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OIL-IN-WATER MICROEMULSIONS BASED ON CHEMODEGRADABLE SURFACTANTS AS REACTION MEDIA

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The reaction of 2-(*p*-nitrophenyl)ethyl bromide with hydroxide ion was studied in oil-in-water (o/w) microemulsions at 50°C. The octane-in-water microemulsion systems were stabilized by chemodegradable cyclic acetal-type cationic surfactants as [(2-alky-1,3-dioxolan-4-yl)methyl]trimethylammonium bromides Ia–c (alkyl: a = *n*-C_9H_{19}; b = $C_{11}H_{23}$; c = $C_{13}H_{27}$) and butan-1-ol as co-surfactant. The rate constants were also determined in the corresponding aqueous micelles and in water. The hydrolytic lability of Ia–c in the microemulsion systems was achieved at 50 °C by acid hydrolysis of the 1,3-dioxolane ring. Systematic synthetic studies of the dehydrobromination were performed in order to develop a preparative approach for the product separation without unfavourable process such as foaming and emulsification.

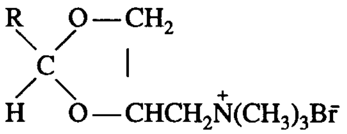
INTRODUCTION

Microemulsion systems offer a very convenient way to investigate the kinetics of processes taking place at an oil/water interface owing to the high volume fraction occupied by the disperse phase and the very high interfacial area.[1] Their potential as reaction media has been demonstrated with increasing interest for various organic and inorganic reactions.[2] Microemulsions, both oil-in-water and water-in-oil, can change reaction rates. In this respect, they behave like micelles, and the factors that control chemical reactivity in micelles are also at work in microemulsions.[3] As reaction media, microemulsion droplets have the major advantage over micelles that they incorporate relatively large amounts of added solute, whereas micelles generally have much less capacity.

However, when surfactants are used for micellar catalysis purposes, they often form an emulsion in the reaction mixture that causes difficulties during isolation of the desired products, and the surfactant remaining in the product can damage its character.[4]

One of the most promising solutions is to construct the micellar systems by means of chemodegradable surfactants,[5] which are susceptible to chemical reactions that decompose them into non-surface-active intermediates. Of the functional groups present in these surfactant molecules, the acetal group is the most common.[6]

The main purpose of this work was to perform kinetic and systematic studies of the model basic dehydrobromination reaction of 2-(*p*-nitrophenyl)ethyl bromide[7] in oil-in-water droplets stabilized by chemodegradable cationic surfactants containing a 1,3-dioxolane group as a linkage between the hydrophobic and hydrophilic units:



Ia: R = C_9H_{19}; **Ib**: R = $C_{11}H_{23}$; **Ic**: R = $C_{13}H_{27}$

The role of the 1,3-dioxolane moiety as a portion of surfactant has been a subject of recent studies.[5g,6f–i] Its presence in micelles introduces a hydrophobic character comparable to the effect of more than two methylene groups of the hydrophobic alkyl chain.[5f,8] Moreover, the 1,3-dioxolane ring does not seem to introduce noticeable changes in the micelle catalytic ability in comparison with the 'classical' hexadecyltrimethylammonium bromide.[9]

In this work, the reaction was followed in o/w microemulsions of chemodegradable surfactants **Ia–c**, *n*-octane and butan-1-ol in comparison with the respective micelles and water at 50 °C. Owing to the acid decomposition of the surfactant microemulsion components, which leads to non-surface-active compounds, we could avoid unfavourable processes such as foaming or emulsification during a preparative approach

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appropriate for organic synthesis, allowing one to isolate the dehydrobromination product from the microemulsion medium.

EXPERIMENTAL

Materials. 2-(*p*-Nitrophenyl)ethyl bromide was available from our previous studies.[7c] It was purified before use by recrystallization from light petroleum. The preparation and purification of surfactants **Ia–c** has recently been described.[6i] The salts obtained were recrystallized several times from acetone–diethyl ether mixtures to a constant melting point. A check of the purity of the surfactants was obtained from the results of surface tension measurements.[5g] Deionized, doubly distilled water was used throughout. Analytical reagent-grade butan-1-ol and *n*-octane were obtained from Fluka.

Phase diagrams. All phase diagrams were constructed at 50 ± 0·1 °C with compositions by weight per cent. Phase behaviour was noted by visual inspection. The butan-1-ol/surfactant weight ratio was 2·00. The phase boundary was determined by titration with 0·02 M NaOH (Figure 1). All solutions with compositions inside the boundary domain are clear and optically transparent.

