

# AN AGGREGATION NUMBER-BASED DEFINITION OF THE IONIZATION OF A MICELLE

*Demonstration with TRFQ, SANS, and EPR*

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## Abstract

The degree of ionization of a micelle,  $\alpha$ , is defined by asserting that the aggregation number,  $N$ , is dependent only on the concentration of counterions in the aqueous pseudophase whether supplied by the surfactant or added salt. Employing different combinations of surfactant and salt that give the same value of  $N$  leads to a straightforward definition of  $\alpha$ . The value of the aggregation number is not needed in the method; the experiment need only assure that the value of  $N$  is the same for two combinations. The definition is demonstrated with time-resolved fluorescence quenching, (TRFQ) small-angle neutron scattering (SANS), and electron paramagnetic resonance (EPR).

## 1. Introduction

It has been well accepted for many years[1] that a fraction,  $\alpha$ , of an ionic surfactant's counterions are dissociated from the micelles leaving them charged[2, 3]. A quantitative measure of the value of  $\alpha$  is crucial in order to understand many aspects of the behavior of micelles. Nevertheless, there is not a satisfactory consensus as to the value of  $\alpha$  for any surfactant, not even the often studied surfactant sodium dodecylsulfate (SDS). To illustrate, Table I of Romsted's review[4] compiles 30 determinations of  $\alpha$  for SDS near the cmc. These values vary from a low of  $\alpha = 0.14$  to a high of  $\alpha = 0.70$ . Romsted[4] noted that the variability in the values of  $\alpha$  using a particular technique was less than the variability from technique to technique. That a particular technique would lead to distinct values of  $\alpha$  is not surprising in view of the fact that each technique is likely to measure a different definition of what is meant by "dissociated" counterions. A decision must be made about the location of the counterions--are they in the micelle or not? Further, an assumption must be made concerning whether counterions take part in a particular experiment as micelle-associated or not.

It would clearly be an important step forward to define  $\alpha$  in a way that is independent of any particular experimental method. In a recent paper, we proposed[5] such a definition based on the value of  $N$  and demonstrated the method with EPR. The purpose of this paper is extend the demonstration to TRFQ and SANS using data from the

literature. We also report another EPR study using a different spin probe in order to establish that the method does not depend on any particular features of the spin probe.

## 2. Theory

The fundamental hypothesis is that  $N$  is uniquely given by the concentration of counterions in the aqueous pseudophase,  $C_{aq}$ , which, according to the conventional pseudophase ion exchange mass balance relationship[2, 6] as modified by Soldi[7] is given by

$$C_{aq} = F(S_t)\{\alpha S_t + (1-\alpha)S_f + C_{ad}\}, \quad (1)$$

where  $S_t$ ,  $S_f$ , and  $C_{ad}$  are the molar concentrations of total surfactant, surfactant in monomer form, and added common counterion in the form of salt respectively. Equation 1 expresses formally the concentration of counterions associated with the micelle in the sense that governs the value of  $N$ . It makes no statement about their physical location. The factor within the brackets would give the concentration of counterions in the aqueous phase if that phase occupied the entire sample; however, at higher surfactant concentrations the excluded volume effect becomes important[7]. Following Soldi et al.[7], we correct for this excluded volume effect by including the factor  $F(S_t)$

$$F(S_t) = \frac{1}{1 - VS_t}, \quad (2)$$

where  $V$  is the molar volume of the anhydrous surfactant in moles per liter assuming that the density of the surfactants is approximately 1.0 g/mL[7]. For the two surfactants reported here,  $V = 0.272$  and 0.288 liters/mole for lithium dodecylsulfate and sodium dodecylsulfate, respectively.

