

Antonio Cipiciani\* and Stefania Primieri

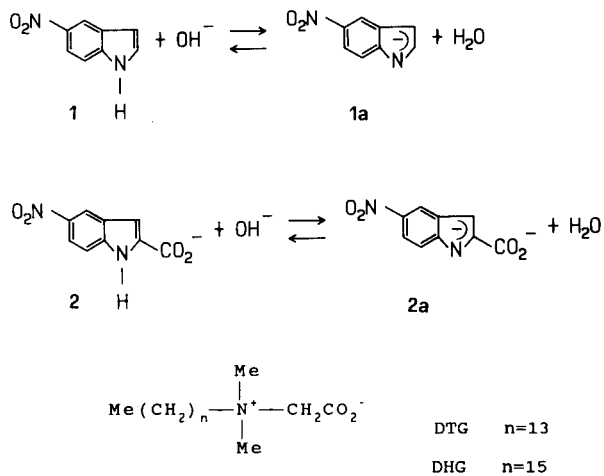
Dipartimento di Chimica, Università di Perugia,  
Via Elce di Sotto 8, Perugia 06100, Italy

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Deprotonations of 5-nitroindole (**1**) and its 2-carboxylate ion **2** at high pH have been examined in solutions of *N,N*-dimethyl-*N*-tetradecylglycine (DTG) and *N,N*-dimethyl-*N*-hexadecylglycine (DHG). We have compared the surfactant effects with those of single- and twin-tailed ionic surfactants.

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Micellar effects upon indicator equilibria are well known and cationic micelles of single- and twin-tailed surfactants increase deprotonation of weak acids at high pH [1-3]. The increased deprotonation can be accounted for quantitatively in terms of binding of OH<sup>-</sup> and indicators to the colloidal self-assemblies. We have examined deprotonations of 5-nitroindole (**1**) and its 2-carboxylate ion **2** in solutions of *N,N*-dimethyl-*N*-tetradecylglycine (DTG) and *N,N*-dimethyl-*N*-hexadecylglycine (DHG) with sodium hydroxide.



The study of micellar effects of zwitterionic surfactant systems, such as DTG and DHG, on deprotonation of weak acids in solutions of OH<sup>-</sup> is of interest since the presence of both a carboxylate group and an ammonium group in these molecules induces important changes which may affect the activity of micelles and their use as models in, for example, enzymatic reactions. Attention is also drawn to the study of the effects of activity of zwitterionic surfactant systems in an attempt to rationalize the various abilities of different surfactants to discriminate between different substrate orientations [4].

With this in mind we have examined deprotonations of 5-nitroindole, neutral indicator, and 5-nitroindole-2-carboxylate ion, charged indicator. The anion of 5-nitroindole should bind to the quaternary ammonium centres of zwitterionic micelles, but both 5-nitroindole and OH<sup>-</sup> will

be distributed between aqueous and micellar pseudo-phases, therefore the extent of deprotonation of 5-nitroindole in zwitterionic surfactant systems can be related to the concentrations of **1** and OH<sup>-</sup> in zwitterionic aggregates. On the other hand, the hydrophobic anion **2** should bind to the cationic centres of zwitterionic colloidal self-assemblies; therefore on the assumption that (**2**) and its dianion are micellar-bound the extent of deprotonation of (**2**) can be related to the amount of micellar-bound OH<sup>-</sup> [2].

In water the dianion **2a** is a slightly stronger base than the anion **1a**, in fact  $K_b = 5.6 M$  for **1a** and  $K_b = 8.3 M$  for **2a** [5].

## Results and Discussion.

### Deprotonation of 5-nitroindole in DTG and DHG.

The extent of deprotonation, *f*, of 5-nitroindole in DTG + sodium hydroxide at different concentrations, are shown in Figure 1. For the system DTG + sodium hydroxide 0.01 *M* the maximum extent of deprotonation is below the critical micelle concentration (CMC) which is  $1.5 \cdot 10^{-4}$  mol dm<sup>-3</sup> in water [4]. The extent of deprotonation decreases with increasing [DTG]. With increasing sodium hydroxide concentration (0.3-0.7 *M*) the extent of deprotonation, *f*, increases with increasing [DTG] and goes to a plateau at high concentrations of DTG. In sodium hydroxide 0.1 *M* the variation of *f* with surfactant concentration traces a borderline between the above-mentioned behaviours. Extents of deprotonations, *f*, of 5-nitroindole in DHG + sodium hydroxide at different concentrations, are shown in Figure 2. It is possible to note the similarity of DHG + sodium hydroxide system with that DTG + sodium hydroxide in deprotonation of 5-nitroindole.

