

Scavenging of hydrated electrons by hydrophobic solutes in ionic micellar solutions

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Abstract

Pulse radiolysis has been used to investigate scavenging of hydrated electrons (e_{aq}^-) by hydrophobic acceptors in anionic micellar solutions of dodecylsulfates and cationic micellar solutions of alkyltrimethylammonium halides. It is found that the rate of e_{aq}^- decay depends not only on the charge of micelles but also on the kind of scavenger, micellar size and the nature of counterions. The results are discussed in terms of scavenger effectiveness, its distribution between aqueous and micellar phases and location in the aggregates of different structure.

INTRODUCTION

Micellar solutions are regarded as primitive models of cell membranes (ref. 1). Information obtained for these systems may be relevant for understanding mechanisms of the processes occurring in more complex biological media. Numerous works have been aimed to elucidate how microheterogeneity of the system affects such processes as: charge separation, electron transfer, excited state formation and energy transfer etc, cf. recent reviews (ref. 2). Although photochemical methods are most widely used in these studies, pulse radiolysis appears a useful complementary technique (ref. 3-6). In particular, it enables to follow electron transfer between aqueous and lipoidic phases of the membrane mimetic systems. We have studied by pulse radiolysis reactivity of hydrated electron (e_{aq}^-) towards hydrophobic solutes bound to ionic micelles in aqueous solutions.

EXPERIMENTAL

Sodium and lithium dodecyl sulfates, NaDS and LiDS resp., were used to prepare anionic micelles. The former was studied in neat water solution and in those containing NaCl, tetramethylammonium chloride, TMAC, or tetrabutylammonium bromide, TBAB. Dodecyl- and hexadecylammonium bromides, DTAB and HTAB resp., as well as dodecyltrimethylammonium chloride, DTAC, were used to prepare cationic micelles. The examined scavengers were: CCl_4 ; benzyl chloride, BzCl; benzyl alcohol, BzOH; N,N,N',N'-tetramethylbenzidine, TMB; 3,3'-dimethylbiphenyl, DMBP; and hexadecylpyridinium chloride, HPC. Details on sample preparation and pulse radiolysis equipment can be found elsewhere (ref. 7-11). The pseudo-first order reaction of e_{aq}^- with a scavenger was examined by following the decay of e_{aq}^- absorption. If possible, the growth of scavenging product was also followed.

RESULTS AND DISCUSSION

Cationic micellar solutions

In the presence of cationic micelles reactions of e_{aq}^- with hydrophobic acceptors are catalysed with respect to homogeneous water solution. This is explained in terms of solute incorporation into micelles and electrostatic interactions of e_{aq}^- with the aggregates (ref. 5, 6).

According to the mechanism proposed by Grätzel et al., hydrated electron is accelerated in the positive potential field of a cationic micelle and becomes trapped on its surface with the rate constant approaching the order of $10^{12} \text{ M}^{-1}\text{s}^{-1}$. The process is reversible and at low probe/micelle concentration ratio, $[S]/[M] < 1$, e_{aq}^- migrates between aggregates until it finds the one containing a scavenger molecule. Finally, intermicellar electron transfer occurs leading to the micelle bound product (ref. 12-14).

In the presence of very efficient HPC scavenger the rate of e_{aq}^- decay is governed by intermicellar electron transport. HPC itself is a surfactant molecule. If added at low concentration to micellar solution of alkyltrimethylammonium halide it becomes incorporated into host aggregates and the pyridinium ring, reactive towards e_{aq}^- , remains anchored in the head-group layer. In such a case intramicellar electron transfer to the acceptor occurs on micellar surface and is very fast, so it does not contribute to the observed kinetic pattern (ref. 14).

Migration of e_{aq}^- between cationic aggregates leads to a multiexponential decay which can be described by the pseudo-first order equation of dispersive kinetics with the time-dependent rate coefficient: $k(t) = B t^{\alpha-1}$; where $B = cts$, and $0 < \alpha < 1$ is the parameter characterizing distribution of e_{aq}^- life-times (ref. 15). At low $[S]/[M]$ ratio the data for all the examined scavengers, but TMB, are best fitted with $\alpha = 0.8$ (ref. 8-10).

As shown in Fig. 1 the mean rate constant of e_{aq}^- decay, \bar{k} , changes with scavenger concentration and surfactant concentration (cf. the data for HPC) parallelly to the variations in the fraction of occupied micelles ($[S]/[M]$), i.e. in the probability of finding an aggregate containing a scavenger molecule; in accordance with the migration mechanism.

