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CHEMICAL AND PHOTOCHEMICAL REACTIVITY IN MICROEMULSIONS AND WATERLESS MICROEMULSIONS

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PART I Waterless microemulsions as reaction media

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Aggregation in Formamide Solution: Reactivity and Structure of Non-Aqueous Microemulsions

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ABSTRACT

Relatively little attention has been paid to molecular aggregation phenomena in structured non-aqueous solvents compared to that devoted to such processes in aqueous media. This paper is a review concerning our work with formamide in place of water.

The following observations showed that formamide has sufficient cohesive force to favor molecular aggregation: (1) critical micellar concentrations (c.m.c.) were determined with various ionic and non-ionic surfactants; (2) the phase diagram of CTAB in formamide shows two mesomorphic phases closely resembling those found in aqueous systems; (3) X-ray scattering demonstrated the presence of molecular aggregates, and gave an indication of their structure, and (4) a variety of microemulsions were prepared in formamide.

Such non-aqueous microemulsions represent valuable media for synthetic purposes. For example, Diels-Alder reactions, photoamidation of olefins, and the Wacker process can be carried out readily in such media. The observed discontinuities in reaction selectivity indicate the presence of structured phases. (AW) X

INTRODUCTION

Molecular aggregation phenomena are usually investigated under the following conditions: in aprotic organic solvents of low dielectric constant, or in structured protic solvents (nearly always water). In this case, the nature of the interactions is particularly dependent on the nature of the solvent. The protonic nature favors hydrogen bonding which would also be expected to occur in a solvent such as formamide.

We report here the results of our investigations on micellization and the formation of microemulsions in formamide and analogues.

The hydrophobic interactions observed in aqueous systems are, in fact, a particular example of solvophobic interactions in general [1]. The ability of some amphiphilic molecules to form micelles in non-aqueous media indicates that a water replacement should have the following properties: (1) a high po-

larity (high dielectric constant), (2) a high solvating power, and (3) highly structured. The structural nature of a solvent can be evaluated from two main parameters: the internal pressure P_i , and the density of the cohesion energy D_{ce} . Tables 1 and 2 show physicochemical parameters for various potential solvents [2].

Examination of these parameters suggested that formamide would be suitably structured. Sinanoglu and Abdunur [3] have established the following order of solvophobicity from empirical observations of molecular associations in different solvents: water > glycerol, formamide \gg ethylene glycol > *n*-butanol, methanol, *n*-propanol, ethanol > *t*-butanol. Herskovits and Bowen also found this order for the stability of DNA double helices in the same solvents [3]. It can be seen that formamide stands out from the other non-aqueous solvents. This has also been confirmed by X-ray diffraction, showing the highly structured nature of liquid formamide [4].

TABLE 1

Physicochemical characteristics of various solvents

Solvents	D_{ce}^a (J cm ⁻³)	P_i^b (J cm ⁻³)	ϵ/ϵ_0^c	M^d	ϵ_T^e
Water	2302	150.6	78.5	1.8	63.1
Formamide	1574.9	554.4	109.5	3.4	56.6
Ethylene glycol	892.0	502.1	37.7	2.0	56.3
Methanol	873.6	288.3	32.6	1.65	55.5
<i>N</i> -Methylformamide			182.4	3.8	54.1
<i>N</i> -Methylacetamide			175.7	4.3	52.0

^aDensity of cohesion energy.

^bInternal pressure.

^cDielectric constant.

^dCharge dipole moment.

^eKosower's parameter.

TABLE 2

Surface tension γ of various solvents

Solvents	γ (mN m ⁻¹)	T (°C)	Solvents	γ (mN m ⁻¹)	T (°C)
Water	70	20	Methanol	22.55	20
Formamide	58.5	20	<i>N</i> -Methylformamide	37.96	30
Ethylene glycol	48.9	20	<i>N</i> -Methylacetamide	33.67	30
Et.NHNO ₂	46.3	50			

FORMAMIDE: A WATER SUBSTITUTE

We compared water and formamide in various situations: (1) in a structural investigation of molecular associations (micellization, formation of microemulsions) [5], and (2) in various reactions in phase transfer or in microemulsions.

Self-association in formamide

Non-ionic amphiphiles (Pluronic) [6] as well as ionic amphiphiles such as cetyltrimethylammonium bromide (CTAB) and phosphonium salts $(C_6H_5)_3P^+C_nH_{2n+1}X^-$ ($X=Br,I$) [7] have been used as surfactants. The phosphonium salts with large polar heads are, however, insoluble in water and cannot be used to prepare aqueous microemulsions under normal experimental conditions. Furthermore, contradictory results have been reported on the production of micelles in formamide using ionic surfactants [8]. We therefore carried out a series of investigations using formamide as a solvent. We first demonstrated molecular aggregation in formamide of large ions, $(C_6H_5)_3P^+C_nH_{2n+1}I^-$ and their fluorinated homologues $(C_6H_5)_3P^+CH_2CH_2R_F I^-$, which are insoluble in water even at high temperatures [9]. However, they are soluble in formamide, and micellization was indicated from measurements of surface tension and conductance. The Krafft temperature in formamide for such derivatives are nevertheless quite high (around $60^\circ C$), and so the surface tension and conductance measurements were carried out at $64^\circ C$.

There are no reports in the literature of measurements of Krafft temperatures for classical ionic surfactants (water-soluble surfactants) in formamide. We determined the Krafft temperatures in formamide for two classical ionic surfactants, SDS and CTAB, and we also investigated the surfactant action of these compounds above the Krafft temperatures.

The change in surfactant solubility in $HCONH_2$ with temperature was found to be similar to that of such compounds in water [10].

The Krafft temperatures of these surfactants are found to be much higher in formamide than in water (Table 3). Evans et al. [11] have reported high Krafft temperatures for alkyltrimethylammonium bromides in ethylammonium nitrate ($48^\circ C$ for CTAB). Such high values can be explained in terms of the structure of the medium. The structure of liquid formamide and solvated salts in formamide probably resemble the fused salt structure of compounds like ethylammonium nitrate.

The c.m.c. for both SDS and CTAB are much higher in formamide than in water (about $\times 100$). Our results indicate that solvophobic interactions are weaker in formamide than in water, which could explain the higher c.m.c. val-

TABLE 3

Krafft temperatures and c.m.c. of SDS and CTAB in formamide and water

	Krafft temp. ($^{\circ}\text{C}$)		c.m.c. (mol l^{-1})	
	SDS	CTAB	SDS	CTAB
Water	16	26	$9.7 \cdot 10^{-3}$	$1.03 \cdot 10^{-3}$
Formamide	55	43	$2.2 \cdot 10^{-1}$	$9 \cdot 10^{-2}$

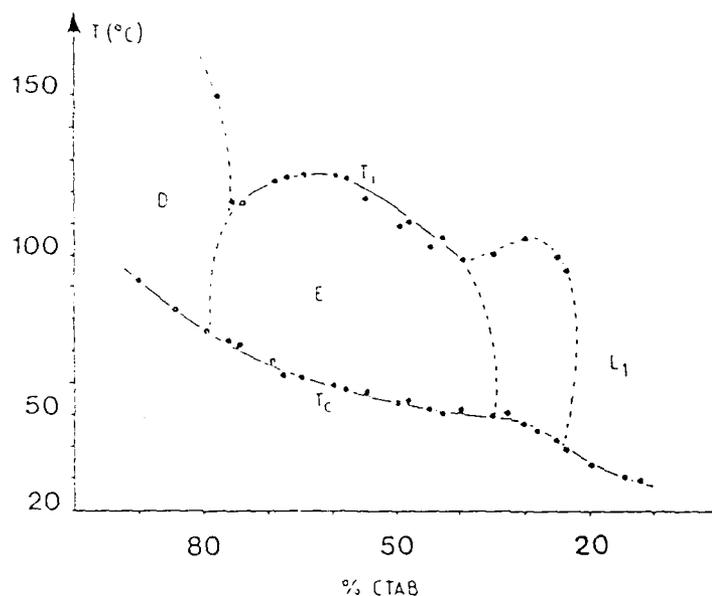


Fig. 1. Phase diagram of CTAB in formamide. The dotted lines indicate poorly defined boundaries.

ues. Similar increases have been observed between water and ethylammonium nitrate.

We concluded that in order to produce micelles of ionic surfactants in formamide one must work above the Krafft temperature and, under this condition, the c.m.c. values are higher in formamide than in water. Formamide would seem to confer the properties of a low-melting anhydrous salt similar to ethylammonium nitrate.

Phase behavior of CTAB in formamide

We studied in more detail the phase behavior of CTAB in formamide [12] (Fig. 1). Two mesomorphic phases could be clearly identified: an hexagonal phase (E) and a lamellar phase (D). The textures closely resembled those seen in water/surfactant systems. The CTAB/formamide system involves the same

phases as the CTAB/D₂O system with, however, a small concentration shift towards higher values.

The aggregation stage of CTAB in the isotropic phase was also characterized by ¹H NMR and compared to the results obtained from surface tension measurements. The longitudinal relaxation time (T_1) of the main resonance in the proton spectrum was measured. This peak corresponds essentially to the methylene groups in the aliphatic chain, this relaxation time should fall at the c.m.c. This was in fact observed at 60°C with a c.m.c. value of $9.4 \cdot 10^{-2} \text{ mol l}^{-1}$ (c.m.c. in D₂O = $2 \cdot 10^{-3} \text{ mol l}^{-1}$). From surface tension measurements, we obtained a c.m.c. value of $9.0 \cdot 10^{-2} \text{ mol l}^{-1}$, which is in good agreement with the NMR value. These results further demonstrate that formamide can replace water in systems involving molecular aggregation.

Structural analysis by X-ray scattering of formamide aggregates in CTAB

X-ray scattering was used to analyze the structures of aggregates of CTAB in various formamide-containing media [13]. As in aqueous solutions, micelles can be observed in the supercooled state. The aggregation number N , the surface area per polar head at the micelle/solvent interface (Table 4) and the number of micelles can be deduced from the size and density of the micelle.

The aggregates were assumed to be spherical as they were very small. However, they increase in size as the concentration increased, although there was no change in their overall number ($n = 5.7 \cdot 10^{18} \text{ micelles cm}^{-3}$). They remain spherical at least up to 2.5 times the c.m.c. on the assumption that they are spherical at lower concentrations. They were observed over the temperature range 40–70°C (70°C being the highest temperature used in these studies).

The small size of the aggregates at low concentrations would appear to be a characteristic of the formamide systems. Moreover, results from experiments in progress have shown that the parameters of the hexagonal and lamellar phases in the CTAB/formamide system are lower than those for water, and are relatively small given the chain length of CTAB.