Kinetic procedure. The basic dehydrobromination of 2-(*p*-nitrophenyl)ethyl bromide was followed in a thermostatically controlled cell compartment of a Hewlett-Packard HP 8452 A diode-array UV–visible spectrophotometer at 50 °C within 0·1 °C by measuring the increase in absorbance of *p*-nitrostyrene (318 nm). The starting concentration of the organic reagent was 1×10^{-4} M. In the presence of 0·02 M NaOH, the observed pseudo-first-order rate constants (k_ψ) calculated from ln(absorbance) versus time functions using a linear regression program are the averages of at least three determinations. All reactions followed first-order kinetic for at least four half-lives.

For the kinetic measurements, the microemulsions were prepared by mixing appropriate weights of the four components under the conditions indicated by the phase diagram locations in Figure 1.

The conductivity of microemulsions (Figure 2) was measured on a Teleko N5772 conductivity meter connected to a thermostated cell (cell constant 0·634 cm^{-1}) capable of regulating the sample temperature at 50 ± 0·1 °C. The constant of the conductivity cell was determined against 0·01 M KCl solution.

Hydrolysis of Ia–c in a microemulsion. The lability of the 1,3-dioxolane moiety was determined by gas chromatography (GC) (Chromatron GCHF-18·3, 2 m × 4 mm i.d. column, 5% DEGS on Chromosorb G-AW) with UV–visible spectrophotometric detection (280 nm). A given microemulsion (1 ml) and 50 μl of 2 M HCl was heated in a sealed tube at 50 °C. After the required time, the reaction mixture was cooled. The microemulsion phase separation occurred readily under the experimental conditions, giving rise to an organic layer which was separated, diluted with *n*-octane and submitted to GC analysis. The butan-1-ol/appropriate aldehyde ratio was determined for every kinetic run, allowing one to determine the total surfactant decomposition. A similar microemulsion sample was analysed spectrophotometrically following the appearance of the respective aldehyde until phase separation of the microemulsion occurred.

GC/MS technique. All analyses for the synthetic studies were carried out with a Hewlett-Packard HP 5890 Series I gas chromotograph equipped with an HP 5971 A mass-selective detector. A glass capillary column (15 m × 0·2 i.d.) containing a cross-linked methylsilicone gum was used.

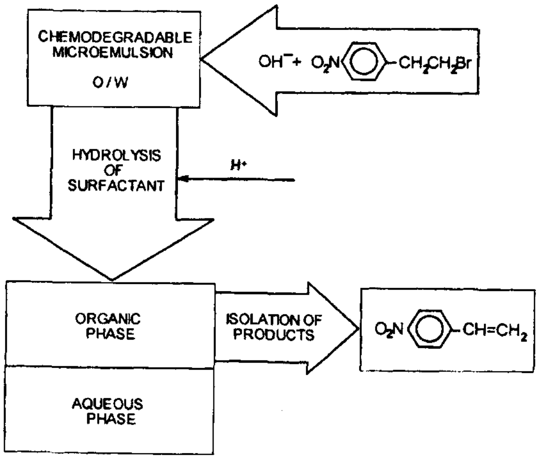
RESULTS AND DISCUSSION

For the initial kinetic and synthetic studies in chemodegradable microemulsion media, we selected the base-induced dehydrobromination of 2-(*p*-nitrophenyl)ethyl bromide as an example since this reaction has been studied in detail in micellar systems including chemodegradable micelles.[7,9]

To approach the systematic methodology necessary for organic synthesis we constructed a schematic work-up as illustrated in Scheme 1.

Phase diagrams

The microemulsion systems that we chose for these experiments were made of surfactant **Ia–c**–butan-1-ol–*n*-octane–0·02 M NaOH at 50 °C. The compositions



Scheme 1.

