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abstract

Because of the trend towards "micellar" formulations, surfactant manufacturers often get requests to prove the existence of micelles and/or provide values for Critical Micelle Concentrations (CMC). Therefore, the CESIO Working Group "Test Methods of Surfactants" and the TEGEWA Working Group "Surface Active Substances" have conducted round robin tests using "technical" surfactants, i.e. surfactants having alkyl chain length distributions: A) fatty alcohol ethoxylates with 9EO and different alkyl chain lengths (C12-C18) and B) two alkylamidopropyl betaines (coco vs. C12). The methods employed were the standard procedures established in industry, e.g. Wilhelmy Plate, du Noüy Ring or Pendant Drop. Two aspects have been the focus of this work: A) the effect of alkyl chain length variations on the CMC values, and B) the influence of the experimental procedures on the results of the surface tension measurements. There is indeed a significant influence of the experimental procedure on the surface tension values – especially for surfactants with broad alkyl chain distribution. Since these differences are mostly below CMC, the values of the CMCs itself are somewhat consistent. However, giving more "precise" values than one significant digit does not make much sense. But this should be sufficient, since in practical applications one is always well above CMC.

Introduction

In the last few years, there was a trend towards "micellar" formulations such as micellar water or micellar shampoos. As a consequence, surfactant manufacturers often get requests by formulators to provide both proof of the formation of micelles and/or values for Critical Micelle Concentrations (CMC) of their products. There are long established procedures and norms how to measure surface tensions (Wilhelmy Plate or du Noüy Ring Method [1, 2] Pendant Drop Method [3]), which can also be applied to determine CMCs by measuring the surface tension as a function of concentration [4]. Nowadays, corresponding computer-controlled equipment is commercially available and well-established in the industry, including autodilution functions to determine CMCs automatically. These norms, however, mainly describe how to perform test methods in terms of equipment, chemicals used for cleaning or calibrating, the exact procedure and how to calculate the results – usually there is less information concerning scope, limitation and the applicability to certain surfactant classes. In scientific studies dealing with CMCs, either ultra-pure surfactants (without homologes) or surfactants with unknown homologe distribution are used. Accordingly, often there is quite a variation in the CMC values reported [5]. Therefore, the CESIO Working Group "Test Methods of Surfactants" and the TEGEWA Working Group "Surface Active Substances" have asked themselves if and how the usual methods to determine CMC values can be applied to "technical" surfactants used in the industry, i.e. surfactants based on broad alkyl chain length distributions (e.g. coco C8-C18) instead of e.g. pure C12.

For the experiments in this study, which were conducted as Round Robin tests, two types of model surfactants having different chain length distributions were examined, i.e. a series of fatty alcohol ethoxylates with 9 EO (C12, C12/C14, C12-C18, C10+C18) as well as two alkylamidopropyl betaines (coco vs. C12). The equipment was commercially available standard tensiometers typically used in the industry, i.e. DuNoüy ring or Wilhelmy plate (mostly using the autodilution feature), as well as Pendant Drop Tensiometry of individually prepared solutions. Two aspects have been the focus of this work: On the one hand, the influence of the experimental procedures on the results of the surface tension measurements. On the other hand, the effect of alkyl chain length variations on the CMC values determined.

Materials & Methods

The nonionic surfactants were all laboratory products prepared at Schärer&Schläpfer, basically variation on the theme C12E9 with different alkyl chain length (distributions). Since the same ethoxylation conditions have been used for all products, it can be expected that the EO chain length distribution is pretty much identical, and there is only a variation in alkyl chain length distributions: C12E9 (>98% C12), C12/14E9 (70% C12, 30% C14), C12-18E9 (55% C12, 22% C14, 11% C16, 12% C18), C10E9 (>98% C10) and C18E9 (>98% C18).

As amphoteric surfactants, Cocamidopropyl Betaine (CAPB; 7% C8, 7% C10, 50% C12, 18% C14, 10% C16, 8% C18) and Lauramidopropyl Betaine (LAPB; >99% C12) have been used; both were laboratory products prepared at Evonik under the same experimental conditions; the levels of residual amidoamine was quite low (0.037% for CAPB; 0.057% for LAPB), and the active matters were 31.1 and 30.0%, respectively.