The maximum extent of deprotonation is lower than that found with cationic single- and twin-tailed surfactants [1-3]. The fact indicates a low bond of OH<sup>-</sup> to micellar surface, and this is consistent with weak binding of OH<sup>-</sup> by the zwitterionic micelles. Zwitterionic micelles are formally neutral, but coulombic interactions between micelles and free ions depend, to a high degree, upon the charge density at the micellar surface. According to 'smooth' micellar model [4,6], the charge density at the spherical

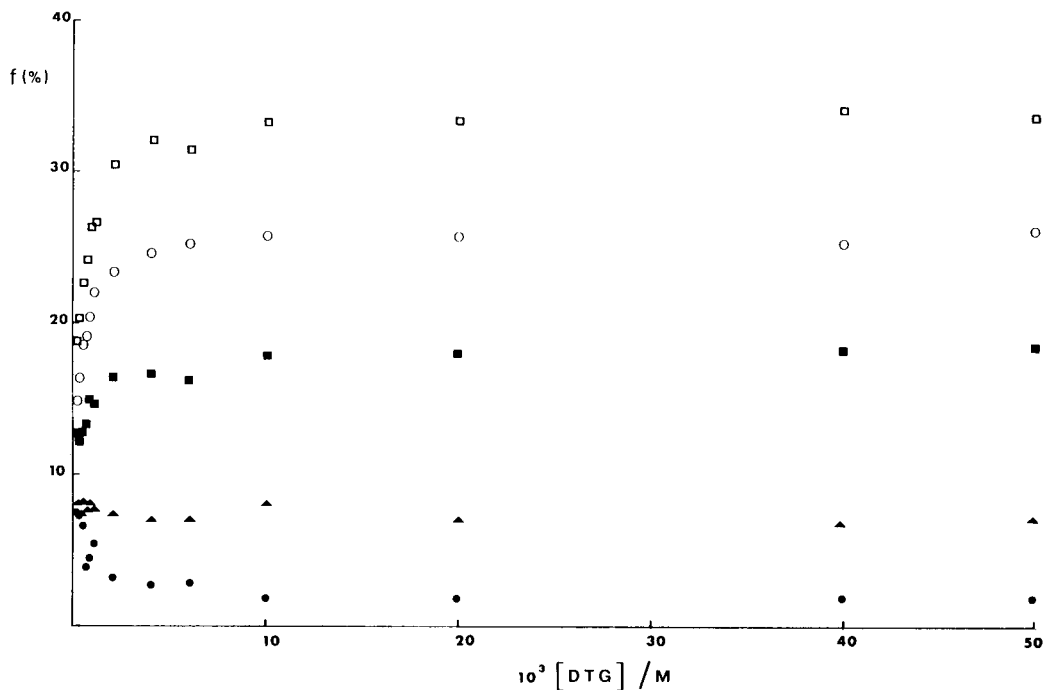


Figure 1. Extent of deprotonation of 5-nitroindole in DTG + NaOH: (●) NaOH 0.01 M, (▲) NaOH 0.1 M, (■) NaOH 0.3 M, (○) NaOH 0.5 M, (□) NaOH 0.7 M.

