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The Effect of Surfactants on the Kinetics of Diazocoupling Between *p*-Methoxybenzenediazonium Ions and α-Naphthylamine†

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SUMMARY

The effect of anionic, cationic and non-ionic surfactants on the reaction rate between p-*methoxybenzenediazonium ions and α-naphthylamine is examined.*

Strong catalytic activity is shown by the micelles of sodium lauryl sulphate, while limited variations of the rate of reaction could be detected in the presence of micelles of Triton X-100 and cetyltrimethylammonium bromide.

INTRODUCTION

Few references have appeared in the literature[1] on the effects of micelles on electrophilic aromatic substitution reactions and no general rules have been suggested.

In some cases (e.g. coupling of *p*-nitrobenzenediazonium ions with naphthols[2]) micelles of both ionic and non-ionic surfactants decrease the observed rate constants while in other cases (e.g. coupling of substituted benzenediazonium ions with naphthylamines[3]) micelles of sodium lauryl sulphate (NaLS) increase the reaction rate dramatically and, vice versa, micelles of cetyltrimethylammonium bromide (CTAB) decrease it. The

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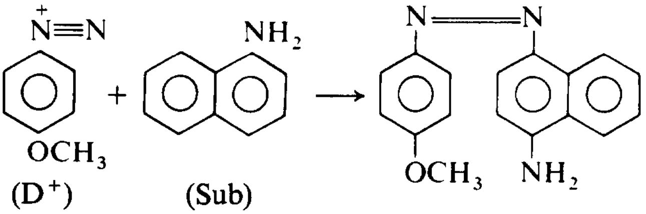
results of Rufer[3] seem to fit the model based on localized overconcentration or overdilution of reactants due to electrostatic interactions between the substrate–micelle complexes and the positive diazonium ions. This model accounts for the results obtained with different substrates (different substituents in the aromatic ring) with different surfactants. However, no complete investigation of the effect of different surfactants has been carried out for the same single reaction.

Accordingly, the purpose of this paper is to examine in some detail the effect of NaLS, CTAB and a non-ionic surfactant (Triton X-100) on the reaction between *p*-methoxybenzenediazonium ion (D^+) and α-naphthylamine (Sub.) (Scheme 1).



Scheme 1

The intrinsic properties of the system investigated impose unusual experimental conditions in the study of micellar effects on reaction rates. For example, in order to avoid double coupling it is necessary to have a stoichiometric excess of the hydrophobic substrate and this makes it difficult to realize the usual condition of large excess of micelles with respect to the substrate without significantly changing the ionic strength.

Moreover, the high concentration of salts necessary to buffer the medium does not allow an exact evaluation of the critical micellar concentration (cmc) of ionic surfactants with the usual conductometric techniques. Consequently, it is beyond the limits of this paper to present any quantitative model and the experimental results are discussed only on a qualitative basis. The discussion will refer also to the general second-order kinetic equation for micelle-catalyzed reaction rate:

$$\begin{aligned} R &= K_{\text{obs}}[\text{Sub}][\text{D}^+] \\ &= K_{\text{w}}(1-F)[\text{Sub}][\text{D}^+] + K_{\text{m}}F[\text{Sub}][\text{D}^+] \end{aligned}$$

where K_{obs} is the observed kinetic constant, K_{w} and K_{m} are the kinetic constants in water and in the micellar phase respectively and F is the fraction of Sub dissolved into the micellar phase.

EXPERIMENTAL

Materials

NaLS (Fluka 99 %), CTAB (Fluka 98 %), Triton X-100 (Fluka) and α-naphthylamine (Fluka 99 %) were used as received without any purification; *p*-methoxybenzenediazonium tetrafluoroborate was prepared from *p*-anisidine and purified by general, published procedures.[4]

Buffer solutions were prepared from reagent-grade $NaH_2PO_4H_2O$ and $Na_2HPO_42H_2O$.

Kinetic measurements

The reactions were followed spectrophotometrically at 22 °C with an SP-1800 Pye–Unicam spectrophotometer.

All kinetic runs were carried out at pH 7 in buffered solution with a concentration of D^+ varying from $0{\cdot}5 \times 10^{-5}$ to 1×10^{-5} M and a stoichiometric excess of Sub varying from 2 to 100. In such conditions the resulting dye did not precipitate in the time-scale of the experiments and its absorbance was linearly dependent on the concentration (molar extinction coefficient equal to 12·000 M^{-1} cm at 470 nm according to ref. 3); D^+ did not decompose appreciably in the same time-scale.