The difference between micellization of CTAB in water and formamide is

TABLE 4

X-ray scattering analysis of micellization of CTAB in formamide

C_{M}	$C \text{ (mol l}^{-1}\text{)}$	$R \text{ (\AA)}$	N	A^2
2.88	$9.0 \cdot 10^{-2}$			
5	0.154	9	7	145
10	0.312	13.6	24	97
20	0.624			

probably due to differences in affinity of the solvent for the hydrocarbon chains, as well as differences in the interactions between the polar heads.

The standard free enthalpy ΔG_m^0 for micellization of the monomer can be calculated fairly accurately at 5°C (close to the c.m.c., at zero micelle concentration) by:

$$\Delta G_m^0 = RT \log C_{cmc}$$

giving $\Delta G_m^0 = 5 \text{ kJ mol}^{-1}$ in formamide, quite different from the value determined in water (-29 kJ mol^{-1}). The free enthalpies per CH_2 in formamide and water are also quite different (1.5 kJ mol^{-1} for formamide [14] versus -2.9 kJ mol^{-1} for water). Formamide can be seen to have, therefore, a much higher affinity for hydrocarbon chains.

In these two solvents, the change in enthalpy per CH_2 in micelle formation is -1 kJ mol^{-1} in water, and only $-0.25 \text{ kJ mol}^{-1}$ in formamide [15]. Formamide thus behaves as a liquid that is highly structured round the hydrocarbon chains, and the low value of ΔH seems to indicate that the exothermic chain interaction only just overcomes the endothermic destructuration of formamide. On the other hand, in both solvents, micellization is accompanied by a large increase in entropy ($5.8 \text{ J mol}^{-1} \text{ K}^{-1}$ in water and $4 \text{ J mol}^{-1} \text{ K}^{-1}$ in formamide) [16]. This entropy-driven micellization phenomenon observed in both water and formamide is rather different from that found in other solvents in which micellization is studied. In hydrazine for example, Evans has shown that micellization is essentially enthalpy-driven [17].

Non-aqueous microemulsions

It occurred to us that it should be possible to prepare microemulsions with formamide. We used transparency criteria to determine the microemulsion monophasic areas on the pseudo-ternary phase diagrams [18]. With cyclohexane as oil, 1-butanol as cosurfactant and formamide, we studied two surfactants; (1) cetyltrimethylammonium bromide (CTAB), and (2) cetyltributylphosphonium bromide (CT_bPB).

No microemulsions were obtained with CT_bPB and water. Figures 2 and 3 show the pseudo-ternary phase diagrams of 1-butanol/surfactant/formamide/cyclohexane mixtures. Figure 4 shows another type of pseudo-ternary phase diagrams for formamide/CTAB/1-butanol/cyclohexane mixture. In addition, electrical conductivity measurements were carried out following the procedure described by Dvolaitzky et al. [19] for water.

A discontinuity in electrical conductivity along the phase boundary was observed, indicating the presence of a microscopically heterogeneous medium (probably with percolation) rather than just a case of cosolubility. The low values of the volume fraction of formamide ($\phi = 0.02$) can be attributed to the solubility of the cosurfactant in formamide.

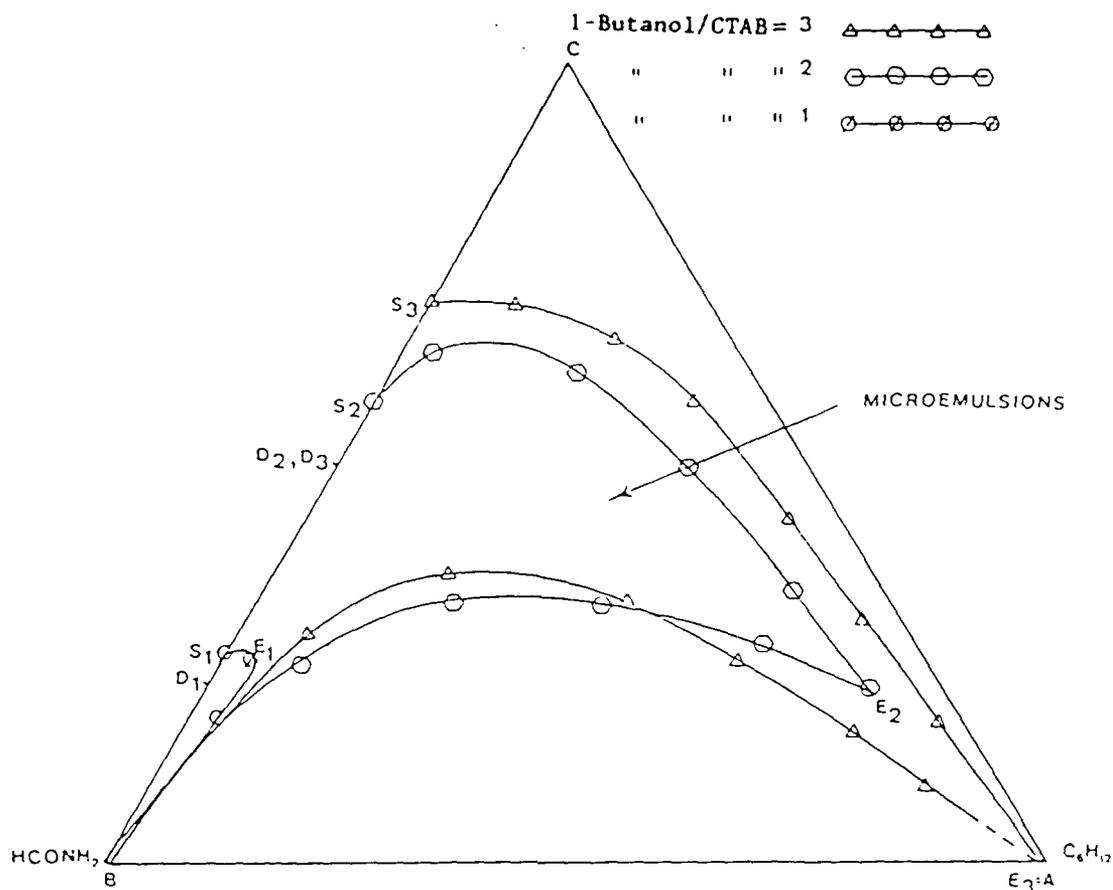


Fig. 2. Pseudo-ternary phase diagrams of 1-butanol/CTAB/formamide/cyclohexane.

With perfluorinated compounds we also obtained large continuous monophasic areas of microemulsion [20] (Fig. 5). As with the hydrogenated compounds, there was a discontinuity along the phase boundary. Percolation was observed at a volume fraction of formamide $\phi = 0.12$, which was commonly found in this type of experiment. Our systems are not true solutions since triphasic areas are observed in the phase diagrams which indicate the presence of organized systems. Moreover, the interfacial surface tensions were always extremely low for the triphasic system (10^{-5} mN m⁻¹).

Formation of Winsor I, II and III systems

We also investigated the salinity effect in the perfluorinated water-free microemulsions, using potassium iodide instead of sodium chloride as salt, due to its high solubility in formamide. The results are summarized in Fig. 6.

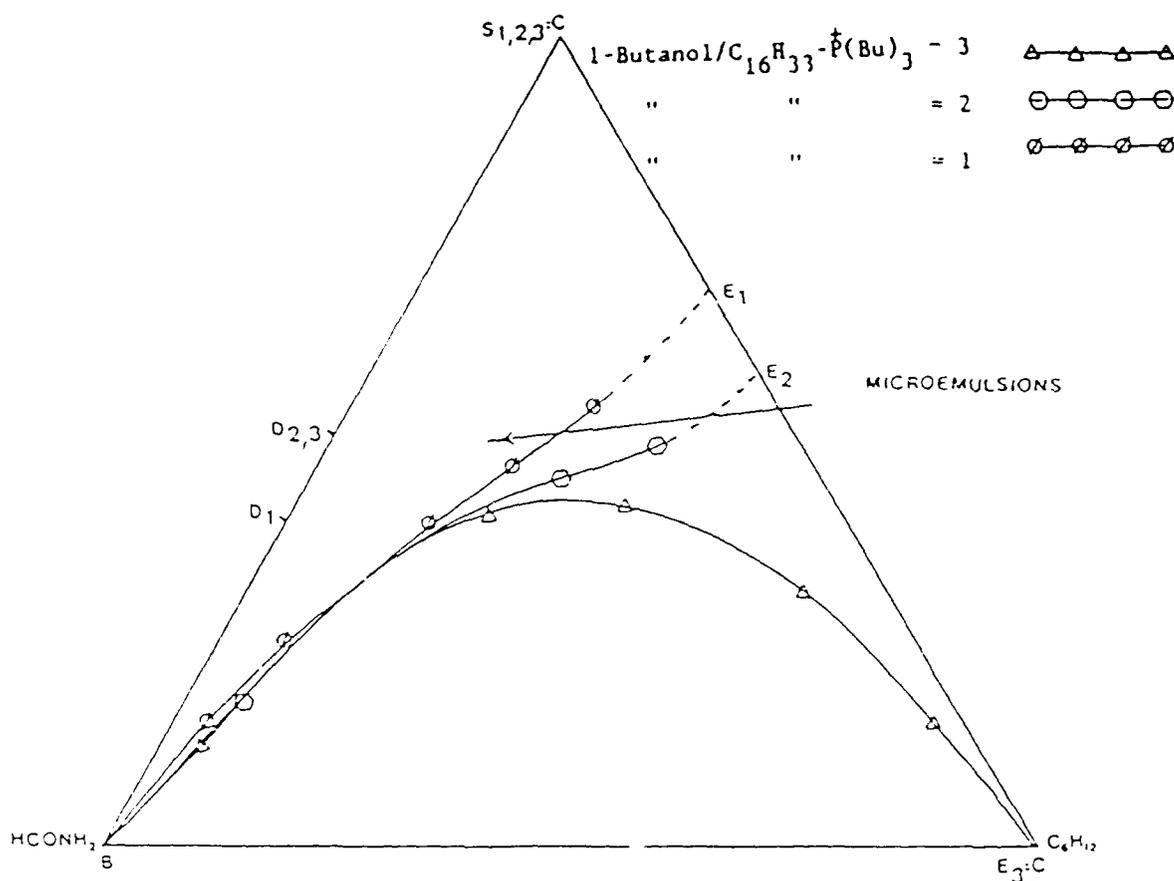


Fig. 3. Pseudo-ternary phase diagrams of 1-butanol/CT₆PB/formamide/cyclohexane.

Structure of the formamide/CTAB/isooctane/1-butanol system

The structure of the microemulsion of the system (formamide/CTAB = 2) was studied by X-ray scattering. It was assumed that there were no droplets or vesicles.