For each neutral scavenger the apparent second-order rate constant (slope of the respective \bar{k} vs $[S]$ straight line) is significantly lower than that for cationic HPC. The difference cannot be accounted for by incomplete solubilization of DMBP, BzCl and BzOH in micelles, since we would have to admit that the fraction of micellized scavenger is not higher than 30%, 20% and 2% respectively. These percentages are quite unreasonable in view of very low water solubility of DMBP (the order of 10^{-5} M) and the available data on distribution of BzCl (see below) or BzOH in ionic micellar solutions (ref. 16).

Thus, our results directly reveal that reactivity of e_{aq}^- towards acceptors bound to cationic micelles depends on the kind of scavenger. This finding denies the earlier suggestion of Patterson that a strong positive electrostatic effect is the only factor determining the rate of e_{aq}^- decay (ref. 6).

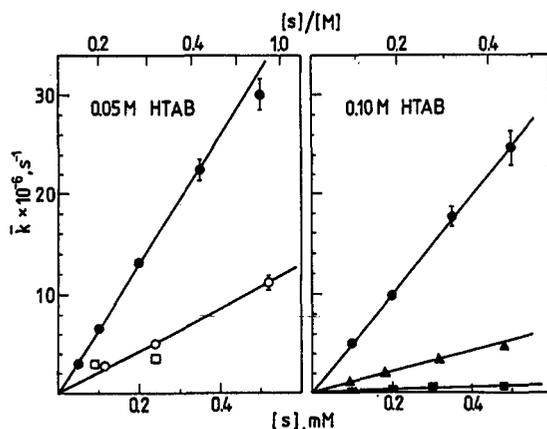


Fig. 1. Mean rate constant of e_{aq}^- decay in HTAB solutions vs concentration of scavengers: ● - HPC, ○ - DMBP, □ - TMB, △ - BzCl, ■ - BzOH.

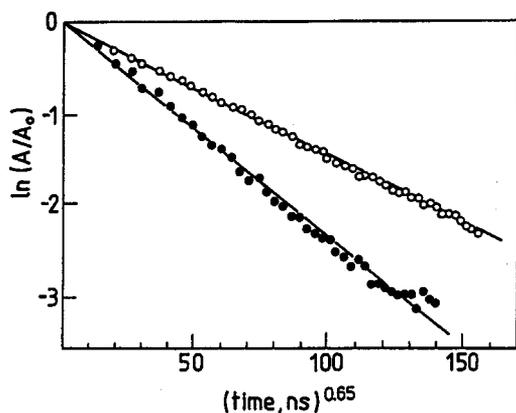


Fig. 2. Time dependence of e_{aq}^- absorbance in fresh (●) and 1 week aged (○) 0.05 M DTAB / 0.09 mM TMB solutions.

We postulate that in the presence of neutral scavengers intramicellar electron transfer is relatively slow, so not every encounter of e_{aq}^- with an occupied micelle leads to scavenging, contrary to the case of cationic HPC scavenger; cf. the data on the yields of reaction products (ref. 9, 10). The effect of the kind of acceptor may be related to its effectiveness and/or location within aggregates. To distinguish between these two possible explanations we have studied the influence of micelle aging on the rate of e_{aq}^- decay.

As observed previously, some processes involving entry or exit of reactive species to or from micellar phase become slow down on storage of the solutions over few days. This was interpreted in terms of a change of alignment of surfactant molecules leading to a smaller separation of heads and higher viscosity in the aggregate interior (ref. 17). Thus, in aged micellar solutions one could expect lower permeability of the interface for e_{aq}^- and slower intermicellar electron transfer if the probe was located below the head-group layer. We do observe such an effect in the presence of TMB, cf. Fig. 2, but with HPC or DMBP as scavengers the same kinetic results are obtained for fresh and aged micellar solutions (ref. 9).

Hence, we conclude that DMBP, similarly to the pyridinium ring of HPC, is located in the surface region, while TMB molecule is buried somewhat deeper in micelles. This would be consistent on the one hand with specific interactions between arenes and quaternary ammonium groups (ref. 18, 19), and on the other hand with more hydrophobic character of TMB in comparison to DMBP (water solubility of the former an order of magnitude lower). For BzCl and BzOH surface locations are still more probable as they are more hydrophilic than DMBP. Apparently, deeper location of the probe in micelles leads to a wider distribution of e_{aq}^- life-times, since in the case of TMB the kinetic α parameter is lower than 0.8; cf. Fig. 2 and (ref. 8).

Our results indicate that e_{aq}^- reactivity depends on the scavenger effectiveness, in spite of a strong positive electrostatic effect of cationic micelles. For the probes located in the surface region the rate of intramicellar electron transfer decreases in the sequence: HPC < DMBP \leq BzCl < BzOH, which parallels variations in the second-order rate constants of the respective e_{aq}^- reactions in homogeneous water solutions (ref. 10).