Samples of these surfactants have been sent to the seven participating laboratories; not every laboratory possesses or has used all methods discussed here. Also, we did not agree on an experimental protocol - every laboratory used its inhouse standard procedures. For the Du Noüy Ring or Wilhelmy Plate method there exist three different standard procedures, namely (i) stepwise addition of surfactant stock solution (e.g. 5 g/L) to water, (ii) preparation of individual solutions, and (iii) the auto-dilution feature in the inverse mode, i.e. stepwise dilution of a surfactant stock solution with water. The latter option, often called "inverse" CMC determination, seems to be the most frequently used for routine measurements, since there is less cleaning of equipment required – the titration apparatus is only filled with pure water rather than a surfactant stock solution. In the Pendant Drop method, the surface tension is recorded as a function of time. The values reported here are the equilibrium values, either after 600 s or until a constant surface tension has been reached. The water used to prepare the surfactant solutions was either doubly-distilled or MilliQ water.

Results & Discussion

The results of the surface tension measurements using the nonionic surfactant C12/14E9 (**Fig. 1**) might look confusing at first sight. The data points with filled brown symbols are all from individually prepared solutions using the Pendant Drop method. Especially close to the CMC and above, the surface tension values are pretty consistent, and independent of the laboratory in which the measurements have been conducted. One advantage of the Pendant Drop method is that the surface age is well defined, and hence the values detected are equilibrium surface tension values. Since the surface tension is determined as a function of droplet lifetime, in principle the diffusion kinetics of the slower, more hydrophobic components to a freshly created air/water interface can be observed as well. This, however, goes beyond the scope of this study. In the Du Noüy Ring or Wilhelmy Plate method, using stepwise dilution or addition of surfactant, the surface age is not defined. Hence, the surface tension values (below CMC!) are somewhat lower, most probably because of the accumulation of the most hydrophobic components at the surface over time. Another reason, why the Pendant Drop values are higher, could be depletion effects [6]. Looking at the open symbols, it is obvious that the „reverse" CMC method (i.e. stepwise dilution of concentrated surfactant solution) is especially problematic. Above CMC, the data are quite consistent, but there are large deviations below CMC. This is not totally unexpected, since the most hydrophobic components are enriched at the surface, and upon dilution, their tendency to leave the surface is low. There is obviously no real mixing, but just an exchange of the "subphase", and the more or less insoluble monolayer of surfactants persists. Independent of the method, the CMC value for C12/14E9 is ≈ 0.02 g/L; giving a more precise value is hardly possible and does not make sense, also considering the log scale of the concentration axis.

There was initial hope to obtain more consistent CMC curves and hence more "precise" CMC values using C12E9, the "purest" ethoxylate in our series of nonionics, but these results look pretty much identical (data not shown). This means that the variation in the alkyl chain length (C12-C14) is not the main cause for the "confusing look" – it is rather the distribution in the hydrophilic headgroup, i.e. the presence of homologes carrying different numbers of EO. As a consequence, there is still a mixture of species of different hydrophilicity present, despite the well-defined alkyl chain length.

The results for the ethoxylate with a rather broad alkyl chain length distribution, C12-18E9, are given in **Fig. 2**. As expected, the broader alkyl chain distribution makes the

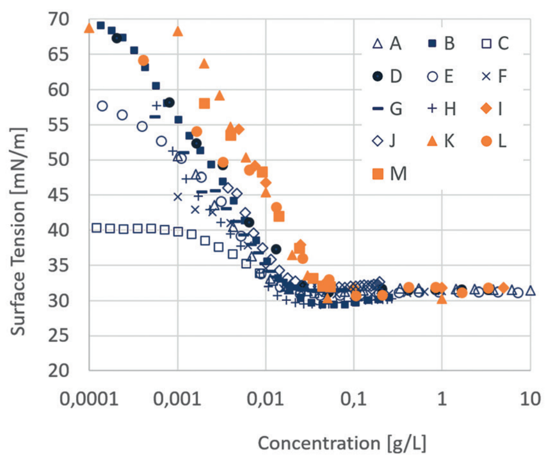

Fig. 1 Surface tension of C12/14E9 as a function of concentration; filled symbols in blue: Automated CMC by stepwise addition of surfactant stock solution to water; filled symbols in brown: Pendant Drop method of individually prepared surfactant solutions; open symbols: Automated „reverse" CMC. (Different shapes are a code for the different participants, e.g. data D, E and L have been determinded in the same laboratory).