There was a continuity in the change in scattered intensities between the different solutions. Overall, the results may be explained in terms of the presence of formamide filaments, since observations are comparable to those in semi-dilute solutions of polyelectrolytes.

Small angle X-ray scattering showed that the microemulsions obtained in formamide were quite different from those observed in water-in-oil microemulsions. Dispersed formamide filaments were observed rather than the globular particles seen in aqueous microemulsions.

A complete analysis of the structure has been published elsewhere [13].

Water-free microemulsions as reaction media

Various studies have shown the value of aqueous microemulsions as reaction media [21], although their scope has been limited by the lack of solubility of

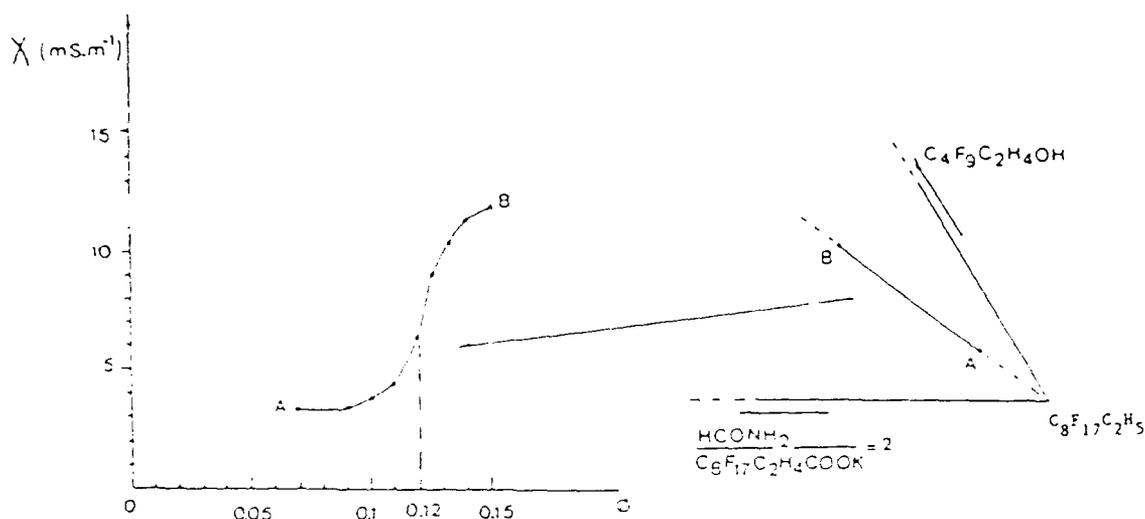


Fig. 5. Conductivity χ versus volume fraction ϕ of formamide, along the linear part of the phase boundary, in the oil-rich region for the system $\text{HCONH}_2/\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{COOK}/\text{C}_8\text{F}_{17}\text{C}_2\text{H}_5/\text{C}_4\text{F}_9\text{C}_2\text{H}_4\text{OH}$.

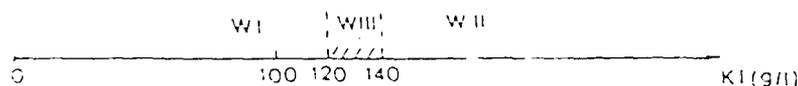
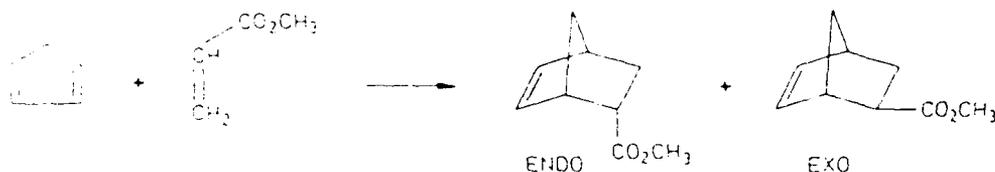


Fig. 6. Formation of WI, WII, WIII, with increase in KI concentration in initial system [HCONH_2 (44%), $\text{C}_8\text{F}_{17}\text{C}_2\text{H}_5$ (44%), $\text{C}_4\text{F}_9\text{C}_2\text{H}_4\text{OH}$ (4%), and $\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{CO}_2\text{K}$ (8%)].

many reagents in water. Formamide would appear particularly useful in such situations.

Diels-Alder reactions

Using the Diels-Alder reaction between methyl acrylate and cyclopentadiene as a chemical probe, we were able to explore the monophasic areas of both ionic and non-ionic surfactant solutions in formamide [22,23].



The two isomers (endo and exo) are produced via two different transition states of different polarity. It is known that the endo/exo selectivity increases with increasing polarity of the solvent. We carried out a preliminary study of the influence of the various constituents of the microemulsion on the reaction (see Table 5).

We were thus able to exploit the high solubility of substrates in formamide to investigate the complete formamide microemulsion phase diagram (Fig. 7).

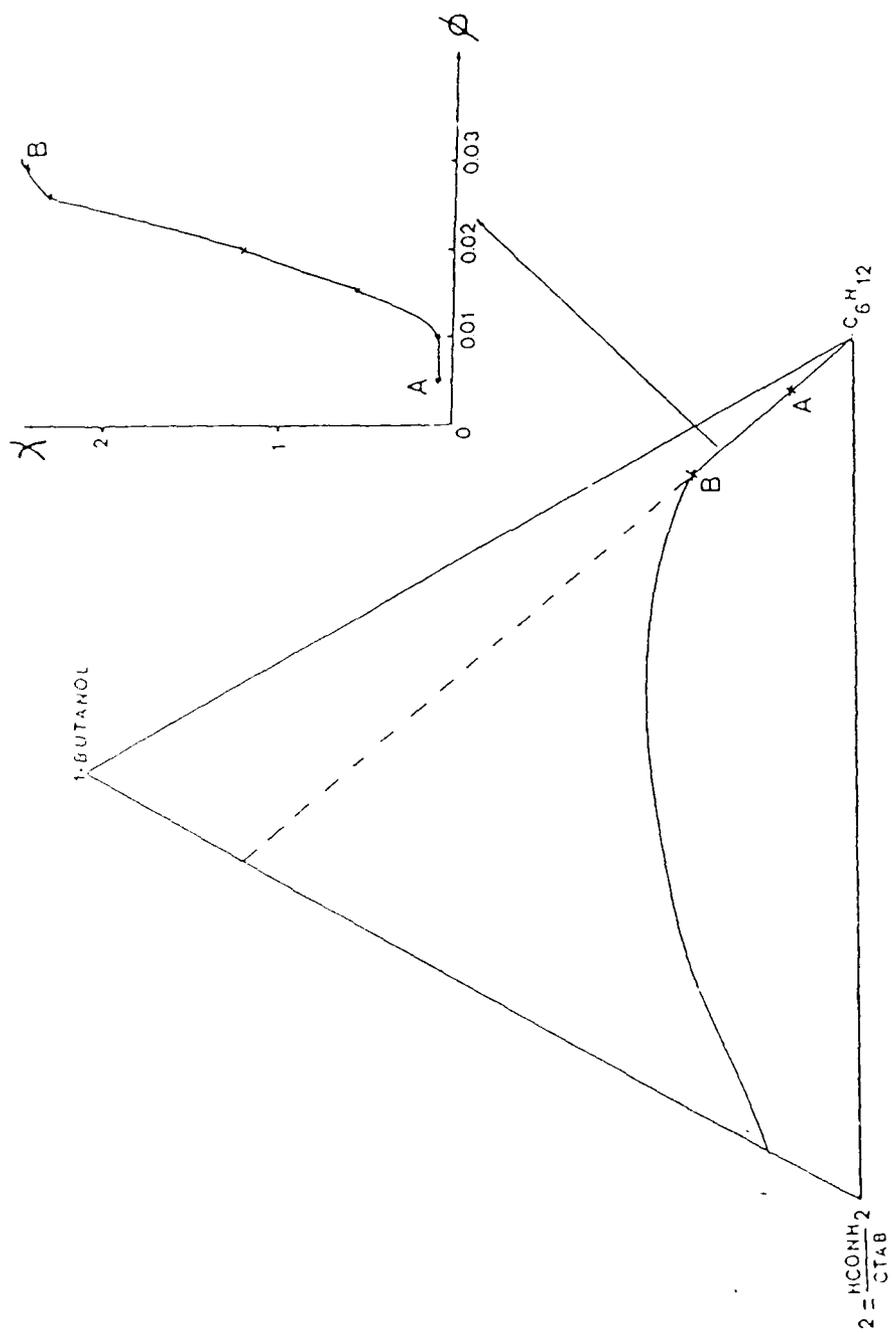


Fig. 4. (a) Pseudo-ternary phase diagram of formamide/CTAB/1-butanol/cyclohexane; (b) Conductivity χ versus volume fraction ϕ of formamide.

TABLE 5

Endo/exo product ratios in organic media and in water

Solvent	Dielectric constant	Concentration of diene and dienophile (<i>M</i>)	Endo/exo
Isooctane	2.0	0.15	2.3
1-butanol	17.1	0.15	5.0
Water	78.5	0.15	7.4
Formamide	109.0	0.15	6.7

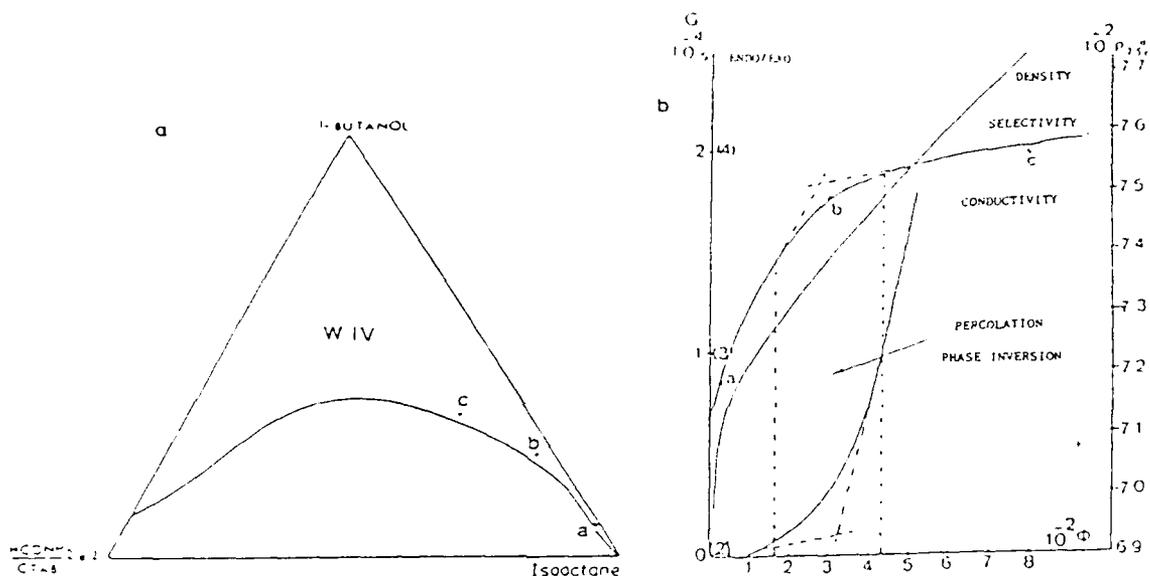


Fig. 7. (a) Pseudo-ternary phase diagram of the system formamide/CTAB/isooctane/1-butanol. (b) Density, selectivity and conductivity versus volume fraction ϕ of formamide.