In a typical experiment, 10 ml of 2×10^{-3} M Sub solution in phosphate buffer containing the appropriate concentration of surfactant were rapidly mixed with 10 ml of 2×10^{-5} M D^+ solution in the same buffer at pH 7; after 2–3 min a clear portion of the mixed solution was placed in a cuvette and this was inserted in the cell compartment of the spectrophotometer. The absorbance at 470 nm was recorded as a function of time. Rate constants for reactions with half-life of the order of 15 min were reproducible to at least ±5 % while much more uncertain were the rate constants obtained in the presence of micelles of NaLS, where the half-life of the reactions was of the same order of magnitude as the time of foam decay after mixing.

Conductometric measurements

Conductometric measurements were carried out in order to obtain evidence of ionic coupling between D^+ and LS^-; the pH of all solutions, except HBF_4, was adjusted to 7 and increasing amounts of DBF_4 or HBF_4 were added once to pure water and once to NaLS solution.

The conductivity was measured with a General Radio 1608 A Impedance Bridge equipped with a General Radio 1232A Null Detector.

RESULTS AND DISCUSSION

Experimental conditions and results are shown in Table 1, where the last column represents the ratios between the observed second-order kinetic constants in surfactant solution (K_{obs}) and in the buffered, surfactant-free solution (K_w). The kinetic constant in the latter case was $0{\cdot}40\,\text{M}^{-1}\,\text{s}^{-1}$. The most striking feature of the data in Table 1 is the contradictory role played by NaLS: at a concentration definitely lower than cmc it inhibits the reaction almost completely while at a concentration close to or higher

TABLE 1
Experimental Conditions and Kinetic Results

Run	*Surfactant* (M)	*DBF_4* (M)	*Sub* (M)	*Buffer*[a]	K_{obs}/K_w
1	None	1×10^{-5}	1×10^{-3}	1	—
2	NaLS 5×10^{-4}	1×10^{-5}	1×10^{-3}	1	$\simeq 0$
3	NaLS 2×10^{-3}	$0{\cdot}5 \times 10^{-5}$	1×10^{-5}	1	$\simeq 500$
4	NaLS 1×10^{-2}	$0{\cdot}5 \times 10^{-5}$	1×10^{-5}	1	$\simeq 1400$
5	Triton X-100 1×10^{-4}	1×10^{-5}	1×10^{-3}	1	0·9
6	Triton X-100 5×10^{-3}	1×10^{-5}	1×10^{-3}	1	2·7
7	CTAB 1×10^{-4}	1×10^{-5}	1×10^{-3}	1	1·1
8	CTAB 5×10^{-3}	1×10^{-5}	1×10^{-3}	1	1·5
9	CTAB 5×10^{-3}	1×10^{-5}	1×10^{-3}	2	1·6
10	CTAB 1×10^{-2}	1×10^{-5}	1×10^{-4}	1	0·9

[a] Buffer 1, $1{\cdot}55 \times 10^{-2}\,\text{M}\ Na_2HPO_42H_2O + 1{\cdot}12 \times 10^{-2}\,\text{M}\ NaH_2PO_4H_2O$; Buffer 2, $1{\cdot}3 \times 10^{-3}\,\text{M}\ Na_2HPO_42H_2O + 0{\cdot}9 \times 10^{-3}\,\text{M}\ NaH_2PO_4H_2O$.

than cmc it increases the kinetic constant as much as three orders of magnitude. Some comments on the value of the cmc of NaLS are required before any discussion of the experimental results.

The cmc of NaLS in the presence of 5×10^{-2} M Na^+ solutions (very close to our experimental conditions) is reported to be $2{\cdot}3 \times 10^{-3}$ M at 25 °C.[5] However, some facts may contribute to reduce this value.

The temperature of our experiments was slightly different (22 °C) and, in addition, it is known that polar organic compounds reduce the cmc of ionic surfactants;[6] α-naphthylamine and, possibly, small amounts of impurities could have acted in that sense. Moreover, cmc cannot be defined as a precise point but rather as a narrow concentration range and consequently it is quite possible that aggregates of surfactant are already present in a 2×10^{-3}M NaLS solution.