of the microemulsion used as the reaction medium are indicated in Figure 1 by points X_{ij} (i = **a**, **b** and **c** for surfactants **Ia** and **Ib**, respectively, and j = 1, 2, 3, 4, 5) and are summarized in Table 1. The 1 : 2 microemulsions are fluid, easy to prepare and offer an appreciable region of clarity. Figure 2 shows the electrical conductivities of the studied microemulsions as a function of oil content for a constant surfactant-to-water ratio. Microemulsions X_{i1} (i = **a**, **b**, **c**) of low oil content appear to have a high conductance, which after addition of *n*-octane decreases following path X_{i1}–X_{i4}–X_{i5}. According to the literature,[8] butan-1-ol is displaced from the core to the surface as *n*-octane is added to the o/w microemulsion. The droplets increase in size and their mobility decreases while their concentration remains constant. After enough oil has been added to displace all of the alcohol, additional oil causes the size to increase with a concomitant decrease in droplet concentration. Thus, lowering of the electrical conductance of microemulsions X_{i4} and X_{i5} is demonstrated here by the decreases in aggregate concentration and droplet mobility. Conductivity data suggest that the studied microemulsions are most likely an o/w system in which oil microdroplets are dispersed in an aqueous continuous phase.

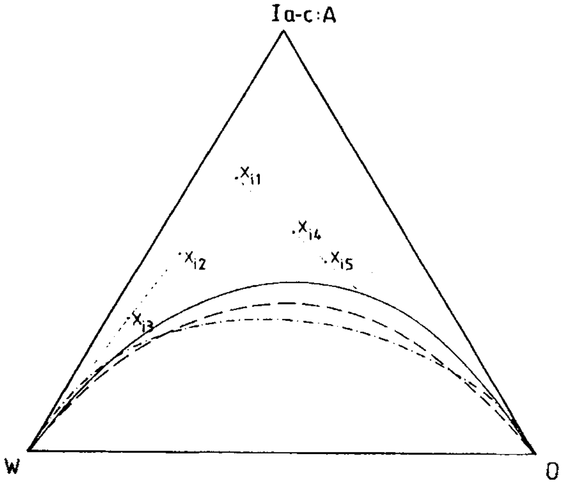


Figure 1. Pseudo-ternary phase diagrams at 50 °C for the system formed by **Ia**–**c** [(———) a; (---) b; (-·-·-) c]–butan-1-ol (A)–*n*-octane (O)–0·02 M NaOH (W). **Ia**–**c**: A = 1 : 2 (w/w). The points X_{ij} (i = **a**, **b**, **c**; j = 1, 2, 3, 4, 5) are indicative of the compositions studied

Table 1. Compositions of microemulsions

	Microemulsions (wt%)			
PDL[a]	**Ia**–**c**	Butan-1-ol	*n*-Octane	Water
X_{i1}	21·6	43·2	8·1	27·1
X_{i2}	15·5	31·2	6·5	46·8
X_{i3}	10·3	20·6	5·0	64·0
X_{i4}	17·3	34·6	26·0	22·0
X_{i5}	15·5	31·1	34·0	19·5

[a] Phase diagram location (Figure 1), were i = **a**, **b**, **c**, for the surfactants **Ia**, **Ib** and **Ic**, respectively.

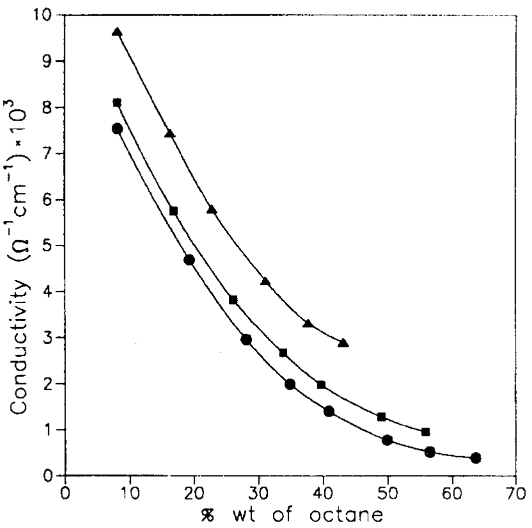


Figure 2. Specific conductivity [$\sigma(\Omega^{-1}\,\mathrm{cm}^{-1})$] as a function of oil content at 50 °C for the surfactant–water–butan-1-ol–*n*-octane microemulsion system: (▲) **Ia**; (■) **Ib**; (●) **Ic**

Kinetic studies

The observed pseudo-first-order rate constants (k_ψ) for the reaction of 2-(*p*-nitrophenyl)ethyl bromide with hydroxide ion in microemulsions of the synthesized surfactants **Ia**–**c** are given in Table 2. We examined the effect of changing the microemulsion composition on the dehydrobromination reaction, i.e. the variation of the observed rate constant at a fixed concentration of sodium hydroxide when the microemulsion composition is changed following the paths indicated in Figure 1. It can be seen (points X_{i1}, X_{i4}, X_{i5}) for all surfactants that k_ψ begins to decrease when the amount of octane in the microemulsion is increased. Following paths X_{i1}–X_{i2}–X_{i3} a slight decrease in the k_ψ value is also observed. The kinetic data indicate that the dehydrobromination is only slightly faster in the **Ic** microemulsions than in **Ia** and **Ib** microemulsions, which leads to the conclusion that the average microenvironment of the organic reagent in the microdroplets **Ia**–**c** is essentially the same.