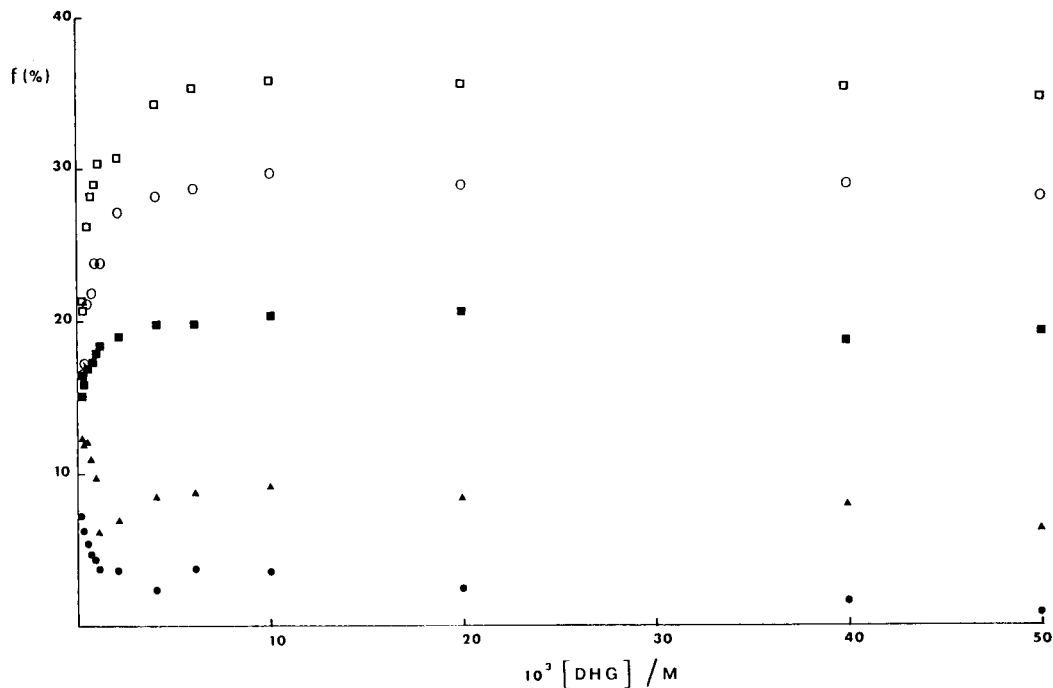


Figure 2. Extent of deprotonation of 5-nitroindole in DHG + NaOH: (●) NaOH 0.01 M, (▲) NaOH 0.1 M, (■) NaOH 0.3 M, (○) NaOH 0.5 M, (□) NaOH 0.7 M.

surface through the cationic centres will be greater than that at the spherical surface through the anionic centres; this model, even though it is an approximation, indicates how zwitterionic micelles could bind  $\text{OH}^-$ , albeit weakly.

Different behaviour of  $f$  with surfactant concentration, at different sodium hydroxide concentrations, can be related to a concentration effect of  $\text{OH}^-$  ions. For example, very high concentrations of  $\text{OH}^-$  in the aqueous pseudo-

phase could change not only the micellar structure but also the distribution of indicator between the pseudo-phases. Therefore at high sodium hydroxide concentrations (0.3-0.7 *M*) zwitterionic micelles could be well formed also at low surfactant concentrations and the extent of deprotonation of 5-nitroindole increases with [surfactant] and goes to a plateau under conditions such that **1** (and its anion) should be essentially fully micellar bound and the micellar surface is saturated with OH<sup>-</sup>. On the other hand, in dilute sodium hydroxide solution (0.01 *M*) at low [surfactant], hydrophobic **1** may bind to monomeric surfactant or small submicellar aggregates and be in a location which promotes the deprotonation and then *f* decreases as the [surfactant] increases and micelles form.

In any case, the systems DTG or DHG + sodium hydroxide + 5-nitroindole indicate how zwitterionic micelles weakly bind OH<sup>-</sup>.

#### Deprotonation of 5-Nitroindole-2-carboxylate Ion in DTG and DHG.

The extent of deprotonation, *f*, of **2** in DTG + sodium hydroxide at different concentrations, is shown in Figure 3. For systems DTG + sodium hydroxide 0.01-0.7 *M* maximum extents of deprotonation are below the CMC and then *f* decreases to low values with increasing [DTG] in sodium hydroxide 0.01-0.1 *M*, and to less low values in sodium hydroxide 0.3-0.7 *M*. The extent of deprotonation of **2** in DHG + sodium hydroxide at different concentrations, is shown in Figure 4. Again it is possible to note the

similarity of DHG + sodium hydroxide system with that DTG + sodium hydroxide in deprotonation of **2**. It therefore seems that these surfactants have a common behaviour independent of the structural features of their hydrocarbon chain, and that the physical-chemical properties of such colloidal systems have a great dependence on their charge distribution and the experimental conditions.