Good agreement between changes in conductivity and endo/exo selectivity can be seen in the plot of conductivity versus formamide volume fraction ϕ . With ionic surfactants the abrupt changes in selectivity and conductivity along the demixing line can be attributed to phase inversion from reverse micelles (formamide in oil) to direct micelles (oil in formamide). It can also be seen that there are discontinuities in density, indicating structural rearrangements.

With microemulsions based on non-ionic surfactants, the absence of charged products makes the investigation of the physicochemical characteristics of the monophasic area more difficult. The chemical probe reaction is thus particularly suited for this type of analysis. With Pluronic F 68 (MW = 3750) $[\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{80}-(\text{CH}_3\text{CHCH}_2\text{O})_{30}-(\text{CH}_2\text{CH}_2\text{O})_{80}\text{H}]$, the density changed monotonically from one end of the diagram to the other as the continuous phase changed from toluene to formamide (Fig. 8).

From the values of the endo/exo ratios observed, there is a discontinuity in

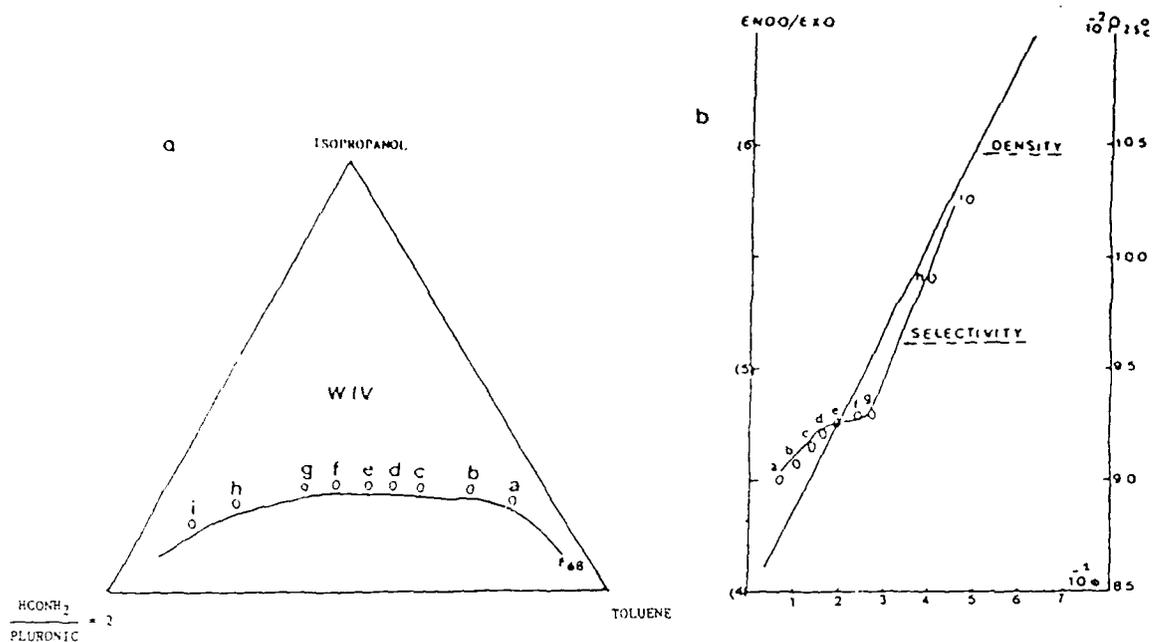
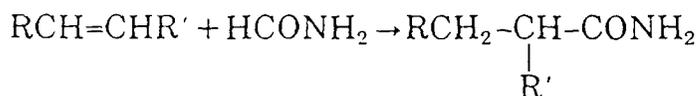


Fig. 8. (a) Pseudo-ternary phase diagram of the system formamide/Pluronic F 68/toluene/isopropanol. (b) Density and selectivity versus volume fraction ϕ of formamide.

reaction selectivity (Fig. 8), indicating the presence of structured phases which would have been impossible to detect by measurements of density.

Amidation of olefines

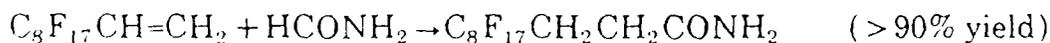
Gamma radiation- and light-induced amidation of olefines have been reported



This reaction provides a good route to the higher amides, which can be readily converted to surfactant compounds (carboxylic acids, amine derivatives, etc.).

However, the mixture of olefins and formamide was homogenized with *t*-butyl alcohol, and yields were often low. Furthermore, this reaction cannot be used with perfluorinated olefins which are not soluble.

One way round this problem is to use water-free systems as reaction media. Use of a solvent such as formamide with its high dielectric constant can thus provide a valuable medium for many reactions. For example, new perfluorinated amides can be obtained with a perfluorinated microemulsion:



The reaction only seems to take place in the bicontinuous part of the phase

diagram, showing the importance of the structure of microemulsion on the reactivity [24].

Wacker process in formamide microemulsions [25]

The Wacker process for the catalytic oxidation of alkenes is an important industrial process which has been in widespread use for the last 20 years. It involves the transformation of a terminal olefin, $\text{RCH}=\text{CH}_2$ into a ketone RCOMe by water, using a palladium(II) salt as a catalyst:



We investigated the Wacker process in; (1) biphasic media, replacing the usual dimethylformamide by formamide, and, (2) homogeneous media using a standard formamide microemulsion (the pseudo-ternary phase diagram is shown in Fig. 9). The results obtained in DMF-H₂O, HCONH₂ and H₂O, and in microemulsions M and N are shown in Fig. 10.

The reaction carried out in DMF-water started after an induction period of around 100 min. This delay can be attributed to poor contact between the reactants and the catalyst.

No reaction could be detected in the HCONH₂-water mixture, owing either to poor contact with the catalyst or strong complexation of palladium by formamide.

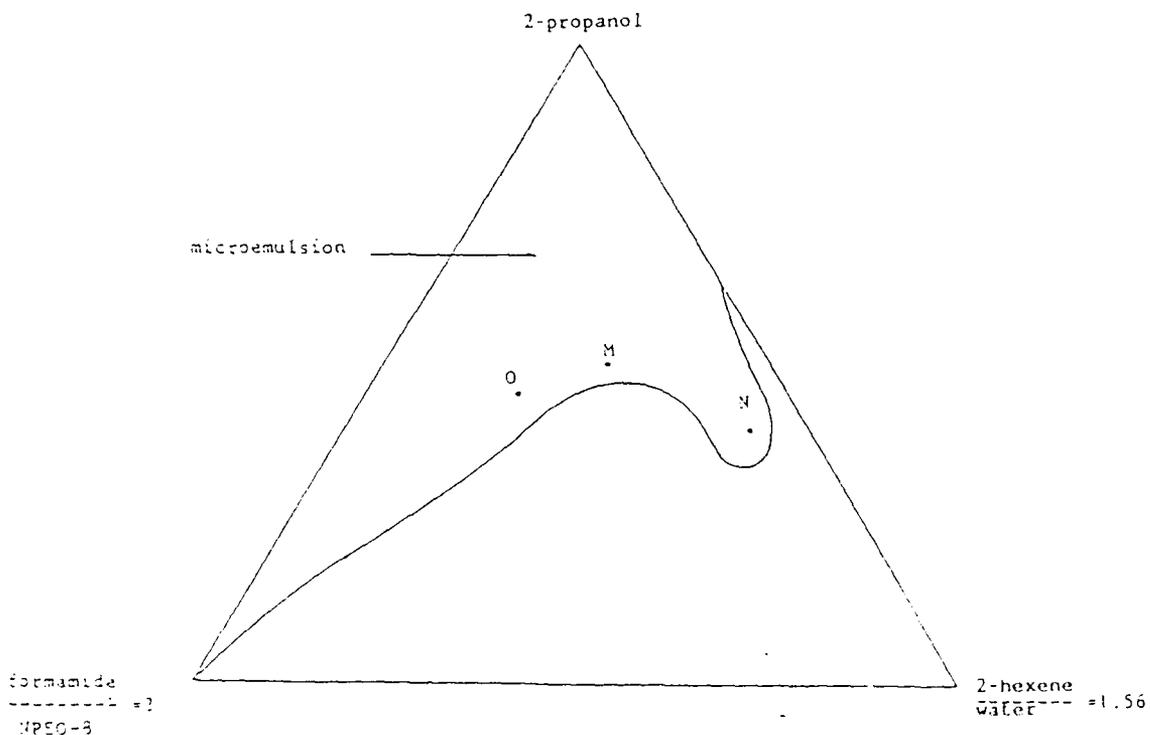


Fig. 9. Phase diagram of the Wacker catalytic microemulsion system HCONH_2 - $\text{C}_6\text{H}_{11}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_8\text{OH}$ (2:1 w/w)-propan-2-ol-hex-1-ene/water (1.56:1 w/w).