Table 2. Basic dehydrobromination of $p\text{-}NO_2C_6H_4CH_2CH_2Br$ in different systems and 0·2 M NaOH at 50 °C

System	PDL[b]	SL[c] (M)	10^3k_ψ (s^{-1})	k_{rel}
Water			0·72	1
Ia (micelles, $k_{\psi\,max}$)[a]		0·0040	9·55	13·2
Ib (micelles, $k_{\psi\,max}$)[a]		0·0042	24·80	34·4
Ic (micelles, $k_{\psi\,max}$)[a]		0·0048	35·7	49·5
Microemulsion	X_{a1}	0·24	3·68	5·1
	X_{a2}	0·17	2·65	3·7
	X_{a3}	0·10	2·47	3·4
	X_{a4}	0·20	1·63	2·3
	X_{a5}	0·21	0·75	1·0
	X_{b1}	0·30	4·15	5·7
	X_{b2}	0·20	3·66	5·1
	X_{b3}	0·11	3·00	4·2
	X_{b4}	0·23	2·15	3·0
	X_{b5}	0·25	0·93	1·3
	X_{c1}	0·35	4·85	6·7
	X_{c2}	0·23	4·33	6·0
	X_{c3}	0·13	3·76	5·2
	X_{c4}	0·27	2·19	3·0
	X_{c5}	0·29	1·08	1·5

[a] Reaction in micelles:[9] $[\mathbf{Ia}]_{max} = 0·03$, $[\mathbf{Ib}]_{max} = 0·0125$ and $[\mathbf{Ic}]_{max} = 0·0075$ M

[b] Phase diagram location (Figure 1). The compositions of the microemulsion used are summarized in Table 1.

[c] Solubility of 2-(*p*-nitrophenyl)ethyl bromide.

Rate enhancements (k_{rel}) are also presented in Table 2. It is seen that the k_{rel} values are about one order of magnitude higher in **Ia–c** micelles than in the respective microemulsion systems. The kinetics in micelles are greatly enhanced at low concentrations of surfactant owing to the classical micellar catalysis effect. This is related to the increased concentration of reagents at the micelle surface, but this effect progressively disappears at higher surfactant concentrations because the reagents are distributed on a greater number of micelles.[10] When the reaction between 2-(*p*-nitrophenyl)ethyl bromide and OH^- is carried out in **Ia–c** microemulsions, the concentration of OH^-in the microemulsion droplets is considerably lower than that in cationic micelles of **Ia–c**. Further, the hydroxide ions are distributed over a larger phase volume in the microemulsion droplets than in micelles. In the reaction medium the butan-1-ol co-surfactant, partially converted into a butoxide ion, can also be reactive in promoting the studied *E*2 process. It is difficult to interpret quantitatively the effects of hydroxide and butoxide ions on the observed reaction rates because of the problems related to the deprotonation of butan-1-ol. The extent of butan-1-ol at high pH cannot be estimated and the presence of butan-1-ol in a droplet reduces the charge density at the surface of the droplet and its ability to attract ions.

Hydrolysis of microemulsions

The cyclic acetal—type cationic surfactants **Ia—c** are stable under neutral and basic conditions but readily hydrolyse under acidic conditions to non-surface-active aldehydes and diols. The mechanism and kinetics of acetal hydrolysis have been investigated in detail both in homogeneous[6i,11a,b] and micellar systems.[6h,9,11c] The specific acid hydrolysis of the 1,3-dioxolanes proceeds with a rate-determining step, involving cleavage of the protonated acetal or ketal grouping.[11] The hydrolytic reactivities of aggregated chemodegradable surfactants in acidic solutions are much smaller than those of unaggregated forms, which may indicate that the reaction microenvironment of the micellar aggregates causes electrostatic repulsion of hydronium ions by positively charged head groups.[9,11c] Additionally, the hydrolytic lability is decreased in micellar aggregates in comparison with aqueous systems as the result of a lower Stern layer polarity relative to the aqueous phase.