The maximum extent of deprotonation of **2** in zwitterionic surfactants is lower than that found with cationic single- and twin-tailed surfactants [1-3], and is at low [surfactant] where monomeric surfactant or small submicellar aggregates should be present. Again this fact indicates how zwitterionic surfactants weakly bind OH<sup>-</sup> and how indicator-monomeric surfactant or small submicellar aggregates interaction promotes the deprotonation of **2** better than indicator-zwitterionic micelle interaction. The action of submicellar aggregates of surfactants has been described also in other papers [3,4].

Indicator **2** more than **1** prefers indicator-small submicellar aggregates interactions in deprotonation with sodium hydroxide in the presence of DTG and DHG, to such a point that the formation of zwitterionic micelles seems an unfavourable process. This fact can be related directly to the different physical-chemical nature of two indicators and their conjugate bases and consequently to the different type of indicator-zwitterionic system interaction and therefore to different location of indicators and their conjugate bases at the zwitterionic system.

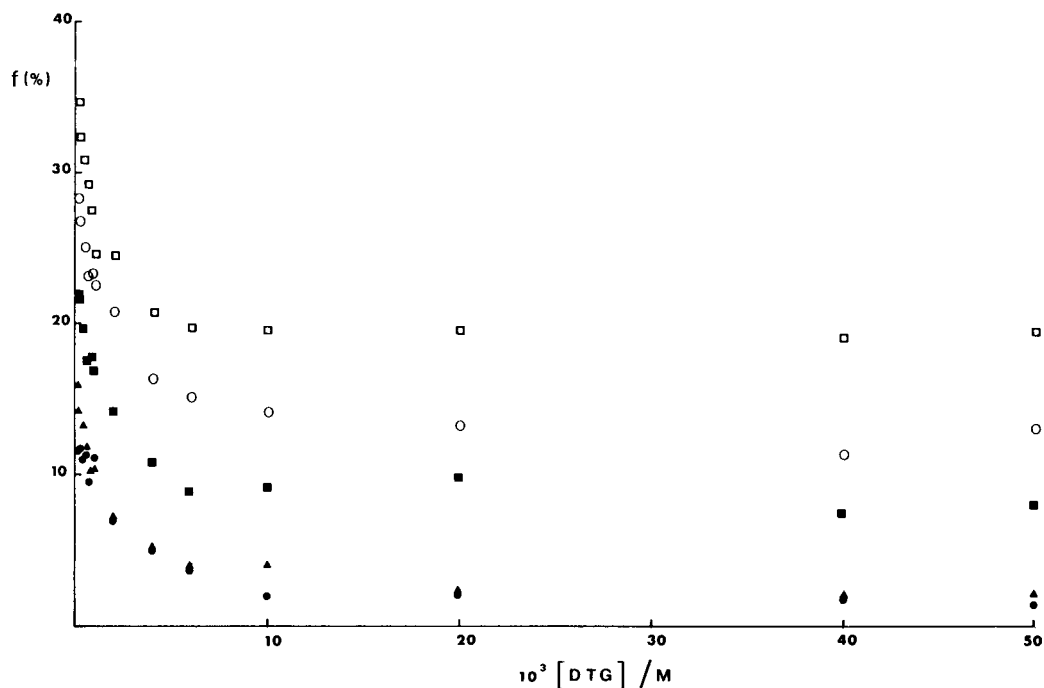


Figure 3. Extent of deprotonation of 5-nitroindole-2-carboxylate ion in DTG + NaOH: (●) NaOH 0.01 *M*, (▲) NaOH 0.1 *M*, (■) NaOH 0.3 *M*, (○) NaOH 0.5 *M*, (□) NaOH 0.7 *M*.