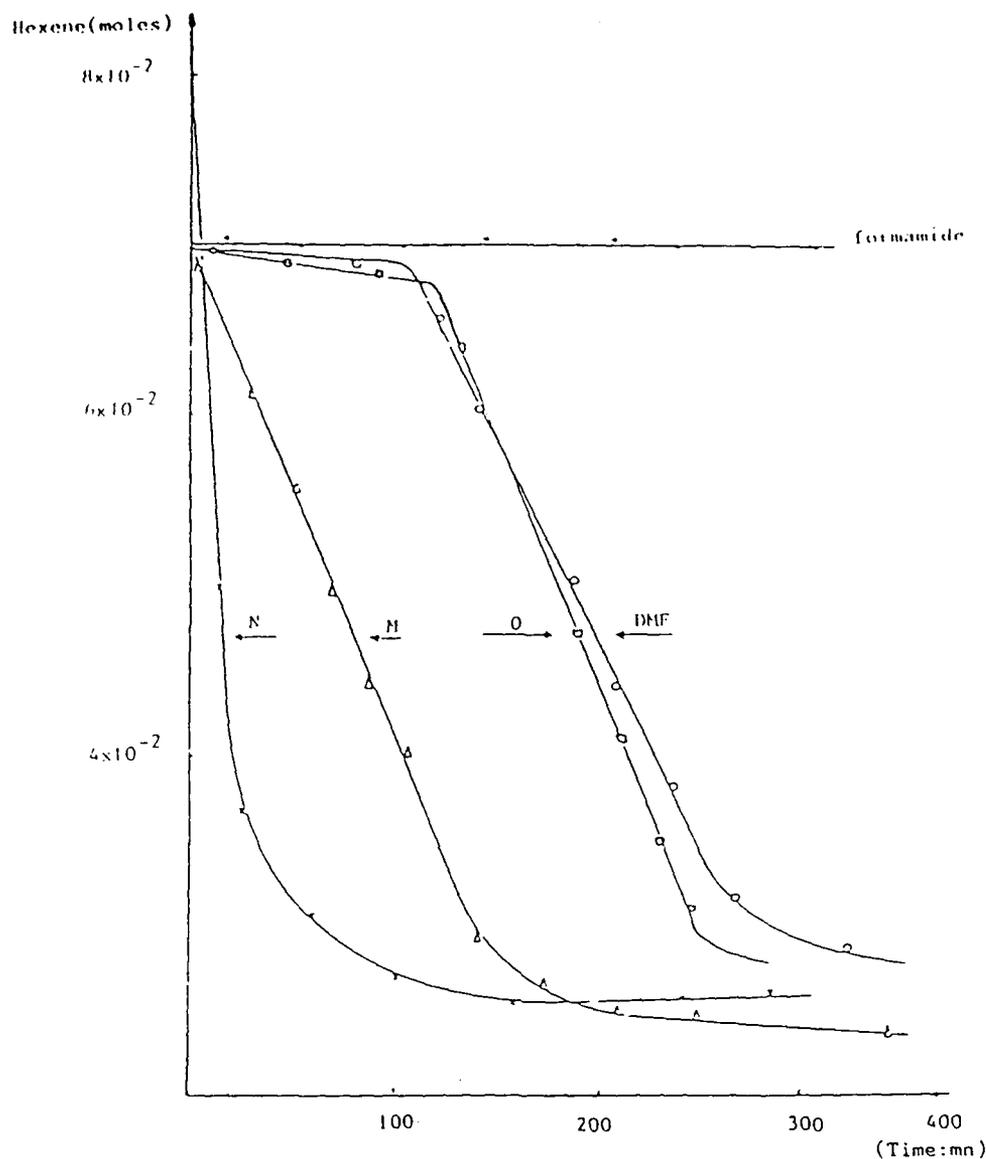


Fig. 10. Kinetics of Wacker oxidation of hex-1-ene in DMF-H₂O (O), HCONH₂-H₂O (+) and microemulsions M (Δ) and N (×).

In the microemulsion (M and N) the main feature was the absence of an induction period. In such homogeneous media, there is good contact between reactants and catalyst and the reaction starts immediately. It should also be noted that the overall reaction was faster than in the water-DMF mixture, particularly in the olefin-rich microemulsion N with a three-fold increase in reaction velocity over the classical medium. This approach shows considerable promise owing to the absence of an induction period and an increase in overall reaction velocity. The difference in reactivity depending on the nature of the

microemulsion represents another example of the relationship between structure and reactivity.

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PART II - OXIDATIONS BY HYDROPEROXIDES IN MICROEMULSIONS

E. OLIVEROS and M.-T. MAURETTE

INTRODUCTION

Microemulsions may be used to influence pathways, yields and rates of organic reactions. Due to the microheterogeneous nature of these systems, different solubilization sites (oil phase, water phase, interface) are available to a large variety of substrates and microemulsions have a high solubilizing capability. Moreover, interaction of water soluble reactants and organic substances sparingly soluble in water is made possible by the dynamic structure of these systems.

In our project, we planned to test different ionic microemulsions for a potential catalytic effect on the oxidative degradation of model compounds solubilized in microemulsions containing hydroperoxides, such as hydrogen peroxide and *tert*-butyl hydroperoxide or sodium perborate. We did not aim at a direct application of the results to practical purposes of decontamination, however the information gained from model investigations could be valuable for the preparation of new decontamination mixtures.

Our work contains two main topics:

1) The preparation of four components microemulsions based on cationic or anionic surfactants and containing hydrogen peroxide, *tert*-butyl hydroperoxide or perborate, and the study of the effect of the hydroperoxides on the pseudo-ternary phase diagrams of microemulsions.

2) Kinetic investigations on the reactivity of the hydroperoxides towards solubilized organic substrates, mainly 1,4-naphthoquinone, and comparison of the efficiencies of these oxidation reactions in homogeneous and microheterogeneous media.

As indicated in the project submitted for the third year of contract, the work on the hydrogen peroxide reactivity has been done in close collaboration with Dr. A. M. Braun (EPFL, Lausanne, Switzerland).

PREPARATION OF MICROEMULSIONS

1) Microemulsions containing H_2O_2

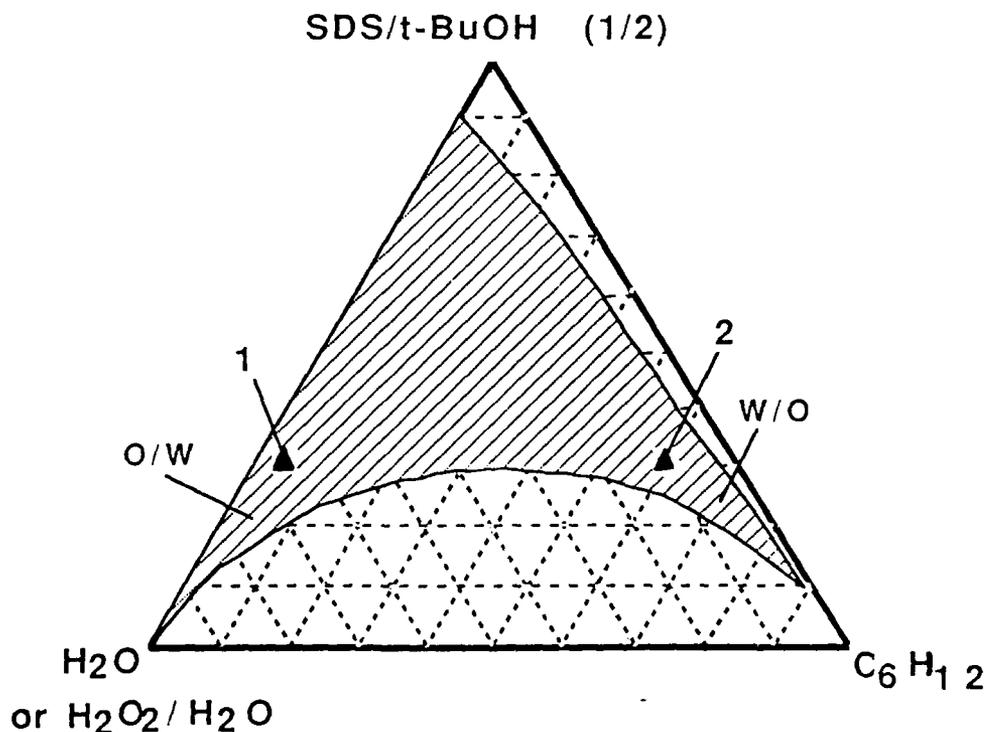
The effect of the addition of H_2O_2 on the pseudo-ternary phase diagrams of four components systems (surfactant, cosurfactant, hydrocarbon, water) has been studied. A possible modification of the extent and shape of the monophasic domain of microemulsions, O/W (micellar-like) as well as W/O (reversed), has been checked.

Different anionic and cationic surfactants have been used:

- sodium dodecyl sulfate (SDS) and lithium dodecyl sulfate,
- benzyl dimethyl tetradecyl ammonium chloride (BDMTAC) and cetyl dimethyl pyridinium chloride.

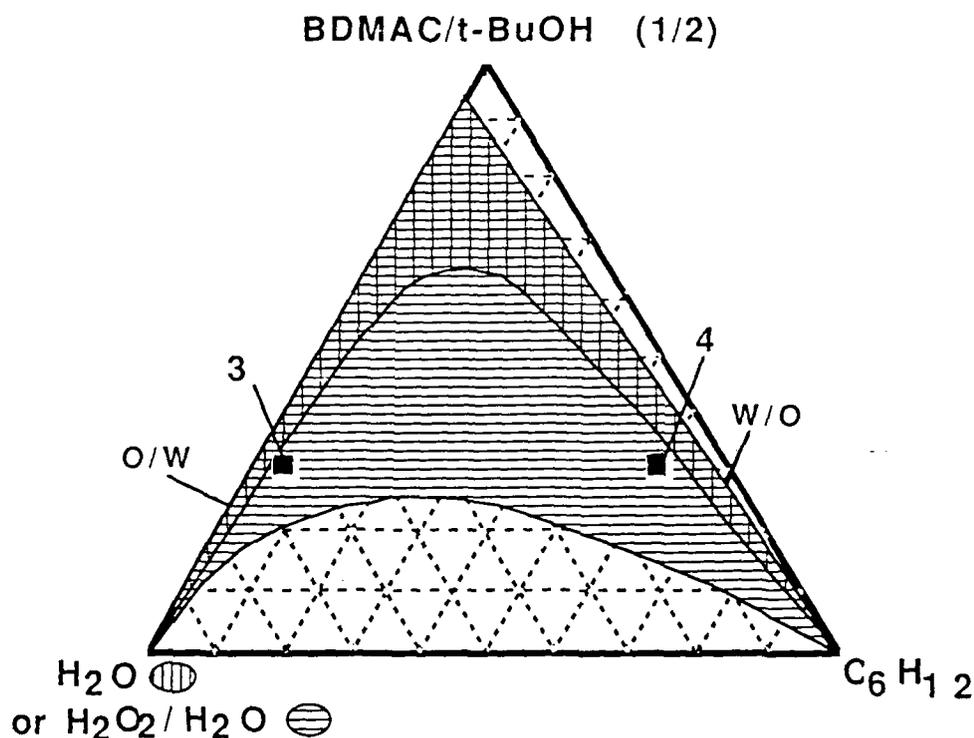
n-Butanol (BuOH) or *tert*-butanol (t-BuOH) have been used as cosurfactants and cyclohexane as hydrocarbon.

Figure 1. Pseudo-ternary phase diagram of microemulsions containing sodium dodecyl sulfate (SDS) as surfactant, t-BuOH as cosurfactant, cyclohexane, H_2O or 30% H_2O_2/H_2O (diagram in weight %); ▲: composition of the microemulsions used for the kinetic experiments.