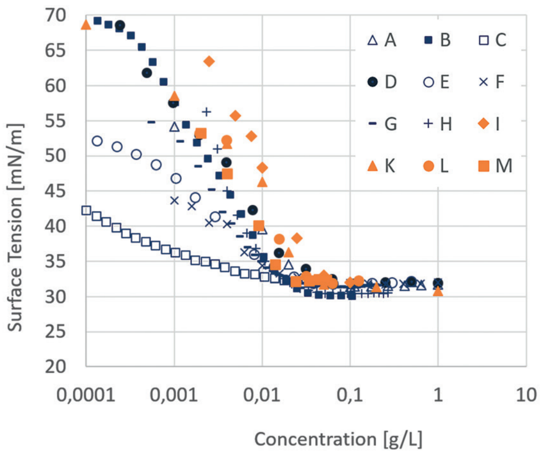

Fig. 2 Surface tension of C12-18E9 as a function of concentration; filled symbols in blue: Automated CMC by stepwise addition of surfactant stock solution to water; filled symbols in brown: Pendant Drop method of individually prepared surfactant solutions; open symbols: Automated „reverse" CMC. (Different shapes are a code for the different participants, e.g. data D, E and L have been determinded in the same laboratory).

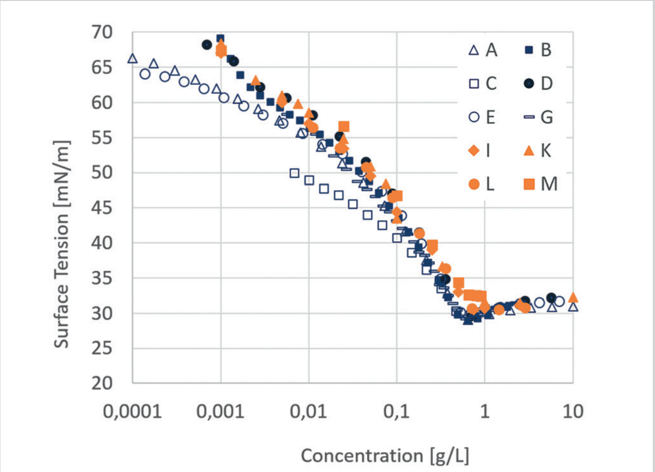

Fig. 3 Surface tension of C10E9 as a function of concentration; filled symbols in blue: Automated CMC by stepwise addition of surfactant stock solution to water; filled symbols in brown: Pendant Drop method of individually prepared surfactant solutions; open symbols: Automated „reverse" CMC. (Different shapes are a code for the different participants, e.g. data D, E and L have been determinded in the same laboratory).

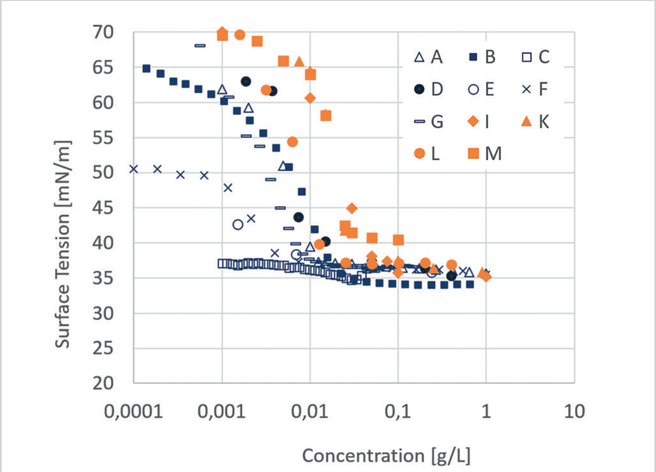

Fig. 4 Surface tension of C18E9 as a function of concentration; filled symbols in blue: Automated CMC by stepwise addition of surfactant stock solution to water; filled symbols in brown: Pendant Drop method of individually prepared surfactant solutions; open symbols: Automated „reverse" CMC. (Different shapes are a code for the different participants, e.g. data D, E and L have been determinded in the same laboratory).

situation worse – especially using the autodilution feature („reverse" CMC). The most hydrophobic components (C18) really have problems leaving the surface upon dilution. Also, some Pendant Drop data below CMC are quite high; the diffusion of the most hydrophobic components to the surface seems to be challenging. The CMC value itself, however, is quite similar (≈ 0.02 g/L) as compared to the one of C12/C14E9.

The results for the shortest, i.e. most hydrophilic nonionic surfactant, C10E9, look more like what can be found in a surface chemistry textbook; even the "reverse" CMC gives quite comparable results, except at concentrations much lower than CMC (**Fig. 3**). The surface tension values seem to be more or less independent of the method used, and corresponding to the considerably higher hydrophilicity and/or solubility, the CMC is significantly higher than for C12E09, ≈ 0.8 g/L instead of 0.02 g/L.