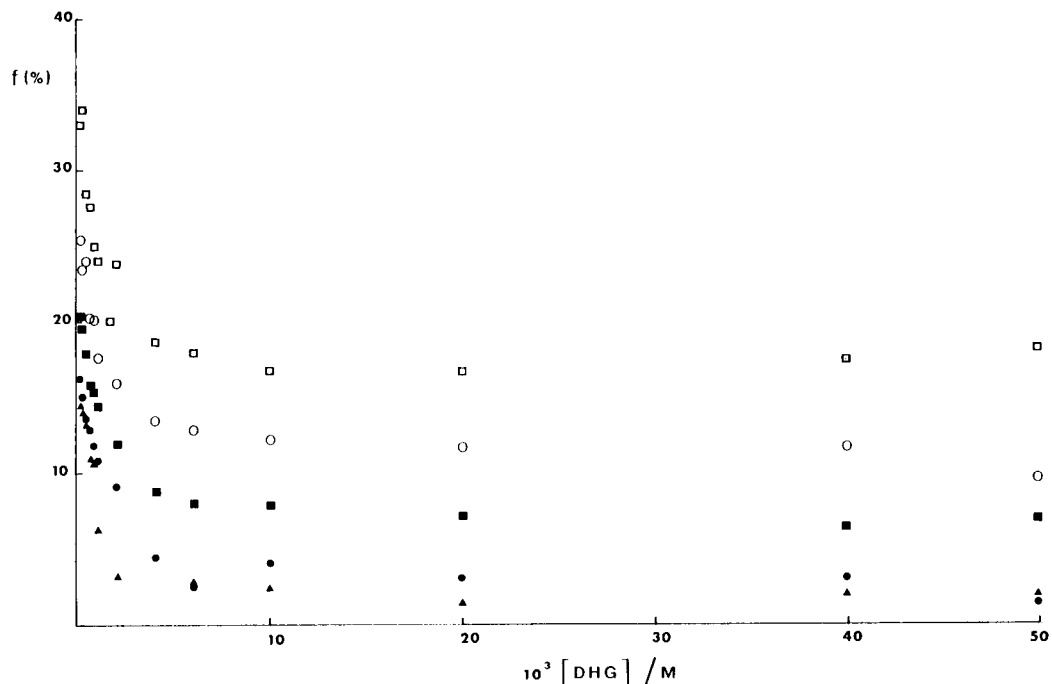


Figure 4. Extent of deprotonation of 5-nitroindole-2-carboxylate ion in DHG + NaOH: (●) NaOH 0.01 M, (▲) NaOH 0.1 M, (■) NaOH 0.3 M, (○) NaOH 0.5 M, (□) NaOH 0.7 M.

Coulombic interactions between cationic centres of zwitterionic surfactant systems and the dianion **2a** should be very strong; also **2** and **1a** should bind to the cationic centres whereas **1** binds to such surfactant systems because of hydrophobic and dispersive interactions. These different interactions and consequently different location of indicators at the zwitterionic aggregate surface produce for **1** an indicator-zwitterionic micelles interaction which promotes deprotonation of **1** (except at low sodium hydroxide concentration) whereas for **2** an indicator-small submicellar zwitterionic aggregates interaction seems to favour its deprotonation. Moreover in the presence of both DTG and DHG maximum extents of deprotonations for **2** are greater than those for **1** in dilute sodium hydroxide solutions (0.01-0.1 M), whereas are similar at high sodium hydroxide concentrations (0.3-0.7 M).

The important factor underlying this difference of behaviour between **1** and **2** in the presence of zwitterionic surfactants is probably the orientation of the indicators within the different type of zwitterionic aggregates.

Micellar effects of DTG and DHG upon the deprotonation of **1** and **2** have a similar origin to those in normal micelles and they can be mostly related to concentration of reagents in the small colloidal particles. Concentration effect in zwitterionic surfactant systems is small and this fact together with weak bond of  $\text{OH}^-$  to zwitterionic aggregates surface explains why the maximum extent of deprotonation of **1** and **2** in zwitterionic surfactants is lower than

that found with single- and twin-tailed surfactants.

## EXPERIMENTAL

### Materials.

Preparation and purification of surfactants and indicators have been described [1-4]. Solutions were made up in distilled water under nitrogen to exclude carbon dioxide.

### Deprotonation.

The fraction  $f$  of deprotonated indicator was estimated spectrophotometrically at 25° using a Beckman Model 35 or a Perkin-Elmer 551S spectrophotometer.

The indicator concentrations were  $9 \cdot 10^{-5}$  M and  $f = \frac{[\mathbf{1a}]}{([\mathbf{1}] + [\mathbf{1a}])}$  or  $\frac{[\mathbf{2a}]}{([\mathbf{2}] + [\mathbf{2a}])}$ . The measurements were made at 398 and 393 nm for **1** and **2**, respectively.

### Acknowledgements.

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