With the anionic surfactants, no change in the monophasic domain of microemulsions was observed when water is replaced by 30% H_2O_2 in water (figure 1). However, in the case of cationic surfactants, a larger domain is obtained in presence of H_2O_2 , its shape being similar to the microemulsions based on anionic surfactants (figure 2). It should be noted that ammonium bromides cannot be used as surfactants because they are instantaneously oxidized by H_2O_2 .

Figure 2. Pseudo-ternary phase diagram of microemulsions containing benzyl dimethyl tetradecyl ammonium chloride (BDMTAC) as surfactant, t-BuOH as cosurfactant, cyclohexane, H_2O or 30% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (diagram in weight %); ■: composition of the microemulsions used for the kinetic experiments.



The same pseudo-ternary phase diagrams are obtained with BuOH and t-BuOH. The latter being an efficient trap for HO^\cdot radicals and being less reactive with H_2O_2 , microemulsions containing this cosurfactant have been prepared for the kinetic studies of the reactivity of HOO^\cdot (*vide infra*). Moreover, it has been shown in Dr. Braun's group that the rate of decomposition of H_2O_2 is slower in t-BuOH containing microemulsions than in those containing BuOH.

We tried to determine the concentration of H_2O_2 in microemulsions by density measurements. However, this method is only applicable to O/W microemulsions (aqueous continuous phase). Unreliable results are obtained in the case of reversed (W/O) systems.

The iodometric method was finally chosen for the titration of H_2O_2 . Even if somewhat less accurate than the titrimetric method with potassium permanganate, it presents the advantage of avoiding secondary reactions with the cosurfactant or the surfactant (ammonium salts).

The stability of H_2O_2 in microemulsions depends, as in aqueous solution, on the pH of the medium. At an apparent pH below 5, the H_2O_2 containing microemulsions remain stable for months.

The microemulsions used for the kinetic experiments are numbered from 1 to 4 in figures 1 and 2.

2) Microemulsions containing *tert*-butyl hydroperoxide (t-BuOOH)

We made the hypothesis that t-BuOOH itself can act as a cosurfactant in a microemulsion, as does t-BuOH [1] or *tert*-amyl alcohol [2]. Indeed, microemulsions could be prepared using a commercial aqueous solution containing 70% of t-BuOOH, a cationic or an anionic surfactant, cyclohexane and various amounts of added water. The pseudo-ternary phase diagrams are very close to those obtained with mixtures containing t-BuOH, water and the corresponding surfactant. Microemulsions containing an amount of water lower than 22% of the total weight of surfactant-cosurfactant-water in the mixture cannot be prepared due to the use of an aqueous solution of t-BuOOH. W/O microemulsions of the same composition as 3 and 4 (cationic surfactant, figure 2) and containing t-BuOOH are not monophasic (3 and 4 are not included in the monophasic region of the H_2O/t -BuOOH diagram which is similar to the diagram H_2O/t -BuOH in figure 2).

3) Microemulsions containing sodium perborate

Sodium perborate is a cheap, non-toxic, large scale industrial chemical. It is a stable and easy to handle oxidant and it has been shown that it is an useful reagent for the oxidation of a variety of functional groups under mild conditions in organic synthesis [3]. We made preliminary experiments on the use of sodium perborate in microemulsions.

Sodium perborate is not very soluble in water or microemulsions. As it is a salt, its dissolution into microemulsions induces a change in the extent and shape of the

pseudo-ternary phase diagram: more specifically, microemulsions close to the lower demixing line in the absence of salt can become biphasic or triphasic by adding salt [4]. We could however prepare an O/W microemulsion containing SDS as surfactant and saturated with sodium perborate (the overall composition of the mixture is the same as the one of microemulsion 1, figure 1). Comparative kinetic experiments have been made with this microemulsion. Only qualitative comparisons were possible with mixtures containing cationic surfactants.

KINETICS OF OXIDATION BY H_2O_2 IN MICROEMULSIONS

The intermediates of the decomposition of H_2O_2 are hydroperoxide anion (HOO^-), superoxide anion (O_2^-), and hydroxyl radical (HO^\cdot).

We have focussed our work on the study of oxidative degradations involving as the first step a nucleophilic addition of HOO^- . We have mainly investigated the oxidation of a model compound, 1,4-naphthoquinone (1,4-NQ), in homogeneous solution and in O/W, as well as in W/O, microemulsions containing an anionic or a cationic surfactant.

The sequence of reactions indicated in scheme 1 (see next page) might be proposed for the oxidation of 1,4-NQ by H_2O_2 . The nucleophilic addition of HOO^- to give a red coloured intermediate is followed by epoxide formation and further oxidation.

1) Oxidation of 1,4-NQ by H_2O_2 in homogeneous solutions

The rate of decomposition of H_2O_2 depends strongly on the concentration of the deprotonated H_2O_2 (HOO^-). Hence, the rate of decomposition increases with the pH of the solution (see A.M. Braun, final report, EPFL, Lausanne) and specific reactions of the deprotonated form should be also enhanced. Reference experiments have been performed in homogeneous solution. The solutions consist of a mixture of 65% H_2O_2 and 35% t-BuOH (in weight), t-BuOH being also used as the cosurfactant in the microemulsions. Experiments have been performed at 3 apparent pH: about 3.6, 4.8 and 7.2 (the two latter pH have been adjusted by adding a few microliters of a NaOH solution). Concentrations of 1,4-NQ are about 6.2×10^{-4} mol.l⁻¹ (100 μ l of a methanolic solution in 3 cm⁻³ of H_2O_2 solution).

The consumption of 1,4-NQ and the formation and disappearance of the coloured intermediate have been followed spectrophotometrically (figure 3). At pH 3.6, the oxidation of 1,4-NQ is slow and the total bleaching of the solution is only

observed after several days. The reaction is faster, as expected, at pH 4.8 and, at pH 7.2, the intermediate is formed instantaneously at the time scale of our experiments. The intermediate shows a weak absorption maximum at about 460 nm.

Scheme 1. Reaction of hydroperoxide anion (HOO^-) with 1,4-naphthoquinone (1,4-NQ)

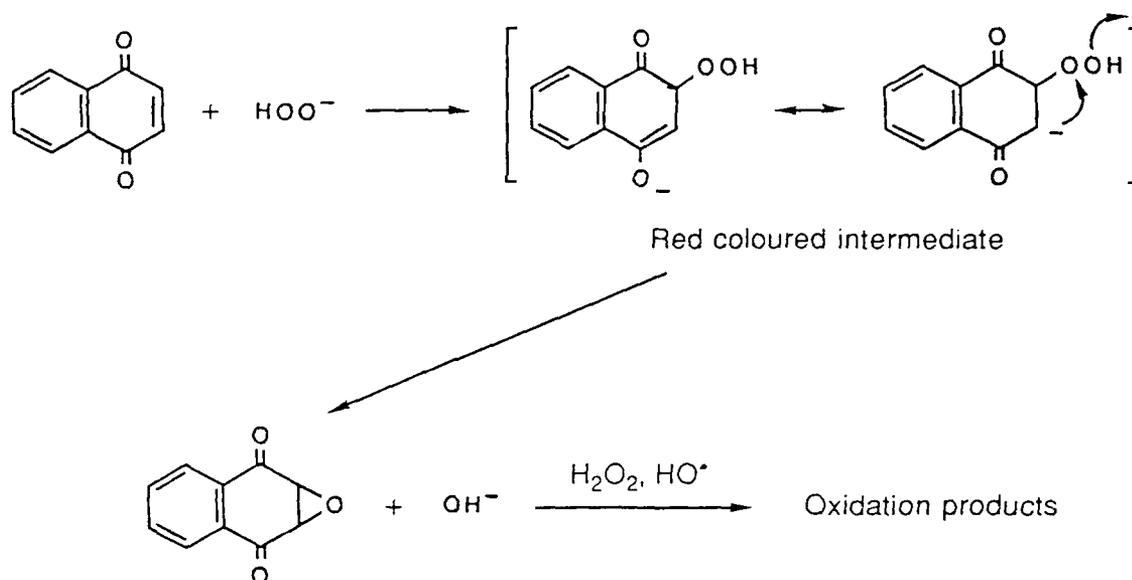
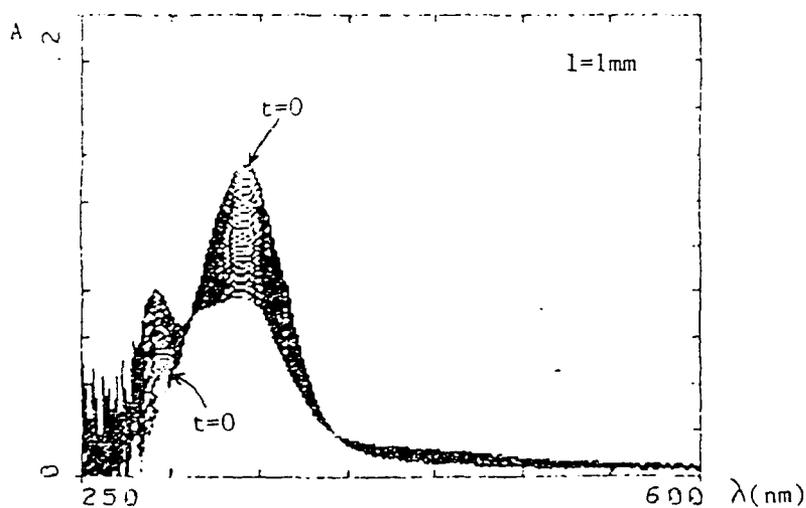


Figure 3. Oxidation of 1,4-NQ by H_2O_2 in a mixture of 30% H_2O_2 in water and *t*-BuOH (65%/35% in weight) observed spectrophotometrically during 14 hours at an apparent pH 3.6.



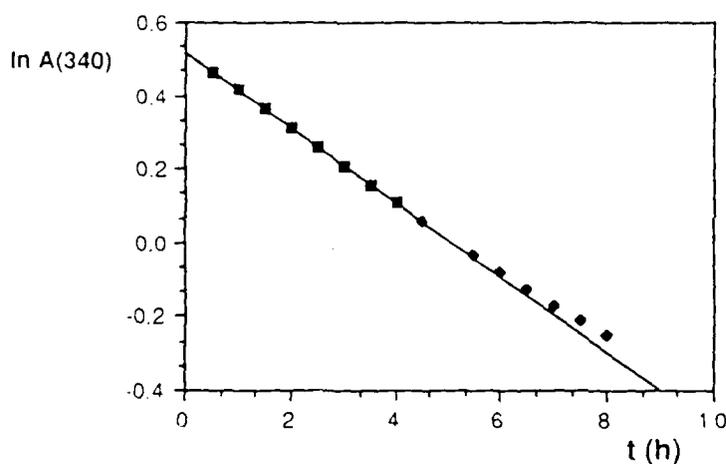
Considering the large excess concentration of H_2O_2 (about 5 mol.l^{-1}), the concentration of HOO^- is remaining practically constant during the observed reaction. Consequently, the kinetics of the consumption of 1,4-NQ (and of formation of the intermediate I) should be pseudo-first order. The kinetic laws of 2 first order consecutive reactions,



could then be used to analyse the oxidation kinetics.