A value of  $\alpha$  is measured by preparing two samples yielding the same value of the aggregation number, but with different combinations of  $S_t$  and  $C_{ad}$ . For these two combinations the hypothesis asserts that the value of  $C_{aq}$  is the same as follows:

$$F(S_t)\{\alpha S_t + [1 - \alpha]S_f + C_{ad}\} = F(S_t')\{\alpha S_t' + [1 - \alpha]S_f' + C'_{ad}\}. \quad (3)$$

As previously discussed [5], the terms involving  $S_f$  and  $S_f'$  cancel in eq 3, thus for an equivalent value of  $N$ , we have

$$F(S_t)\{\alpha S_t + C_{ad}\} = F(S_t')\{\alpha S_t' + C'_{ad}\}. \quad (4)$$

A rearrangement of eq 4 yields the value of  $\alpha$ .

$$\alpha = \frac{F(S_t)C_{ad} - F(S_t')C'_{ad}}{F(S_t')S_t' - F(S_t)S_t}. \quad (5)$$

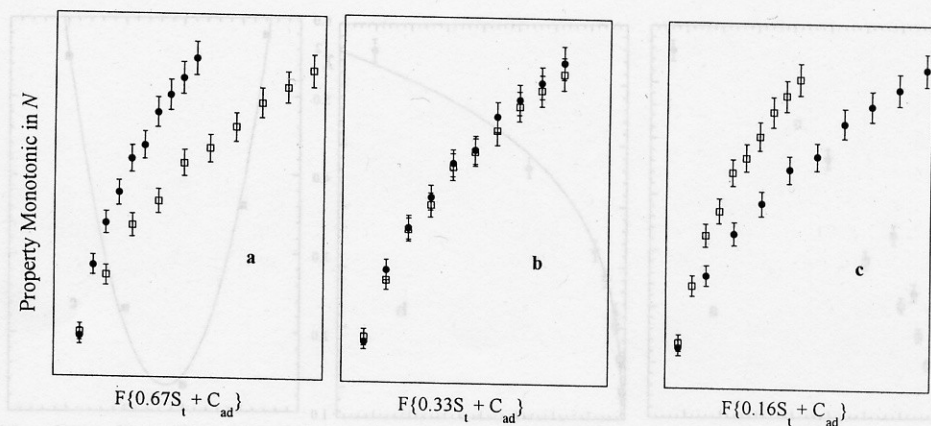
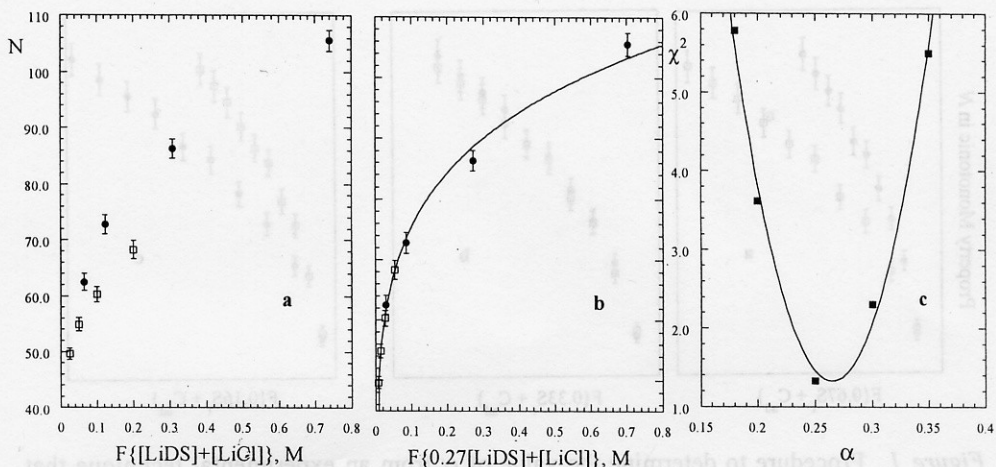


Figure 1. Procedure to determine the value of  $\alpha$  from an experimental technique that detects a quantity monotonic in the value of the aggregation number, the ordinate in each case. The abscissa is the quantity  $F(S_t)\{\alpha S_t + C_{ad}\}$  where  $\alpha$  is adjusted in search of a common curve. Samples are prepared so that the surfactant concentration  $S_t$  is varied in the absence of salt  $\square$  or the salt concentration  $C_{ad}$  is varied  $\bullet$ . A coincidence of the data shows that  $\alpha = 0.33$  is the correct value.