For the most hydrophobic nonionic in our test series, C18E9, the surface tension values depend a lot on the method used, and no reliable CMC values could be obtained (**Fig. 4**). Especially the reverse method fails; a CMC, i.e. a break in the surface tension curve, is hardly detectable. One additional complication using this surfactant is the cloud point [7] (CP); according to the norm [4] on CMC determination, the method is only applicable to nonionic surfactants which are soluble in water and have a CP at least 5°C above the testing temperature. Since CPs are strongly concentration dependent, it could well be that very dilute solutions are clear (<CP), whereas more concentrated solutions are turbid (>CP). In the latter case, the concentration of dissolved surfactant is unknown and the sample should not have been measured at all.

Summarizing the results using the nonionic surfactants, it can be stated that the CMC curves obtained by different laboratories using different methods are quite comparable; the main differences are below CMC and are most probably caused by differences in surface age. The CMC values of C12E9, C12/14E9 and C12-18E9 are pretty similar (≈ 0.02 g/L); more "precise" CMC values can hardly be obtained, since there is no sharp break in the surface tension curve detectable and considering the logarithmic scale of the concentration axis. The chain length dependencies of CMCs which are published (for a good overview see Supporting Info of [5]) could not be verified with the technical surfactants used in our study; in addition to the variations in alkyl chain length, a distribution in the number of EO units of the hydrophilic headgroup (which is almost unavoidable) seems to have a major effect on the results. Most importantly, the automated "reverse" CMC data should be treated with care, especially for more hydrophobic surfactants. Unfortunately, in brochures and data sheets typically only CMC values are given, without mentioning how the values have been generated.

For the two betaines, LAPB and CAPB, the surface tensions of individually prepared surfactant solutions using the Pendant Drop method are shown in **Fig. 5**. The shape of the

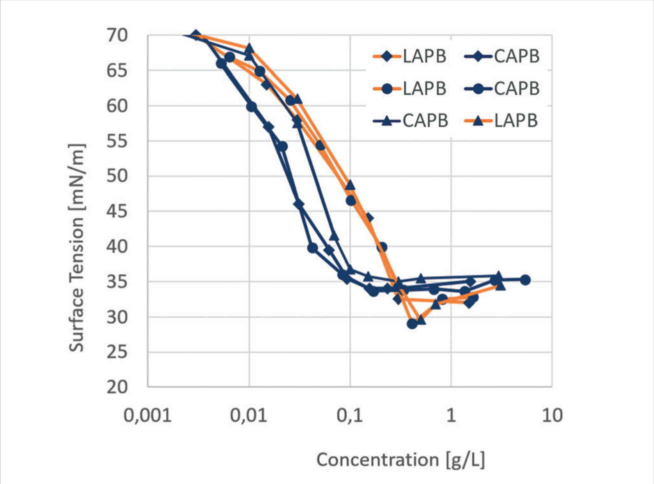

Fig. 5 Surface tension of LAPB (brown) and CAPB (blue) as a function of concentration using the Pendant Drop Method; (Different shapes are a code for the different participating laboratories).

curves (in terms of curvature) is pretty much as expected for a pure (i.e. single chain length) surfactant (LAPB) and a surfactant with alkyl chain distribution (CAPB) and therefore overlapping CMC curves. The CMC values according to these measurements are about ≈ 0.2 g/L for LAPB and ≈ 0.1 g/L for CAPB. The dip in the LAPB curves, as it is usually observed for Sodium Lauryl Sulfate (SDS) [8], is somehow surprising, as it indicates the presence of a hydrophobic impurity. The reason could be the amount of residual amidoamine; although it is quite low, for LAPB it is higher (0.057%) than for CAPB (0.037%).

Looking at the plot summarizing all methods for LAPB (**Fig. 6**), there are quite some discrepancies between the different methods, but hardly between different laboratories using the same method. Pendant Drop gives somewhat higher values than Ring or Plate; the „reverse" CMC method is again problematic, although there is neither an alkyl chain distribution (>99% C12) nor differences in the hydrophilic headgroup. Again, it is hardly possible to give a more precise value than ≈ 0.2 g/L.