In run number 2, no micelles of anionic surfactant were present, and, in principle, no variation of kinetic constant with respect to a surfactant-free medium should be expected. However, D^+ and LS^- are oppositely charged and partially hydrophobic ions, and ionic coupling is likely to occur. Indeed, experimental evidence of ion coupling has been obtained with the aid of conductivity measurements of solutions of DBF_4 in the presence and in the absence of NaLS at pH 7.

Figure 1 represents the conductivity of solutions at different concentrations of DBF_4 in pure water (a, slope $= 9{\cdot}6 \times 10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}\ \mathrm{M}^{-1}$) and in a 5×10^{-4}M NaLS solution (b, slope $= 5{\cdot}9 \times 10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}\ \mathrm{M}^{-1}$): the difference is quite relevant, reflecting a different state of D^+ in the two solutions. For comparison the same experiment has been repeated with the same anion and with a cation not likely to give any ion coupling, at least at low concentration. Figure 2 represents the electrical conductivity as a function of the concentration of HBF_4 in pure water (a, slope $= 3{\cdot}37 \times 10^{-1}\ \Omega^{-1}\ \mathrm{cm}^{-1}\ \mathrm{M}^{-1}$) and in a 5×10^{-4}M NaLS solution (b, slope $= 3{\cdot}36 \times 10^{-1}\ \Omega^{-1}\ \mathrm{cm}^{-1}\ \mathrm{M}^{-1}$): in this case no practical difference is recognizable.

Consequently, the decrease of the electrophilic character of D^+ through ion coupling with LS^- is likely to be responsible for the inhibitive properties of NaLS monomer. As soon as micelles of NaLS start to be present the kinetic pattern changes and the reaction rates increase dramatically.

The differences between K_w and K_{obs} in the presence of micelles (runs 3 and 4) are such that the reaction has necessarily to occur almost completely in the micellar phase and the kinetic constant in run 4, where

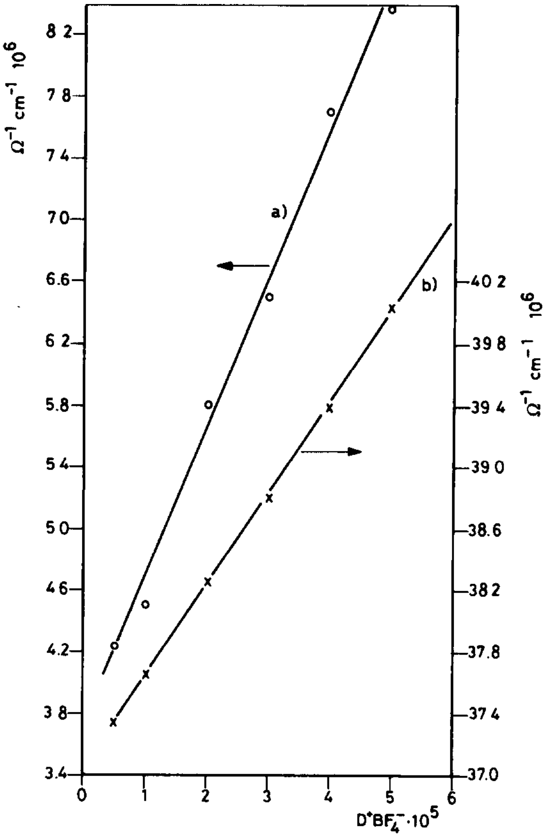


Fig. 1. Electrolytic conductivities of DBF_4 solutions in pure water (a) and in 5×10^{-4} M NaLS (b).

the concentration of micelles is likely to be higher than the concentration of Sub and F close to 1, should represent a good approximation for K_m.

Much less dramatic is the effect of the other two surfactants taken into account. At a concentration lower than cmc (runs 5 and 7), both the surfactants give a kinetic constant within $\pm 10\%$ of K_w. Micelles of Triton X-100 (run 6) result in a definitive increase of the kinetic constant ($K_{obs}/K_w = 27$), a fact that could possibly be explained by a partial hydrophobic character of D^+. In such a case, as a consequence of purely hydrophobic interactions, the core of the micelles would represent a preferential site of dissolution of both reactants, whose over-concentration results in an increase of reaction rate.