Any property that varies monotonically with  $N$  could, in principle, be used. In principle,  $\alpha$  could vary with  $C_{aq}$ ; however, we previously showed that  $\alpha$  is constant for SDS up to  $[SDS] = 600$  mM. This is accord with theory[3] and is certainly a reasonable assumption for the typically encountered surfactant concentrations up to 0.2 M or so. Thus, rather than computing  $\alpha$  for each pair of samples, we illustrate a simpler approach of requiring that all values of the measured property fall on a common curve when plotted versus the variable  $F(S_t)\{\alpha S_t + C_{ad}\}$  where  $\alpha = \text{constant}$ .

One method is illustrated in Figure 1. One series of samples is prepared in the absence of salt, by varying the surfactant concentration and another by holding the surfactant concentration constant and varying the salt concentration. The ordinate in each case in Figure 1 may be any experimental quantity that varies monotonically with the aggregation number. The abscissa is the quantity  $F(S_t)\{\alpha S_t + C_{ad}\}$ . The value of  $\alpha$  is adjusted in the Figure 1a - c in search of a common curve. Figure 1 was prepared with a hypothetical value of  $\alpha = 0.33$ , thus, at this value, a common curve is obtained, Figure 1b. Other combinations of surfactant and salt concentrations may be used as well.

Both TRFQ and SANS measure  $N$  directly, so this is ordinate for these two experimental methods. The EPR method rests upon the fact that the hydration of the polar shell of SDS micelles varies monotonically with  $N$  for aggregation numbers smaller than about  $N = 130$  above which the sphere-to-rod transition occurs[8]. The surface hydration is detected by a spin probe residing in the Stern layer using an electron paramagnetic resonance (EPR) technique detailed in recent papers[8-10].



**Figure 2.** Aggregation numbers for LiDS derived from TRFQ measurements. The symbols have the same meaning as in Figure 1. (a) Data plotted assuming  $\alpha = 1$  and (b) the best fit value  $\alpha = 0.27$ . (c) variation of the mean square deviation from the power law trial function resulting in a best-fit value of  $\alpha = 0.27$ .

The method utilizes the difference in resonance fields of the low- and central-field line of a nitroxide spin probe, denoted by  $A_+$ . Thus, the hyperfine spacing  $A_+$  is a monotonic function of  $N$  for  $N < 130$ . The experimental details are identical to those recently published[5] except that 16-doxylstearic acid methyl ester (16DSE) was used instead of (5DSE).

## Results and Discussion

Figures 2 - 4 are organized as suggested by Figure 1 with  $\alpha=1$  being presented in part *a* and the best fit value of  $\alpha$  used in part *b*. Figure 2 shows aggregation numbers for lithium dodecylsulfate (LiDS) taken from the literature[10]. The best value of  $\alpha$  was determined by calculating the mean square deviations of the data points from a trial function, in this case a power law[10]. A plot of the mean square deviations is plotted versus  $\alpha$  in Figure 2c showing a minimum at  $\alpha = 0.27$ .

Thus, the general scheme of Figure 1 yields  $\alpha = 0.27$  from TRFQ results. Obviously, the statistics are not sufficient to critically analyze this result; nevertheless, it is in line with values found in the literature[10 - 12]. From variations of the critical micelle concentration (cmc) with salt concentration, a value of  $\alpha = 0.32$  has been derived[10], showing that eq 4 leads to reasonable results when implemented with TRFQ. It seems worthwhile to pursue the method using TRFQ, improving the statistics. TRFQ might not be the method of choice to measure  $\alpha$ , but it is important to establish that the definition eq 4 is independent of the experimental method.