The presence of a strong electrolyte such as HCl in the continuous phase strongly changes the diameter of the microemulsion droplets.[12] Accordingly, it decreases with increasing electrolyte concentration. Again the presence of HCl in the continuous phase would reduce the repulsive forces between the head groups of the surfactant molecules, leading to a more efficient packing and, consequently, to a smaller radius of curvature.

The results summarized in Table 3 describe the hydrolytic lability of the studied microemulsion surfactants. The total decomposition time of a surfactant

Table 3. Degradation parameters of **Ia–c** in microemulsions (0·1 M HCl, 50 °C)

Microemulsion PDL[a]	Phase separation time[b] (s)	Total decomposition of surfactant[c] (h)
X_{a1}	5250	7·1
X_{a2}	830	7·3
X_{a3}	6120	12·0
X_{a4}	1080	3·2
X_{a5}	1830	2·5
X_{b1}	5100	7·6
X_{b2}	650	8·3
X_{b3}	5710	12·8
X_{b4}	896	3·6
X_{b5}	1000	3·2
X_{c1}	4360	8·9
X_{c2}	540	10·3
X_{c3}	4890	14·1
X_{c4}	630	4·8
X_{c5}	869	4·1

[a] Phase diagram location (Figure 1).

[b] Determined by the UV–visible spectrophotometry.

[c] Determined by GC.

(last column) corresponds to a hydrolysis conversion of at least 98%, thus providing information when the given medium decomposes almost completely into non-surface-active species. The phase separation time is defined here as the period of time required for a given microemulsion to lose its transparency as indicated by a sharp increase in absorbance. These two parameters were determined for the studied microemulsions **Ia–c** with the component concentrations as given in Table 1. Hydrolysis of surfactants **Ia–c** in microemulsions cannot be described in terms of a rate constant because too many dependables affect the kinetics. Generally, following paths X_{i1}–X_{i2}–X_{i3} and X_{i1}–X_{i4}–X_{i5} there are no linear relationships between values of phase separation and total decomposition times. For all surfactants, the phase separation time is the shortest for X_{i2} but the total decomposition time is shortest for X_{i5}.

Synthetic studies

A preparative dehydrobromination was performed only in **Ic** microemulsions under the conditions used for the kinetic runs in Table 2. 2-(*p*-Nitrophenyl)ethyl bromide [at a concentration 30% less than its solubility limit (SL); Table 2] was dissolved in 40 ml of a given microemulsion X_{cj} ($j = 1, 2, 3, 4, 5$). The SL parameter is based on the total solution volume. Although micelles of **Ic** gave the largest value of k_{rel} they could solubilize much less of the organic reagent and they are therefore the least suited for practical synthesis. In the next step of the work-up presented in Scheme 1, the microemulsion surfactants after the reaction completion were hydrolysed by adding 4 ml of 2 M HCl at 50 °C (conditions are given in Table 3). The upper organic phase, as indicated by the GC–MS analysis, contained *n*-octane, butan-1-ol, *n*-tetradecanal, *p*-nitrostyrene and small amounts of *n*-dodecanal and di-*n*-butyl ether. In order to remove the aldehyde, the organic layer was washed several times with saturated $NaHSO_3$ solution. After the solvents had been removed under reduced pressure, the remaining solid was crystallized from light petroleum and analysed [MS (70 eV), *m*/*z* (relative intensity, %): 149 (M, 31·86), 133 (1·38), 119 (26·55), 103 (25·66), 101 (2·65), 91 (42·03), 78 (6·64), 65 (19·91), 53 (5·31), 51 (55·75)]). The isolation of *p*-nitrostyrene was achieved in more than 90% yield in the case of microemulsions X_{c2}, X_{c3}, X_{c4} and X_{c5}, but only 60% in the X_{c1} microemulsion. If one considers both the catalytic effect and hydrolytic lability of the studied reaction media, the water-rich o/w microemulsions X_{c2} and X_{c3} are the most suitable for synthetic applications in the studied case.

CONCLUSIONS

We have taken advantage of the transparency of microemulsion systems and the degradable character of cyclic acetal-type surfactants to survey a chemodegradable reaction medium. Thus, o/w microemulsions stabilized by surfactants **Ia–c** can be used to catalyse reactions, and subsequent acidification during the work-up procedures convert them into non-surface-active derivatives. The organic product can be isolated from the reaction mixture by an appropriate separation method without any emulsion problems.

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