The Influence of Some Surfactants and Inorganic Salts on the Stability of Diethazine Cation Radical

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Received 28 May 1992

The effect of selected surfactants and inorganic salts on the time stability of perchlorate of diethazine cation radical was studied in an aqueous acid solution (3 M-H_3PO_4). The stability of cation radical was increased only by ClO_4^- in the presence of low concentration of anionic surfactant and nonionic surfactant over the whole studied surfactant concentration region, but the values of time stability are always lower than those observed in the presence of only ClO_4^- without surfactant. In all inorganic salt—surfactant mixtures the stability of diethazine radical cation corresponds, to the first approximation, to superposition of the effects of individual components, where the effect of one of them can predominate at high concentration.

Surfactants are known to alter substantially the physical and chemical properties of a large number of organic compounds. They are widely utilized also in analytical chemistry [1—3] as reaction media increasing the solubility of hydrophobic components in aqueous solutions, affecting the reaction rates, stability of products and changing the spectral, acid-base or electrochemical properties of the analytes [4—8].

Phenothiazine derivatives (PD) are primarily used as drugs in human and veterinary medicine and have also found application in analytical chemistry [9]. In this case their coloured cation radicals ($PD^{+\bullet}$) play a decisive role. However, the stability of these radicals is relatively poor. They are easily converted in aqueous solutions into mixtures of the colourless initial phenothiazine derivative and its sulfoxide (PDO) according to the equation

$$2\ PD^{+\bullet} + H_2O \rightleftarrows PD + PDO + 2\ H^+ \quad (A)$$

The rate of the degradation depends on the type and position of the substituent on the phenothiazine skeleton, on the H_3O^+ ions activity and on the concentration of salts (nucleophilic anions are known to react with $PD^{+\bullet}$) [10].

In our previous papers we dealt with the individual influence of surfactants [11] and salts [12] on the time stability of phenothiazine cation radical and discussed in detail the mechanism of its degradation. This work was devoted to a study of the simultaneous action of surfactants and salts, as the presence of a salt can sometimes completely change the action of surfactants [13, 14]. The effect of salts has already been partly described in a study of electrochemical oxidation of *N*-methyl phenothiazine in micellar media [15—18].

The aim of this paper is to widen our knowledge about the stability of cation radicals in mixed salt—surfactant aqueous solutions, as such model system simulates the conditions for a practical use of these systems. Diethazine was selected as a representative of phenothiazine derivatives.

EXPERIMENTAL

The perchlorate of diethazine (10-(diethylaminoethyl)phenothiazine) cation radical was prepared according to [19] from the standard substance of diethazinium chloride (Research Institute for Pharmacy and Biochemistry, Prague) and stored in the dark in a vacuum desiccator. A stable stock solution of the cation radical ($c = 2 \times 10^{-3}$ mol dm^{-3}) was prepared by dissolving the substance in 85 % phosphoric acid, anal. grade (Lachema, Brno).

Sodium dodecylsulfate (Lachema, Brno) (M_r = 272.38) was purified by washing with diethyl ether followed by multiple crystallization from 96 % ethanol. The purity of the product obtained was checked by indirect alkalimetric titration after hydrolysis with sulfuric acid. A standard solution (c = 0.5 mol dm^{-3}) was prepared by dissolving the substance in distilled water.

Septonex ([1-(ethoxycarbonyl)pentadecyl]trimethylammonium bromide, SPOFA, Prague) (M_r = 422.49) was dried to a constant mass in a vacuum desiccator and used for the preparation of aqueous stock solution ($c = 5 \times 10^{-2}$ mol dm^{-3}) without any further purification. The purity of the substance was tested by a two-phase titration with pure sodium dodecylsulfate.

Triton X-305 (octylphenylpoly(oxyethylene), n = 30, M_r = 1510.0; Erba, Milan) was used for the prepara-

tion of a stock solution ($c = 5 \times 10^{-2}$ mol dm^{-3}) without purification.

Stock solutions of NaCl, Na_2SO_4, $NaNO_3$, and $NaClO_4$ (c = 1 mol dm^{-3}) were prepared by dissolving of anal. grade substances (Lachema, Brno) in distilled water.

