. 3 Surface tension as a function of drop lifetime of 0.1% (open symbols) and 0.5% (closed symbols) aqueous solutions of PEG-120 Methyl Glucose Dioleate using the Pendant Drop Method (DataPhysics OCA 25) at pH 4 (△,▲) and pH 8 (□,■)

The second example is a more hydrophilic, clearly water-soluble associative thickener: PEG-120 Methyl Glucose Dioleate. Methyl glucose has four hydroxyl groups that are ethoxylated by a total of 120 EO, and at least two of the four hydrophilic arms are esterified with oleic acid. The results of the surface tension measurements using the Pendant Drop method are shown in **Figure 3**. This time, the results look as expected, as the material is completely water-soluble and there are no artifacts caused by crystallizable alkyl chains: The surface tension at pH 8 (□,■) is higher than at pH 4 (△,▲), and about the same plateau values are reached sooner or later, depending on the concentration; obviously, both concentrations are above the CMC. For PEG-120 Methyl Glucose Dioleate, the surface tension is just below 45 mN/m, also at pH 8; in this case, the residual oleic acid did not influence the classification as surface-active substance.

Normalization activities

The need to update the standards for the determination of surface tension and the corresponding OECD TG 115 has already been addressed in the ECETOC TR No. 133-3 (Appendix CS6-A.1) [15]; probably not coincidentally, it was also one result of the recent UBA/Fraunhofer/Ramboll project to evaluate which OECD guidelines need to be updated [25]. Since updating OECD Guidelines is a time-consuming endeavor [26], it is easier – as a first step – to develop a standard for the use of the Pendant Drop method for surfactant solutions. The CESIO WG "Test Methods of Surfactants" (TMS) decided to take action on this topic, as most of the members of the CESIO TMS are also members of the relevant standardization groups dealing with surfactant-related test methods (DIN NA 062-05-63 AA „Anwendungstechnische Prüfverfahren für Tenside"; CEN TC 276 WG 2 "Methods of Test"). Fortunately, there was already a good starting point for writing a standard on the Pendant Drop method for surfactant solutions: EN ISO 19403-3 (2020) [27] from the field of paints and coatings formulations, which needs to be modified and supplemented to be suitable for surfactants.

Summary

There are good reasons why the Pendant Drop method has been the state of the art for determination of surface tension in academic and industrial laboratories for decades. The classical ("vintage") methods (du Noüy ring/Wilhelmy plate) have serious shortcomings due to undefined surface age, especially for surfactants consisting of distributions of homologues or surface-active polymers containing hydrophobic impurities. So why are these old methods still being used today, for example in quality control? One reason is the ease of use and the availability of automated equipment. Also, the du Noüy ring and Wilhelmy plate methods are the only ones that are "official" (according to OECD Guideline 115, DIN/EN/ISO standards) in the field of surfactants. However, this is going to change: Normalization activities have already started to develop DIN/EN standards for the Pendant Drop method in the field of surfactants, which is the recommended method in those cases where not only repeatability but also the determination of the correct surface tension value is desired.

Remark

This paper is a joint effort of members of the CESIO Working Group "Test Methods of Surfactants" and the TEGEWA Working Group "Surface Active Substances": Roland Borner (Chemische Fabrik Schärer&Schläpfer AG), Wolfgang Brennich and Katrin Wunderlich (Zschimmer&Schwarz GmbH&Co KG), Karsten Holtin (Kolb Distribution Ltd.), Bernat Pi (Kao Corporation S.A.), Arjan Gelissen (Sasol Germany GmbH), Johannes Bookhold (Clariant Produkte (Deutschland) GmbH), Kati Schmidt (BASF SE), Louis Schwarzmayr (Nouryon Surface Chemistry AB), Michael Stapels (Kao Chemicals GmbH) and Joachim Venzmer (Evonik Operations GmbH).

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