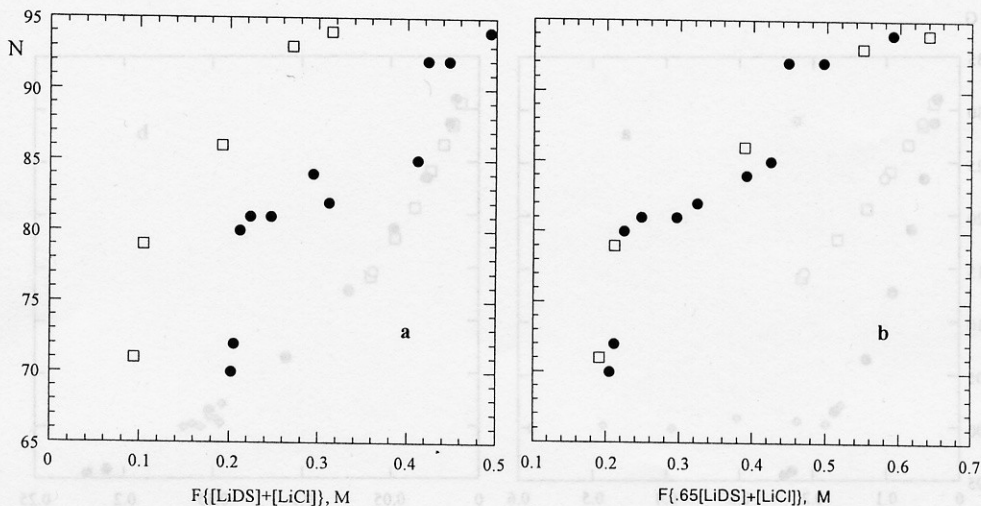


Figure 3. Aggregation numbers for LiDS derived from SANS measurements. The symbols have the same meaning as in Figure 1. (a) Data plotted assuming  $\alpha = 1$ ; (b) assuming the best fit value  $\alpha = 0.65$ .

We note that although there are a number of uncertainties in determining the value of  $N$  using TRFQ, eqs 4 and 5 have the tremendous advantage of being rather insensitive to systematic errors as long as these errors do not correlate with  $S_t$  or  $C_{ad}$ .

Figure 3 shows values of  $N$  taken from the literature for LiDS derived from SANS measurements[13]. A plot of the type shown in Figure 2c (not shown) yields a minimum at  $\alpha = 0.65$ , however this value is clearly out of line with literature values[10] and the TRFQ technique.

Thus, the application of the technique does not seem to work as well for SANS as it does for TRFQ and EPR. One reason for this could be that micelle interactions enter into the calculations for SANS whereas these are to a very high degree of approximation absent in TRFQ and EPR.

Turning to the EPR results, three-line narrow EPR spectra of 16DSE in SDS micelles typical of nitroxide free radicals undergoing approximately isotropic motion in the motional narrowing region were observed for all samples. See, for example, Figure 1(a) of ref[8].

Figure 4 shows values of  $A_+$ . In addition to the types of samples suggested by Figure 1, one other series was prepared such that the value of  $A_+$  was approximately constant. These latter samples were prepared by mixing two samples in various proportions: one with  $[SDS] = 0.500$  M and  $[NaCl] = 0$  and the other with  $[SDS] = 0.025$  M and  $[NaCl] = 0.136$  M. The standard deviations in 3 - 5 runs using the same sample are smaller than the symbols. A value of  $\alpha = 0.29 \pm 0.02$  was found by minimizing the mean square difference between the experimental points and a cubic trial function similar to Figure 2c (not shown). Previously[5], we found  $\alpha = 0.272 \pm 0.017$  using a different spin probe, 5DSE, thus, the value of  $\alpha$  determined by EPR is not probe dependent.