Figure 4 shows that indeed the consumption of 1,4-NQ is *pseudo-first order* at the beginning of the reaction, the deviation from the logarithmic linear plot of the 1,4-NQ absorbance at 340 nm being only observed after the intermediate, which also absorbs in the same region although with a smaller ϵ , is present in appreciable amount.

Figure 4. Kinetics of consumption of 1,4-NQ by reaction with H_2O_2 in a mixture of 30% H_2O_2 in water and *t*-BuOH (65%/35% in weight) at an apparent pH 3.6 (1,4-NQ consumption followed spectrophotometrically).

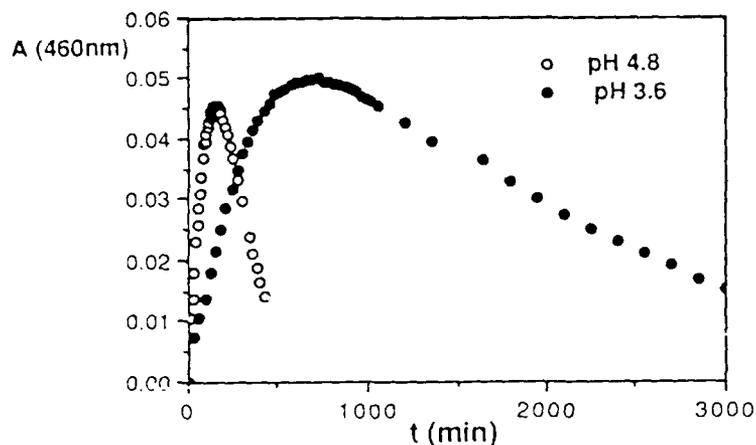


The formation and disappearance of the intermediate follow the kinetic laws of 2 consecutive first order reactions: figure 5 shows two examples of the corresponding plots ($A(460\text{nm}) = f(t)$) for apparent pH 3.6 and 4.8.

The rate constants k_1 and k_2 can be calculated by determining, first, k_1 using equation 2:

$$[\text{NQ}] = [\text{NQ}]_0 \exp(-k_1 t) \quad (2)$$

Figure 5. Reaction of 1,4-NQ with H_2O_2 in a mixture of 30% H_2O_2 in water and t-BuOH (65%/35% in weight) at two apparent pH: formation and disappearance of the intermediate followed spectrophotometrically.



The concentration of the intermediate being given by equation 3,

$$[I]_t = [\text{NQ}]_0 \frac{k_1}{k_2 - k_1} \{ \exp(-k_1 t) - \exp(-k_2 t) \} \quad (3)$$

its concentration is maximum at time t_{max} :

$$t_{\text{max}} = \frac{1}{k_2 - k_1} \ln \frac{k_2}{k_1} \quad (4)$$

Then, knowing k_1 , k_2 can be calculated by measuring t_{max} and solving equation 3.

The nucleophilic addition of HOO^- on 1,4-NQ at $\text{pH} > 7$ becomes so fast that we cannot follow any longer the consumption of the substrate. The intermediate is formed instantaneously at the time scale of our experiments and only the disappearance of the intermediate can be observed (figure 6). We fixed, therefore, a minimum time for the first spectroscopic measurements and evaluated a minimum value of k_1 after experimental determination of k_2 at a reaction time for which we assume that only minor concentrations of the original substrate are present.

The values of k_1 and k_2 in homogeneous solution at different pH are reported in table 1. As expected, increasing the pH increases both rate constants k_1 (nucleophilic addition of HOO^-) and k_2 (epoxidation of the intermediate), the effect being more pronounced for k_1 . Fitting the experimental curves of the absorbance of the intermediate in function of time to the theoretical curve (equation 3) calculated from the values k_1 and k_2 gives a molar absorption coefficient of the intermediate at 460 nm of about $200 \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ at pH 3.6 and 4.8.

Figure 6. Reaction of 1,4-NQ with H_2O_2 in a mixture of 30% H_2O_2 in water and t-BuOH (65%/35% in weight) at an apparent pH 7.2: disappearance of the intermediate.

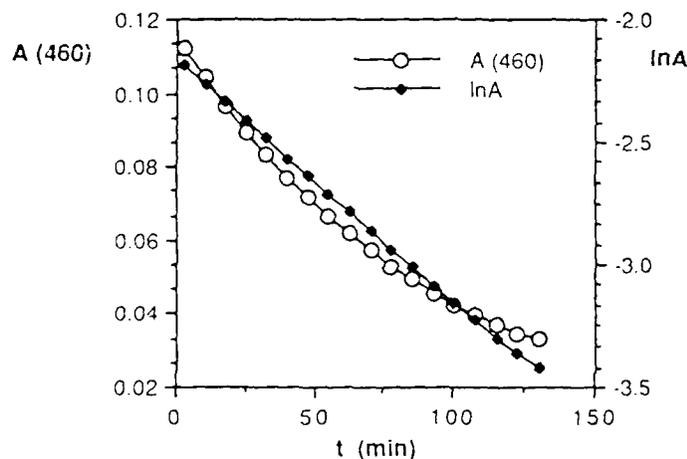


Table 1. Rate constants of the reaction of 1,4-naphthoquinone (1,4-NQ) with H_2O_2 in a solution containing 30% H_2O_2 in water and t-BuOH (65%/35% in weight) at different pH (reaction temperature: 25-27°C).

pH	k_1 [s^{-1}]	k_2 [s^{-1}]	t_{max} [s]
3.6	2.9×10^{-5}	1.7×10^{-5}	43600
4.8	1.6×10^{-4}	8.0×10^{-5}	8820
7.2	> 0.25 b)	1.6×10^{-4}	≤ 30 a)

a) Minimum time required between dissolving 1,4-NQ and the first spectrophotometric measurement.

b) Minimum value calculated from equation 4.

2) Oxidation of 1,4-NQ by H₂O₂ in microemulsions

After having established the reference values of k_1 and k_2 in homogeneous solutions, the same experiments could be carried out in microemulsions.

O/W microemulsions contain 65% H₂O₂/H₂O as in homogeneous solution, 5% cyclohexane and 30% surfactant/cosurfactant (1/2) (figures 1 and 2, microemulsions 1 (SDS) and 3 (BDMTAC)).

W/O microemulsions contain 10% H₂O₂/H₂O (corresponding to a H₂O₂ concentration of about 1 mol.l⁻¹), 60% cyclohexane and 30% surfactant/cosurfactant (1/2) (figures 1 and 2, microemulsions 2 (SDS) and 4 (BDMTAC)).

Apparent pH adjustments [5, 6] and spectrophotometric measurements in microheterogeneous systems are very difficult to achieve in a reproducible manner. The corresponding values of k_1 and k_2 are, hence, calculated with a limit of error of about 20-30%. In the case of W/O microemulsions, we have added the same quantity of NaOH solution as in the corresponding O/W microemulsions to increase the pH of the medium, the measured apparent values of the pH with the microelectrode being unreliable in this case.

Table 2. Rate constants of the reaction of 1,4 naphthoquinone (1,4-NQ) with H₂O₂ in anionic and cationic O/W microemulsions (1 and 3, figures 1 and 2) at different apparent pH (reaction temperature: 25-27°C).

Surfactant	pH	k_1 [s ⁻¹]	k_2 [s ⁻¹]	t_{\max} [s]
HS ^{a)}	3.6	2.9×10^{-5}	1.7×10^{-5}	43600
SDS	3.8	9.2×10^{-5}	6.7×10^{-5}	12600
BDMTAC	3.6	9.8×10^{-5}	7.5×10^{-7}	50000
HS ^{a)}	4.8	1.6×10^{-4}	8.0×10^{-5}	8820
SDS	4.8	3.9×10^{-4}	1.9×10^{-4}	3600
BDMTAC	4.8	2.7×10^{-4}	6.9×10^{-6}	14100
HS ^{a)}	7.2	≥ 0.25 ^{b)}	1.6×10^{-4}	≤ 30 ^{c)}
SDS	7.2	≥ 0.21 ^{b)}	3.7×10^{-4}	≤ 30 ^{c)}
BDMTAC	7.2	9.5×10^{-4}	1.2×10^{-4}	2500

a) Results in homogeneous solution (HS) are given for comparison; b) Minimum value calculated from equation 4; c) Minimum time required between dissolving 1,4-NQ and the first spectrophotometric measurement.

2.1. O/W microemulsions

We deduce from the data in table 2 that the rate constants of both steps of the oxidative degradation of 1,4-NQ (k_1 , nucleophilic addition of HOO^- and k_2 , epoxidation of the intermediate, see scheme 1) are enhanced in SDS microemulsions by a factor of about 2.5 to 4, compared to the reactions in homogeneous solution. The effect of the pH is very similar in both media.

The substrate seems more protected when solubilized in positively charged aggregates. The nucleophilic addition of HOO^- remains more efficient than in homogeneous solution at low pH, but, as the pH increases, the effect is reversed (table 2). Two explanations might be given: a local pH effect near the interface of these microheterogeneous systems, affecting the deprotonation of H_2O_2 , or/and a possible ionic binding between HOO^- and the positively charged aggregate, preventing a nucleophilic addition. The slow reactivity of the negatively charged intermediate in these systems can be well explained by its stabilization by coulombic interactions with the positively charged Stern layer of the microemulsion. This stabilization seems relatively more pronounced at low pH (compare the ratio of the k_2 values in homogeneous solution and in BDMTAC microemulsion at the 3 different pH, table 2). The effect of the pH in the positively charged microemulsions follows the same general trend as in the other media, but in this case, is apparently greater on k_2 than on k_1 .

Table 3. Rate constants of the reaction of 1,4 naphthoquinone (1,4-NQ) with H_2O_2 in anionic and cationic O/W microemulsions (1 and 3, figures 1 and 2) at different apparent pH at 20°C.