For the most popular secondary surfactant, CAPB, the curves measured with different methods do not match at all (**Fig. 7**); however, the values obtained by different laboratories but using the same method are quite consistent. The curvature of the CMC curves is as expected for surfactant with alkyl chain length distribution, but a well-defined CMC value can also not be given – the CMC is somewhere around 0.1 g/L or slightly below. The surface tensions are somewhat higher than for LAPB, and there is hardly any „dip", i.e. no or much lower level of hydrophobic impurity present. Again, Pendant Drop gives slightly higher values than Plate or Ring. Using the „reverse" CMC is even more problematic; considering the presence of hydrophobic species up to C18, this is not unexpected.

There are several potential reasons for the differences in surface tension values determined, among them the material of the flask (plastic, glass) to prepare the surfactant solutions and to perform the measurement, as well as of the syringe used for the Pendant Drop method, and last but not least the pH value of the surfactant solution. Since the pH values were not adjusted and considering the isoelectric point of CAPB is at pH 6.25 [9], a small fraction of CAPB will already be protonated and in its cationic form. Cationic surfactants are known to be challenging during surface tension measurements as they adsorb to most solid surfaces; especially below CMC, there is a lot of surface as compared to the amount of surfactant.

Conclusions

It has been shown that – depending on the alkyl chain length distribution – the influence of the experimental procedure on the surface tension values below CMC is indeed significant. CMC values shown on data sheets are typically determined by using methods corresponding to a norm; however, the applicability of the procedures described there to "real" surfactants is not part of a norm. Depending on the surfactant, its hydrophobicity and homologe distribution (both in the alkyl chain and the hydrophilic headgroup), the surface tension curves might look more or less good. Nevertheless, the CMC values are surprisingly consistent, but considering the logarithmic concentration scale and the fact that there is often no sharp break, more than one significant digit does not make sense. Since practical applications are always well above CMC, one digit should be sufficient.

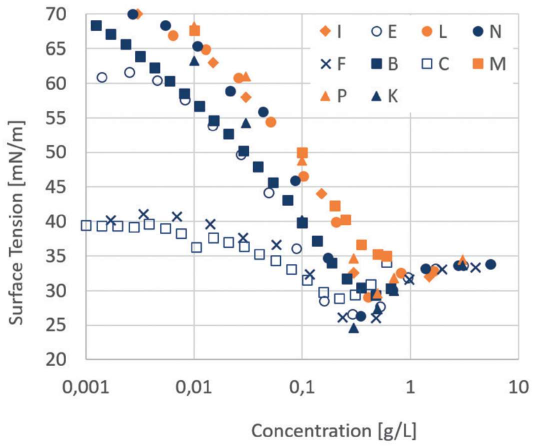

Fig. 6 Surface tension of LAPB as a function of concentration; filled symbols in blue: Automated CMC by stepwise addition of surfactant stock solution to water; filled symbols in brown: Pendant Drop method of individually prepared surfactant solutions; open symbols: Automated „reverse" CMC. (Different shapes are a code for the different participants, e.g. data E, L and N have been determinded in the same laboratory).

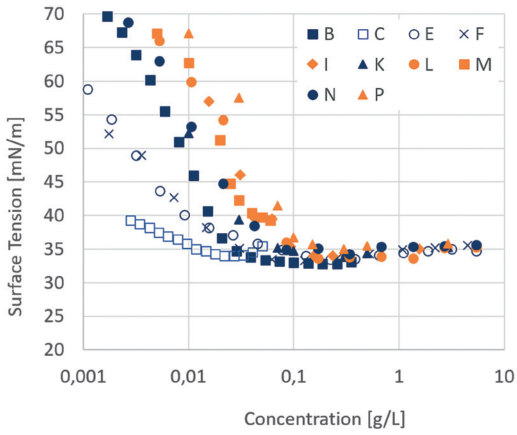

Fig. 7 Surface tension of CAPB as a function of concentration; filled symbols in blue: Automated CMC by stepwise addition of surfactant stock solution to water; filled symbols in brown: Pendant Drop method of individually prepared surfactant solutions; open symbols: Automated „reverse" CMC. (Different shapes are a code for the different participants, e.g. data E, L and N have been determinded in the same laboratory).

All in all, surface chemistry is a delicate beast! Automation should not replace thinking and critical evaluation of the results; especially "reverse" CMC results should be treated with care. Before doing any CMC measurements, one should always ask why a CMC value of a single surfactant is needed at all. In most surfactant mixtures, there is a synergistic interaction between the different surfactants, also affecting the CMC values [10]. Therefore, the relevance of CMC values of single surfactants for formulations containing several surfactants is rather limited.

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