Spectrophotometer SP-800 (Pye—Unicam, Cambridge) with 1 cm quartz cells thermostated at (25 ± 0.5) °C was used. The course of the time dependence of absorbance was recorded with a TZ-4620 chart recorder (Laboratorní přístroje, Prague).

Procedure

To the corresponding mixture of salt, surfactant, and H_3PO_4 in a 25 cm^3 standard flask, 2.5 cm^3 of a fresh cation radical stock solution were added with a syringe. Then the flask was filled up with distilled water to the mark ($c(DE^{+\bullet})_0 = 2 \times 10^{-4}$ mol dm^{-3}; $c(H_3PO_4)$ = 3 mol dm^{-3}) and the absorbance was measured at λ = 512 nm (absorption maximum of diethazine cation radical) against water, within one to thirty minutes after mixing the components. This procedure does not allow determination of the cation radical initial absorbance. This value was obtained by measuring the absorbance of a stable 2×10^{-4} M solution of the cation radical in 85 % phosphoric acid.

Half time τ of decomposition (the time in minutes at which the absorbance of the cation radical decreased to one half of the initial value) was determined as it is obtainable simply from the recorded kinetic curves and adequately characterizes the stability of diethazine cation radical in this complex system. The reproducible values of τ were obtained maintaining the above-mentioned procedure.

RESULTS AND DISCUSSION

The influence of the selected salts on the stability of diethazine cation radical ($DE^{+\bullet}$) in H_3PO_4, which is the medium most commonly recommended for spectrophotometric determinations using phenothiazine derivatives, is demonstrated in Fig. 1. NaCl, Na_2SO_4, and $NaNO_3$ decrease the $DE^{+\bullet}$ stability (decreasing τ). Stabilization was observed only with $NaClO_4$, the anion of which is identical with that of the diethazine cation radical. The rate constants values are given in [12].

The influence of some surfactants on the stability of a $DE^{+\bullet}$ solution is shown in Fig. 2. The shape of the τ—c dependences can be explained in terms of theoretical models of the reaction kinetics in micellar solutions [8]. Below the critical micelle concentration CMC (7.4×10^{-4} mol dm^{-3}) of cationic surfactant Septonex, this does not influence significantly the

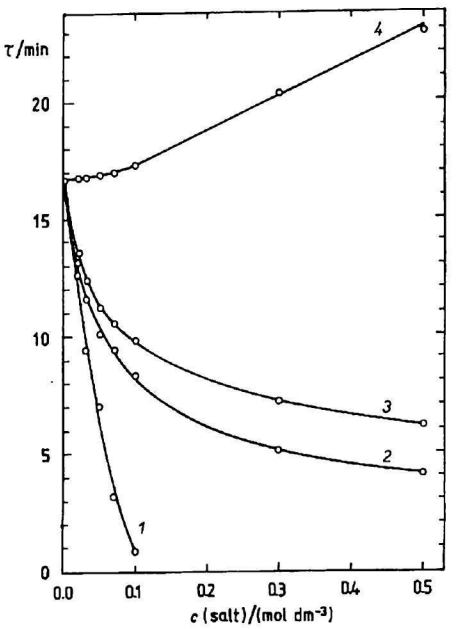

Fig. 1. The dependence of half time of $DE^{+\bullet}$ decomposition on the concentration of salts. *1.* $NaNO_3$, *2.* Na_2SO_4, *3.* NaCl, *4.* $NaClO_4$.

$DE^{+\bullet}$ stability (curve *1*), because there are no interactions between $DE^{+\bullet}$ and dissociated surfactant monomer molecules and the concentration of the Br^- counterions of Septonex is too low to affect the degradation rate. Above the CMC value, the $DE^{+\bullet}$ degradation is catalyzed by Septonex micelles, which are able to bind $DE^{+\bullet}$ particles through hydrophobic interactions, but cannot bind H^+ ions due to electrostatic repulsions. The $DE^{+\bullet}$ degradation, occurring in the micellar pseudophase relatively poor in H^+ ions, is therefore much faster. The effect of the nonionic surfactant Triton X-305 is similar but less significant (curve *3*).