Reaction rates in the presence of micelles of CTAB (according to ref. 3,

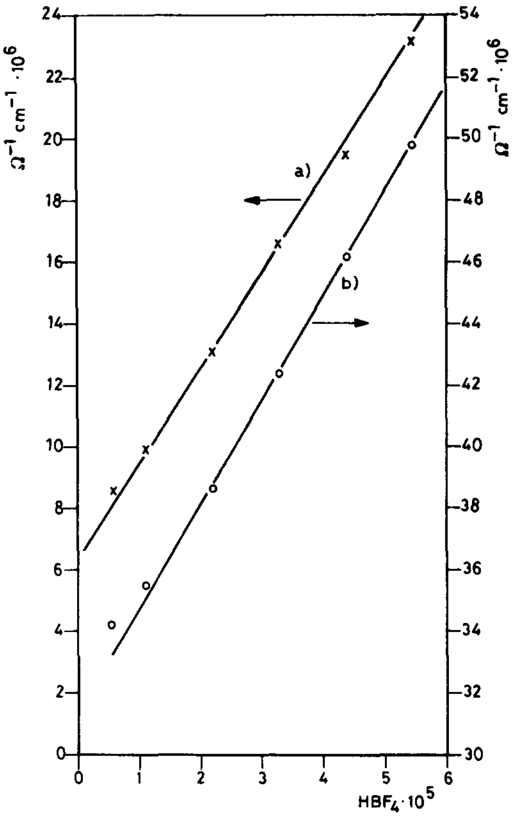


Fig. 2. Electrolytic conductivities of HBF_4 solutions in pure water (a) and 5×10^{-4} M NaLS (b).

cmc should be equal to $9{\cdot}8 \times 10^{-4}$ M) are rather unexpected as they seem not to obey any electrostatic or hydrophobic consideration.

In run 10 the concentration of micelles is higher than the concentration of Sub and, in view of the well-known solubilizing power of CTAB,[5] F in the kinetic expression is likely to be equal to 1.

In such conditions, the reaction appears slightly inhibited ($K_{obs}/K_w = 0{\cdot}9$), a fact that implies either an almost negligible effect of electrostatic repulsion between cationic micelles and D^+ or an influence of hydrophobic interactions on the site of dissolution of D^+, balancing the unfavourable electrostatic conditions.

In runs 8 and 9 the reaction rates appear even greater than in water at the same pH ($K_{obs}/K_w = 1{\cdot}5$ and $1{\cdot}6$ respectively). In these tests, the concentration of micelles is definitely lower than the concentration of Sub and the reaction could in principle occur either in water or in the micellar phase, with a fast transfer of reactant between one phase and the other. However the overall reaction rates are higher than the rates determined in pure water or in micelles (whatever is the kinetic constant in the last case, it has to be lower than in water on the basis of run 10) implying that neither electrostatic nor hydrophobic consideration can fully explain the experimental results.

The fact that electrostatic factors do not really play a significant role in the reaction in the presence of CTAB micelles is additionally confirmed by the actual influence of ionic strength on the kinetic constant. In the run 9 the ionic strength is definitely lower than in run 8 and, as a consequence of electrical double-layer expansion, the concentration profile of D^+ around the CTAB micelles should be more unfavourable for the reaction rate. In spite of this, the kinetic constant is actually the same, with the consequence that some other and yet unknown effect must play a beneficial role in the kinetics of the reaction in the presence of CTAB micelles.

REFERENCES

1. J. H. Fendler and E. J. Fendler, *Catalysis in micellar and macromolecular solutions*, Academic Press, New York, 1975.
2. M. Poindexter and B. McKay, *J. Org. Chem.*, **37**, 1674 (1972).
3. D. A. Rufer, Dissertation No. 6790, ETH, Zurich (1981).
4. G. Schliemann and W. Winkelmüller, *Org. Synth. Coll.*, Vol. II, 188 (1943).
5. M. F. Emerson and A. Holtzer. *J. Phys. Chem.*, **71**, 1899 (1967).
6. M. J. Rosen, *Surfactants and interfacial phenomena*, J. Wiley & Sons, New York, 1978.
7. J. W. Larsew and L. J. Magid, *J. Phys. Chem.*, **78**, 834 (1974).