We have also examined the influence of micelle size and counterion substitution on e_{aq}^- decay. As shown by Table 1, for DMBP the relative apparent rate constant of e_{aq}^- scavenging (with respect to HPC) does not change in going from HTAB to DTAB solution, contrary to the case of BzCl. This can be interpreted in terms of an enhanced BzCl binding to bigger HTAB micelles. Much more hydrophobic DMBP is most probably totally bound, independently of the micelle size as well as of the kind of counterion (although DTAC/DMBP system has not been investigated yet). Furthermore, our data suggests that substitution of Cl^- counterion for Br^- counterion (at the same chain length) brings about a complete solubilization of BzCl in micelles.

Table 1. Apparent second order rate constants of e_{aq}^- scavenging by DMBP and BzCl with respect to the data of HPC.

| system | k^{app}/k_{HPC}^{app} | |
|--------|-------------------------|------|
| | DMBP | BzCl |
| HTAB | 0.33 | 0.20 |
| DTAB | 0.33 | 0.14 |
| DTAC | — | 0.33 |

Anionic micellar solutions

In anionic micellar solution hydrated electron is repelled from the surface of the aggregates and its reaction with a hydrophobic solute is inhibited with respect to a homogeneous system (ref. 5). As shown in Fig. 3, the pseudo-first order rate constant of e_{aq}^- scavenging by BzCl, k' , (determined by the equation of classical kinetics) diminishes with increasing concentration of micelles at $[BzCl] = \text{cts}$, since more and more scavenger molecules become micellized.

Assuming that at the highest surfactant concentration contribution of the reaction in bulk water is negligible, we have estimated from the data of Fig. 3 the equilibrium constants, K_M , for BzCl distribution between the two phases as equal to $2500 \pm 100 \text{ M}^{-1}$ and $5700 \pm 250 \text{ M}^{-1}$ for NaDS and LiDS solutions respectively (ref. 7).

The effect of Li^+/Na^+ counterion exchange in dodecylsulfate micelles is similar to that observed with Cl^-/Br^- counterion exchange in dodecyltrimethylammonium halide micelles. In both cases there is an increased BzCl solubilization in micelles whose counterions are more hydrated.

From the similar kinetic studies for CCl_4 we have concluded that this scavenger is practically totally micellized and remains hardly accessible for hydrated electron in both NaDS and LiDS solutions (ref. 7). Our finding does not coincide with the data of the earlier fluorescence quenching study (ref. 20). However, the different behavior of CCl_4 in comparison to BzCl may be reconciled with smaller size and nonpolar character of the former molecule which most probably locates deeper in micelles.

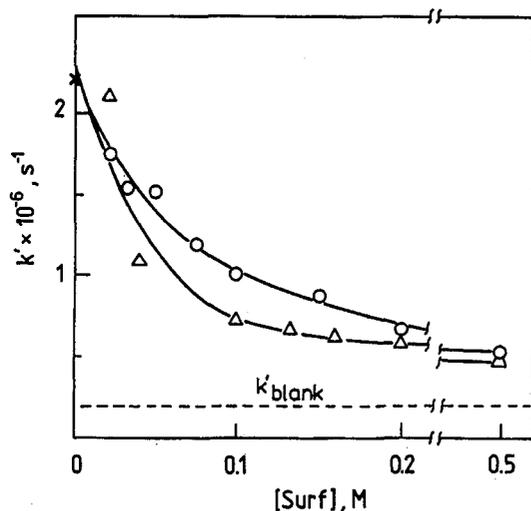


Fig. 3. Rate constant of e_{aq}^- decay in 1 mM BzCl solutions vs surfactant concentration: o - NaDS, Δ - LiDS, + - neat water.

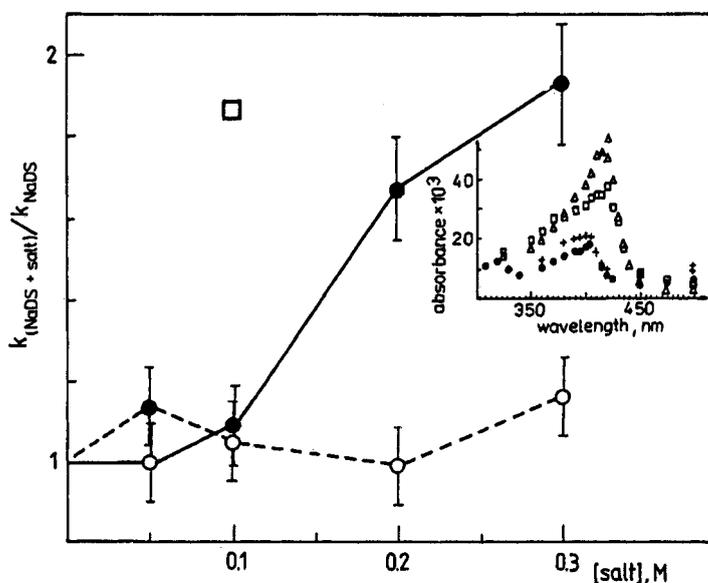


Fig. 4. Relative rate constant of e_{aq}^- decay vs salt concentration in 0.1 M NaDS / 4 mM DMBP solutions and DMBP⁻ spectra : + - no salt, o - NaCl, • - TMAC, □ - TBAB, Δ - DTAB/DMBP system for comparison.