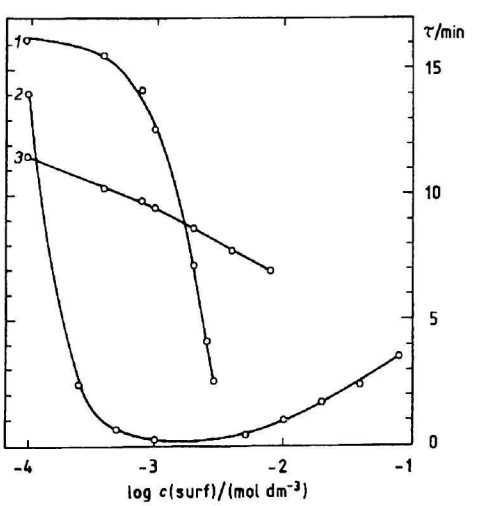

Fig. 2. The dependence of half time of $DE^{+\bullet}$ decomposition on the logarithm of the surfactant concentration. *1.* Septonex; *2.* sodium dodecylsulfate; *3.* Triton X-305.

The influence of the anionic surfactant sodium dodecylsulfate (NaDS) is more complicated (curve 2). It can be assumed that the neutral ionic associates of $DE^{+\bullet}$ with DS^- (or premicelle aggregates) which do not bind H^+ ions are formed below CMC (3×10^{-3} mol dm^{-3} in this system [11]). The τ value quickly decreases with increasing surfactant concentration. For concentrations of NaDS higher than CMC $DE^{+\bullet}$ particles are bound to the negatively charged surface of the micelles, together with H^+ ions. The $DE^{+\bullet}$ decomposition reaction is inhibited at higher surface local H^+ activity and the τ values increase.

The simultaneous influence of a surfactant and a salt on the time stability of $DE^{+\bullet}$ was experimentally studied. The effect of the concentration of the cationic surfactant Septonex and NaCl is shown in Fig. 3. It follows from the τ values that the destabilizing effect of the salt is most significant for low concentrations of the surfactant. For concentrations of Septonex higher than 2×10^{-3} mol dm^{-3}, the τ values become almost constant, independent of the salt concentration, but they are very low. In this concentration range of the surfactant, all $DE^{+\bullet}$ particles are bound in micelles surrounded by Br^- counterions, which react with $DE^{+\bullet}$; the anion of salt added does not affect the degradation. Almost the same conclusions hold for the Septonex—Na_2SO_4 system, the reaction is, however, faster, similar to that in the system without surfactant.

In the presence of nonionic surfactant, the increasing NaCl concentration decreases the τ values in a similar way as in the presence of Septonex. However, the curves of the dependence of τ on the salt concentration retain their original character (*i.e.* the gradual nonlinear decrease of τ values with increasing salt concentration) even at high surfactant concentrations, as the surfactant does not contain any counterions and the rate of the reaction is determined by the concentration of salt alone.

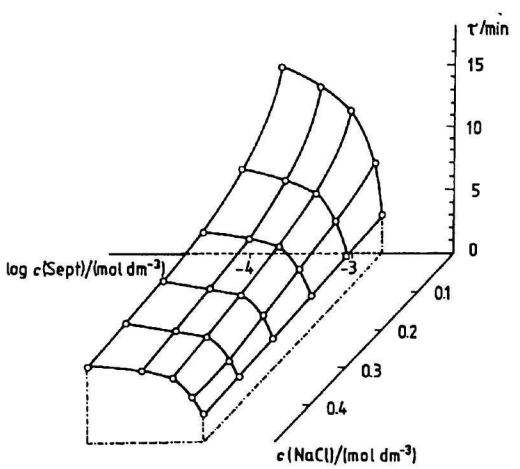

Fig. 3. The dependence of half time of $DE^{+\bullet}$ decomposition on the logarithm of the Septonex concentration and the NaCl concentration.