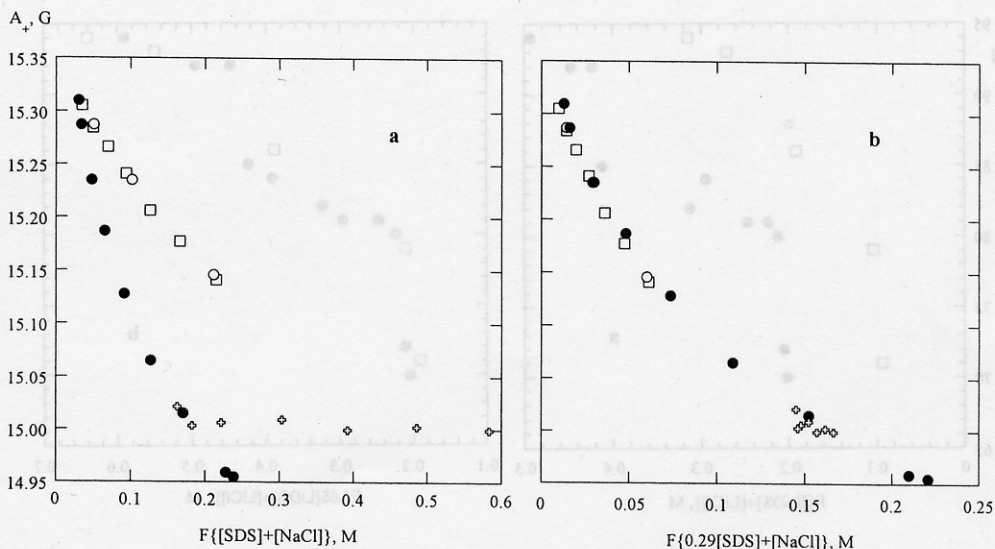


Figure 4. Hyperfine spacing  $A_+$  measurements derived from EPR. The symbols have the same meaning as in Figure 1 with an addition series denoted by the crosses which is due to various mixtures of two samples: one with concentration  $[\text{SDS}] = 0.500 \text{ M}$  and  $[\text{NaCl}] = 0$  and the other with  $[\text{SDS}] = 0.025 \text{ M}$  and  $[\text{NaCl}] = 0.136 \text{ M}$ . (a) Data plotted assuming  $\alpha = 1$ ; (b) assuming the best fit value  $\alpha = 0.29$ .

The values derived from EPR compare well with the value  $\alpha = 0.27$  obtain by Sasaki and coworkers[11] from EMF measurements in a concentration cell which is likely to be reliable because the measurements are almost free of assumptions and approximations[11]. Values of  $\alpha$  obtained from measurements of the dependence of the cmc on the concentration of added common counterion salt,  $\alpha = 0.322$ [12] are similar to the values for LiDS. Light scattering techniques lead to values of  $\alpha$  that are consistent with one another, but lower than those derived from other measurements. For example, from Table 1 of Romsted[4] five determinations of  $\alpha$  from light scattering yielded  $\alpha = 0.17 \pm 0.02$  where the uncertainty is the standard deviation in the five measurements. For the other 25 determinations in the same table, using various techniques,  $\alpha = 0.23 \pm 0.05$ [4] which is within experimental error of the two determinations found using spin probes.

Due to the simplicity of the method, it becomes feasible to investigate large numbers of systems. In addition to studying other surfactants, investigation of the variation of  $\alpha$  with a number of experimental parameters such as temperature, chain length, counterion, and added non electrolytes becomes attractive.

The EPR method ought to be applicable to any micelle that fulfills the general criterion of growing with increasing  $C_{aq}$  and that possesses water in its polar shell that is expelled as the micelle grows. We believe this to include most micelles in the slow growth region where they are approximately spherical; i. e., below the sphere-rod transition.

There are likely to be other experimental techniques that are capable of implementing the definition in eq 4. It is reasonable to assume that the size dispersion of

the micelles is dependent only on  $N$ . Thus, when matching values of  $N$  in order to apply eq 4, the dispersions will also be matched which allows the method to be applied to either a number- or weight-averaged aggregation number. Therefore, any technique that consistently detects the same statistically weighted average aggregation number could be utilized. Any method that must make significant corrections due to the concentration of micelles will be severely handicapped, because to get meaningful measurements, one must extend them over a rather large range of surfactant concentrations.

### Conclusions:

An unambiguous definition of  $\alpha$  results from the hypotheses that the aggregation number and  $\alpha$  depend only on  $Caq$ . In effect, the aggregation number becomes an internal measure of the value of  $Caq$ . TRFQ and SANS results have been applied to the aggregation number based definition of  $\alpha$ , eq 4 for LiDS. The TRFQ results are consistent with other techniques while the SANS results are not. Results for SDS consistent with those recently published[5] and in agreement with literature values were found by EPR using a different spin probe.

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