Tetrahedron Letters, Vol.32, No.16, pp 1881-1884, 1991
Printed in Great Britain

0040-4039/91 $3.00 + .00
Pergamon Press plc

Efficient Catalytic Activity of Polymerized Micelle–Forming Surfactants

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Key Words : Polymerized – Micelles – Surfactants – Micellar–Catalysis

Abstract : Micellar catalysis in the hydrolysis of para–substituted benzaldehyde diethylacetals by sodium 10–undecenyl sulfate is enhanced by polymerization of the surfactant aggregates.

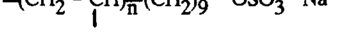
Micellar catalysis generally derives from association of substrate and micelle through electrostatic and hydrophobic interactions with formation of a complex having enhanced reactivity compared to the substrate free in solution[1,2]. It is well known that micelles have a very short lifetime due to the very fast exchange of detergent molecules between aggregates and bulk water[3]. It would be suspected that such a dynamic equilibrium is not favorable to the catalytic process. One efficient way to prevent it should be to polymerize micelles built with polymerizable surfactants molecules. In recent years polymerized micelles have attracted the attention of several groups of workers[4] but the main objectives of their studies were to compare physico–chemical properties of polymerized and unpolymerized micelles (i.e. aggregational behaviour , additive solubilization, intrinsic viscosity, ...) by various methods (fluorescence probing, dye solubility, conductivity measurements, ...). In ionic surfactants, the polymerizable groups (vinyl, allyl, acrylate, methacrylate, ...) can be part either of the lipophilic chain or of the ionic head, leading to two types of polymeric products labeled T (for tail) and H (for head) polymers respectively[5].

From the results reported so far, some studies have been concerned with the catalytic effectiveness of H–polymeric micelles[6] but the catalytic properties of T–polymeric micelles has remained largely unexplored.

In type T–polymers, contraints imposed by the polymeric bonds should be minimal since the hydrophobic backbone can be very well accomodated in the micellar core and the charged ionic heads will be located on the interface in contact with water[5]; the T–polymerized micelles will adopt a structure similar to that its monomeric counterpart. In contrast the behaviour to H–type polymerized micelles, which have a hydrophilic backbone, should be quite different from that of the monomeric micelles[5].

On these basis T–type polymerized micelles are expected to be more able to have an enhanced catalytic activity. We have initiated a series of investigations in this area. The first results, dealing with the hydrolysis of diethylacetals of substituted benzaldehydes in the presence of polymerized micelles of sodium 10–undecenyl sulfate 1[7], are described in this paper.

$CH_2 = CH - (CH_2)_9 - OSO_3^- \, Na^+$ 1



$-\!\!(CH_2 - CH)_{\overline{n}}(CH_2)_9 - OSO_3^- \, Na^+$ 2

Polymerization was accomplished according to the method of LARRABEE and SPRAGUE[9] by a 10 Mrad γ – irradiation of 0,1 M aqueous solution of 1 in a 0,15 Mrad/h60Co γ –ray source. The progress of the polymerization was monitored by ^1H NMR Spectroscopy (in D_2O) as a function of the γ –ray dose. Evidence for the structure of poly(sodium

10-undecenyl sulfate) **2** is provided by comparison of the ^1H spectra of the monomer and polymer; the only observable changes caused by polymerization are the disappearance of absorption due to the vinyl protons (4.5–6.1 ppm) and the broadening of the remaining peaks.

The results are reported in table I[10].