We have also followed the effect of salt addition on e_{aq}^- scavenging by DMBP in NaDS solution (ref. 11). One can see from Fig. 4. that addition of hydrophobic cations, contrary to hydrophilic Na⁺, results in an enhanced rate of e_{aq}^- decay, the effect being stronger for TBAB than for TMAC and increasing with salt concentration. This is accompanied by spectral shift of the scavenging product from 400 nm in neat NaDS to 415 nm in NaDS/TBAB system. Note, that the latter maximum position is identical with that observed in cationic micellar solutions (ref. 9).

Suggested structure of the aggregates

Our results can be rationalized assuming the structure of the examined micelles schematically presented in Fig. 5. Neat NaDS micelles as well as cationic micelles of alkyltrimethylammonium bromides have a relatively compact head-group layer and rather stretched alkyl tails. However, aromatic probes may be located deeper in the former aggregates, since their interactions with H₂O molecules are usually not that strong as in DTAB or DTAC systems (ref. 19, 21). Such different probe locations would be consistent with complex formation between arenes and quaternary ammonium groups (ref. 18, 19), and may be responsible for the spectral shift of DMBP⁻ in going from DTAB to NaDS micelles.

It has been proved that LiDS micelles have a less compact and more hydrated head-group region as well as more disorderd alkyl-chain packing in comparison to NaDS micelles (ref. 22). These structural modifications may bring about higher rate of entry of BzCl molecule into LiDS micelle and consequently, higher K_M value. At the same time LiDS micelle would be more permeable for e_{aq}^- . However, there is no appreciable difference in our kinetic data for LiDS and NaDS at high surfactant concentrations corresponding to practically complete micellization of the scavenger; cf. Fig. 3. Possibly, relatively small molecule of BzCl penetrates LiDS micelles still deeper than NaDS micelles and, although the surface is more permeable, e_{aq}^- has a longer distance to the scavenger locus.

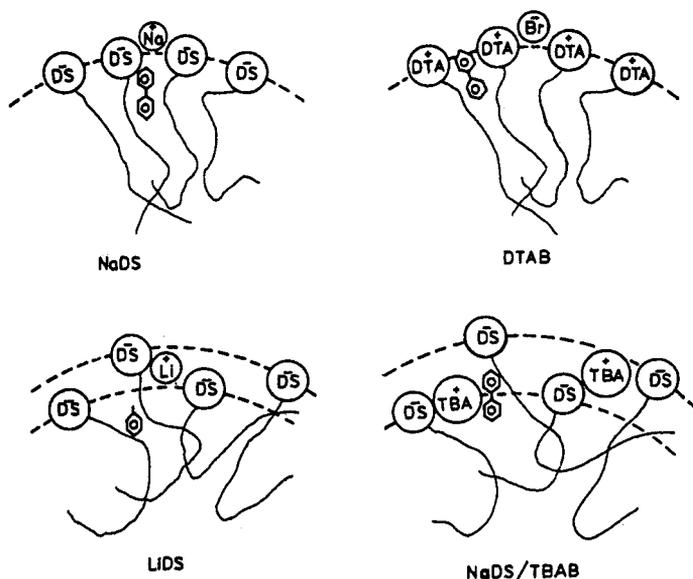


Fig. 5. Schematic representation of micellar structures and probe locations (sections of micelles shown only).

Similar structural modifications are reported for NaDS micelles in the presence of tetraalkylammonium counterions (ref. 23). As shown, in Fig. 5 the effects may be even more pronounced as these cations are hydrophobic and more bulky than Li^+ . However, in the presence of TMAC or TBAB the probe will tend to stay in a close proximity of tetraalkylammonium groups. As the region of such a rough surface is highly hydrated (ref. 23), the local environment of DMBP^- may be fairly polar. Consequently, the absorption maximum of DMBP^- shifts to higher wavelengths in comparison to neat NaDS (cf. Fig. 4). With the more opened structure of a modified dodecylsulfate micelle electron attack on DMBP^- molecule is easier. At the same time, due to complexation by tetraalkylammonium cations, DMBP^- is more stable in TBAB solution than in neat NaDS solution, although in both cases it decays faster than in the examined cationic micellar systems (ref. 11).

Concluding remark

Our results indicate that pulse radiolytic studies not only deliver kinetic parameters of fast reactions in micellar systems, but also enable to infer about solute distribution and location as well as about micellar structure.

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