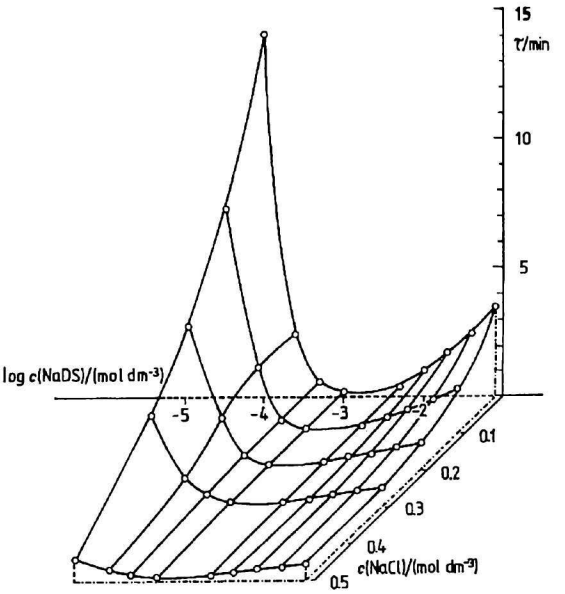

Fig. 4. The dependence of half time of $DE^{+\bullet}$ decomposition on the logarithm of sodium dodecylsulfate concentration and the NaCl concentration.

The simultaneous influence of the anionic NaDS surfactant and NaCl is depicted in Fig. 4. It is evident from the τ values that the rate of $DE^{+\bullet}$ decomposition at lower NaCl concentrations is predominantly influenced by the presence of NaDS. The salt equimolar curves maintain their characteristic shape with a significant minimum at CMC up to NaCl concentration of 0.2 mol dm^{-3}. With increasing salt concentration, the curves become flatter, the catalytic and inhibition effect of NaDS is less pronounced. For the highest NaCl concentration studied (0.5 mol dm^{-3}), the rate of the $DE^{+\bullet}$ decomposition is almost independent on the NaDS concentration. This observation could be explained by competitive blocking of the surface of micelles by Na^+ ions, resulting in restricted accessibility of $DE^{+\bullet}$ particles bound in micelles for H^+ ions.

As mentioned above, the behaviour of ClO_4^- ions is completely different. Unfortunately, it is not possible to measure the kinetics of the $DE^{+\bullet}$ decomposition in mixed $NaClO_4$—Septonex solutions because of the formation of a white precipitate. In the presence of Triton X-305, an addition of $NaClO_4$ substantially increases the half time τ of the decomposition reaction. As the inhibiting effect is almost constant through the whole range of concentrations used, this dependence is illustrative enough in the two-dimensional presentation (Fig. 5). From the comparison of Fig. 2 and 5 it is obvious that the presence of $NaClO_4$ does not completely suppress

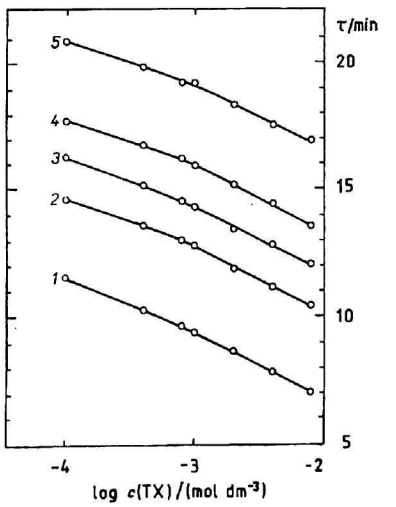

Fig. 5. The dependence of half time of $DE^{+\bullet}$ decomposition on the logarithm of the Triton X-305 concentration at the following $NaClO_4$ concentrations (in mol dm^{-3}): *1.* 0.0; *2.* 0.1; *3.* 0.2; *4.* 0.3; *5.* 0.5.

the catalytic effect of nonionic surfactant on the $DE^{+\bullet}$ degradation. The τ values in mixed salt—surfactant solutions are always lower than those observed in the absence of surfactant for a given $NaClO_4$ concentration.

In anionic surfactant at very low NaDS concentrations (1×10^{-4}—3×10^{-4} mol dm^{-3}), an increase in the concentration of ClO_4^- ions stabilizes somewhat $DE^{+\bullet}$; at c(NaDS) values close to the CMC, the concentration of $NaClO_4$ practically does not affect the τ value. At high surfactant concentration, τ decreases with increasing $NaClO_4$ concentration.

The findings on the effect of surfactants and salts on the stability of cation radicals of phenothiazine derivatives can be utilized in analytical chemistry when searching for optimal conditions of determinations based on the redox properties of phenothiazine derivatives (*i.e.* in spectrophotometric determination of Pt(IV) ions [20]).

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Translated by I. Jelínek