Table I : Rate constants for the hydrolysis of $p-XC_6H_4CH(OEt)_2$ in the presence of **1** and **2** micelles at 25°C

10^2 M [b] 1 or 2	10^{-3} k mol^{-1} dm^3 s^{-1} [a]											
	NO_2 pH = 2.88		CN pH = 2.88		Cl pH = 4.77		H pH = 5.99		CH_3 pH = 5.99		OCH_3 pH = 6.36	
	k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2
0	0.016		0.035		1.90		5.12		20.0		70.5	
0.12	-	-	-	-	-	-	-	-	-	-	-	1290
0.75	-	0.10	-	0.24	-	33.9	-	77.8	-	1009	-	3665
1.5	0.016	0.12	0.036	0.25	2.54	37.0	5.30	96.5	20.52	1199	73.47	4913
3	0.017	0.11	0.036	0.27	2.80	31.8	6.42	108	26.28	1101	407	5450
4.5	0.043	0.12	0.080	0.22	15.4	31.3	32.0	114	207.2	1084	1930	5320
6	0.064	0.11	0.11	0.24	19.20	30.8	70.8	103	493.5	1068	2560	4890

a) $k = kexp/[H_3O]$; each rate is the mean of three independent determinations

b) The polymer concentration is expressed as anionic sulfate group concentration

The catalytic effects observed with **1** are roughly the same as those obtained by CORDES and coll[11] in the presence of sodium dodecyl sulfate micelle. These authors explained their results on the basis of a stabilization of the positively charged transition state by the anionic head-groups of the surfactant. As expected, no catalytic effects is found as long as the monomer concentration is lower than the c.m.c. value. From the table I, it is worthwhile to point out the two specific particularities of the polymeric micelles **2** :

(i) the maximum of the catalytic activity appears at a lower concentration compared to the monomer (**1**) and it is roughly two times higher whatever the substrate. As we assumed, this higher catalytic activity of the polymeric species must reflect stronger micelle–substrate interactions.

(ii) this catalytic power remains even at concentrations much lower than the c.m.c. value of the monomeric species.

For example, with X = OMe, the rate enhancement reaches a maximum value of 78 at a polymeric concentration of 3.0 10^{-2} M and is still equal to 18 at a concentration as low as 1.2 10^{-3} M, a concentration for which no catalytic activity is detected with monomeric micelles **1**.

The results show that polymerized micelles demonstrate micellar behaviour at all concentrations: each polysulfate molecule **2** behaves just like a micelle due to its composition of several repeating surfactant units.

The graphs in figure 1, exemplifies this behaviour; one can see that the maximum catalytic effect provided by **1**, 36, is reached for a 20 times lower concentration of **2**.

In conclusion, T-type polymeric micelles are shown to provide a favorable microenvironment for this reaction since they exhibit rate enhancements greater than those produced by H-type polymer micelles.

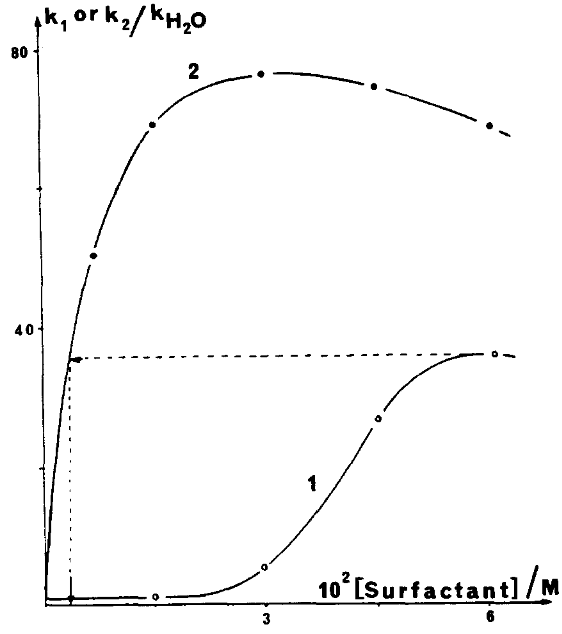


Fig. 1 Catalytic activities of **1** and **2** in the hydrolysis of p-OMe benzaldehyde diethylacetal.

It is interesting to verify whether this observation can be generalized to other reaction systems; work is currently under way in our laboratory to check that point.

Acknowledgements - We thank Mlle N. SCHMITT (L.P.B.-C.N.R.S., Thiais) and Mr J. Rafi (DB/SRA; C.E.N., Cadarache) for carrying out γ-ray irradiations.

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(Received in France 26 November 1990)