Surfactant	pH	k_1 [s ⁻¹]	k_2 [s ⁻¹]	t_{max} [s]
BDMTAC	3.8	1.2×10^{-5}	$< 5 \times 10^{-7}$	>265000
SDS	4.8	2.3×10^{-4}	8.7×10^{-5}	6800
BDMTAC	4.8	2.5×10^{-4}	$< 10^{-7}$	155000
SDS	7.3	$\geq 0.25^{\text{a}}$	1.4×10^{-4}	$\leq 30^{\text{b}}$
BDMTAC	7.3	1.9×10^{-4}	1.2×10^{-5}	15700

a) Minimum value calculated from equation 4.

b) Minimum time required between dissolving 1,4-NQ and the first spectrophotometric measurement.

The degradative oxidation of 1,4-NQ by H_2O_2 is sensitive to the temperature, as shown by comparative experiments made at 20°C (table 3). Experiments in BDMTAC microemulsions at low pH become very slow.

It should be noted that it is possible to form a coloured intermediate, similar to the one resulting from the nucleophilic addition of HOO^- , by dissolving 1,4-NQ in aqueous NaOH at pH 11. This intermediate is formed slowly already at an apparent pH 7.5 in SDS microemulsions. However, the nucleophilic attack of HO^- is, as expected, far less efficient than that of HOO^- .

2.2.) W/O microemulsions

No reaction is observed, even after several days, in W/O microemulsions without addition of NaOH in the reaction medium, despite the fact that the H_2O_2 concentration is similar to the one in O/W microemulsions (the overall concentration is lower, about 1 mol.l^{-1} , but the local concentration in the aqueous dispersed phase should be multiplied by at least a factor of 4). This result might be explained by the absence of a local concentration effect on the 1,4-NQ in the reversed microemulsions, as the quinone is mainly solubilized in the hydrocarbon continuous phase.

By increasing the HO^- concentration, the rate constants k_1 and k_2 increase. However the reactions are not faster than in the corresponding O/W microemulsions (table 4), although the local pH should be higher in the reversed microemulsions (10% aqueous phase).

Table 4. Rate constants of the reaction of 1,4 naphthoquinone (1,4-NQ) with H_2O_2 in anionic and cationic W/O microemulsions (2 and 4, figures 1 and 2) at different NaOH concentration at 20°C.

Surfactant	pH ^{a)}	k_1 [s ⁻¹]	k_2 [s ⁻¹]	t_{\max} [s]
SDS	4.8 ^{a)}	1.1×10^{-4}	3.2×10^{-4}	5000
BDMTAC	4.8 ^{a)}	1.1×10^{-4}	$< 10^{-7}$	100000
SDS	7.3 ^{a)}	4.5×10^{-3}	7.8×10^{-4}	475
BDMTAC	7.3 ^{a)}	1.6×10^{-3}	2.8×10^{-6}	4100

^{a)} Apparent pH of the corresponding O/W microemulsion in which the same volume of NaOH solution has been added

As in O/W microemulsions, the intermediate is stabilized at the positively charged interface of microemulsions containing a cationic surfactant (BDMTAC) compared to those containing SDS.

OXIDATION OF 1,4-NQ BY T-BUOOH IN MICROEMULSIONS

The oxidative degradation of 1,4-NQ has been studied in homogeneous medium (65% t-BuOOH in H₂O) and in O/W and W/O SDS microemulsions. The O/W microemulsion contains 65% H₂O, 5% C₆H₁₂, 30% SDS/t-BuOOH (1/2), the W/O 10% H₂O, 60% , 30% SDS/t-BuOOH (1/2) (see figure 1, microemulsions 1 and 2, t-BuOOH instead of t-BuOH).

Data in table 5 show that t-BuOOH is much less reactive than H₂O₂ towards 1,4-NQ and the reaction could only be studied at an apparent pH 7.3.

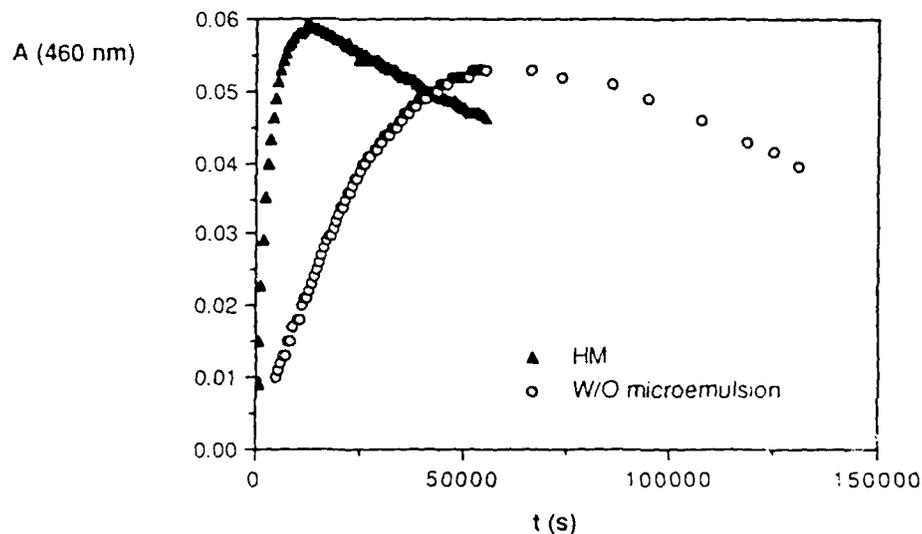
Table 5. Rate constants of the reaction of 1,4 naphthoquinone (1,4-NQ) with t-BuOOH in homogeneous medium (HM) and in anionic O/W and W/O microemulsions (1 and 2, figure 1, t-BuOOH instead of t-BuOH) at an apparent pH 7.3 at 20°C.

Surfactant	k_1 [s ⁻¹]	k_2 [s ⁻¹]	t_{\max} [s]
HM	5.8×10^{-4}	1.8×10^{-6}	10000
SDS (O/W)	1.6×10^{-4}	1.8×10^{-6}	27000
SDS (W/O)	1.6×10^{-5}	1.65×10^{-5}	62400

In homogeneous solution, the reaction follows a similar pattern as already seen for H₂O₂ (figure 7).

In the SDS O/W microemulsions, we might have expected an enhanced rate of the nucleophilic attack of t-BuOOH as both reactants (1,4-NQ and t-BuOOH) are located in the micelles. However, this is not the case due to the fact that the local pH is probably lower than in the bulk aqueous phase and the pH effect is partially lost. The oxidation of 1,4-NQ is even slower in the reversed microemulsion (figure 7), although the intermediate rearranges with a higher rate constant k_2 .

Figure 7. Reaction of 1,4-NQ with t-BuOOH in homogeneous medium (HM) and in a W/O SDS microemulsion at an apparent pH 7.3: formation and disappearance of the intermediate followed spectrophotometrically.



OXIDATION OF MISCELLANEOUS COMPOUNDS BY SODIUM PERBORATE IN MICROEMULSIONS

Solutions and O/W microemulsions saturated with sodium perborate show an apparent pH of about 11. Hence, the oxidative degradation of 1,4-NQ by HOO^- produced *in situ* is very fast.

If the pH is reduced by acidifying, the evolution of the reaction can be followed and is similar to the corresponding media containing H_2O_2 (figure 8).

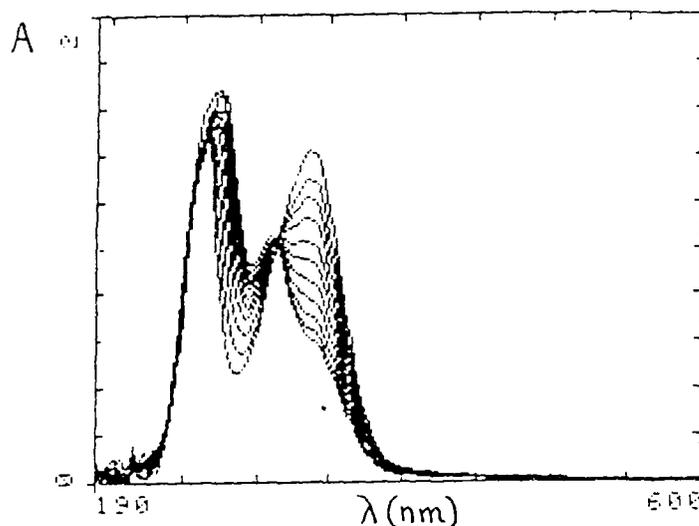
Some qualitative experiments have been carried out concerning the oxidation of sulfides and dihydroxy naphthalenes by sodium perborate in microemulsions.

As for 1,4-NQ, the reactions are much faster than in the same microemulsions containing H_2O_2 .

With 1,3-dihydroxy naphthalene, the first step is the formation of 2-hydroxy naphthoquinone (lawsone) which is then oxidized further in a similar way as 1,4-NQ (see Dr. Braun's report). Phenyl sulfide is degraded but neither phenyl sulfone nor phenyl sulfoxide, obtained in acetic acid [3], are produced in these conditions. In

these cases, the reactions seem faster in cationic microheterogeneous systems. Further studies could not be carried out due to lack of time.

Figure 8. Oxidation of 1,4-NQ in a SDS O/W microemulsion saturated with sodium perborate and acidified to an apparent pH 7.3: the reaction has been followed spectrophotometrically during 14h.



CONCLUSION

Under the present contract, O/W and W/O microemulsions containing hydrogen peroxide, *tert*-butyl hydroperoxide or sodium perborate have been formulated and employed for investigations on the reactivity of hydroperoxide and peroxide anions towards solubilized organic substrates, mainly 1,4-naphthoquinone.

The rate of oxidative degradation by H_2O_2 depends strongly on the concentration of HOO^- , and best results have been found for 1,4-NQ in negatively charged O/W microheterogeneous systems, the pH of which has been adjusted, in order to trigger the reaction. Microemulsions containing cationic surfactants slow down the reaction by stabilizing the negatively charged intermediate. Reversed W/O microemulsions are less efficient than the corresponding O/W systems, due probably to the absence of a local concentration effect on the substrate.

Tert-butyl hydroperoxide reacts more slowly than H_2O_2 and no enhancing effect of the microheterogeneous systems has been found: it is probable that the local pH at the interface, where *t*-BuOOH is mainly located, remains lower than in aqueous phase.

Sodium perborate is an efficient oxidizing agent in microemulsions containing cationic, as well as anionic, surfactants. Further work would be needed to ascertain its potential interest for decontamination applications.

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Financial Statement

As of May 31, 1989, the equivalent of US \$ 65,915 have been paid in salaries and overhead, leaving no unused funds.

Toulouse, June 9, 1989

A handwritten signature in black ink, appearing to be 'A. Lattes', written in a cursive style.

Pr. A. LATTES

A handwritten signature in black ink, appearing to be 'M.-T. Maurette', written in a cursive style.

Dr. M.-T. MAURETTE