

# Analogy between micelles and polymers of ionic surfactants

## A capillary isotachophoretic study of small ionic aggregates in water–organic solutions

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### ABSTRACT

Capillary isotachopheresis (ITP) was applied to monitoring the synthesis of cationic polymers by  $\gamma$ -irradiation of various dodecyl- and hexadecylallyldimethylammonium and dodecylvinylimidazolium salts in aqueous solutions at concentrations considerably exceeding their respective critical micellar concentrations (CMC). The isotachopherograms obtained under both acidic and basic water–methanol electrolyte conditions showed distinctive steps for polymer and monomer surfactants, and also for amine (oxide) degradation products. This enables one to determine the amount of remaining monomer as a function of irradiation time, surfactant counter ion and initial monomer concentration. It was found, as far as the polymerization yield was concerned, that halide counter ions played a special (favourable or unfavourable) part in the polymerization reaction, and that bromide was the most suitable ion associated with allylic surfactants. An optimum irradiation time of *ca.* 25 h was determined for these allylic species, above which the ratio of degradation products was observed to increase markedly. Likewise, the initial monomer concentration should not exceed a second critical concentration, beyond which the polymerization yield would fall drastically. In addition, it was ascertained that when the reaction was allowed to take place in an isotropic medium (*i.e.*, at a concentration below the CMC), only low-mobility degradation products were obtained. ITP also appeared to be well adapted to the physico-chemical characterization of these ionic polymerized surfactants. This method enables polymers to be compared with dynamic micelles. The mobility of the polymers was found to be much greater than that of the starting monomer and close to that of a classical dynamic micelle. The analysis of fractions obtained from ultrafiltration assays revealed that their molecular weight was higher than 5000 g/mol. Hence it can be expected to be of the same order of magnitude than that of dynamic micelles. However, unlike the latter, the polymers remain stable in methanolic solutions and for monomer equivalent concentrations less than the CMC. Lastly, the degree of counter-ion binding, also determinable from isotachopherograms, is much higher for the polymers than for the ionic micelles. Nevertheless, these properties overall justify the term polymerized micelles currently applied to these polymers.

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### INTRODUCTION

During the last decade, the use of surfactants has shown impressive development and, whereas initially it was confined to applications as detergents and for emulsion stabilization, it has recently gained

diversity. The application area of surfactants has even entered the field of fine reagents for analytical

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or preparative chemistry in techniques such as micellar liquid chromatography [1], sodium dodecyl sulphate–polyacrylamide gel electrophoresis (SDS-PAGE) [2], micellar electrokinetic capillary chromatography (MECC) [3], liquid–liquid extraction [4], ultrafiltration [5] and micellar catalysis [6].

Of special interest are the permanently ionic or ionizable surfactants because the aggregates they form in solution (micelles, vesicles) are less disperse than those given by their neutral counterparts. In addition, they are generally commercially available in great purity. Nevertheless, these supramolecular structures have a dynamic character and are chemically fragile, as they must be inevitably in equilibrium with a fixed concentration of the free form of the surfactant. For the case of micelles, this concentration, commonly called the critical micellar concentration (CMC), is typically much higher in organic (or even water–organic) media than in water, so that most of the time the micelle structure can neither be observed nor exploited in those media. Further, non-aggregated species can cross ultrafiltration membranes and hence contaminate ultrafiltrates.

This has been an incentive to investigate ways for stabilizing these aggregates and, among others, the idea of polymerizing surfactants while they are

entangled in a supramolecular structure seemed appealing [7,8]. In this direction, the synthesis of surfactants containing one unsaturated bond was soon realized, leading, for instance, to products such as polyallyldimethyldodecylammonium (poly-ADMDA<sup>+</sup>) bromide [9] and polydodecylvinylimidazolium (polyDVI<sup>+</sup>) iodide [10], as depicted in Fig. 1.

The analytical characterization of the polymers produced is not easy and most often so far, general non-separative techniques have been preferred (<sup>1</sup>H NMR, fluorescence decay, light scattering, etc.). However, capillary isotachoresis (ITP) was recently shown to be an appropriate separation technique for characterizing high-molecular-weight ionogenic polymers and copolymers of various types (with respect to their charge and irrespective of their molecular weight) [11,12]. On the other hand, the lack of a versatile high-performance separation and detection technique allowing the discrimination between surfactant homologues or compounds of the same group recently prompted us to develop closely related ITP methods which are suitable for most groups of monomeric ionic surfactants [13]. In addition, ITP was shown to provide an easy means of estimating the physico-chemical parameters per-

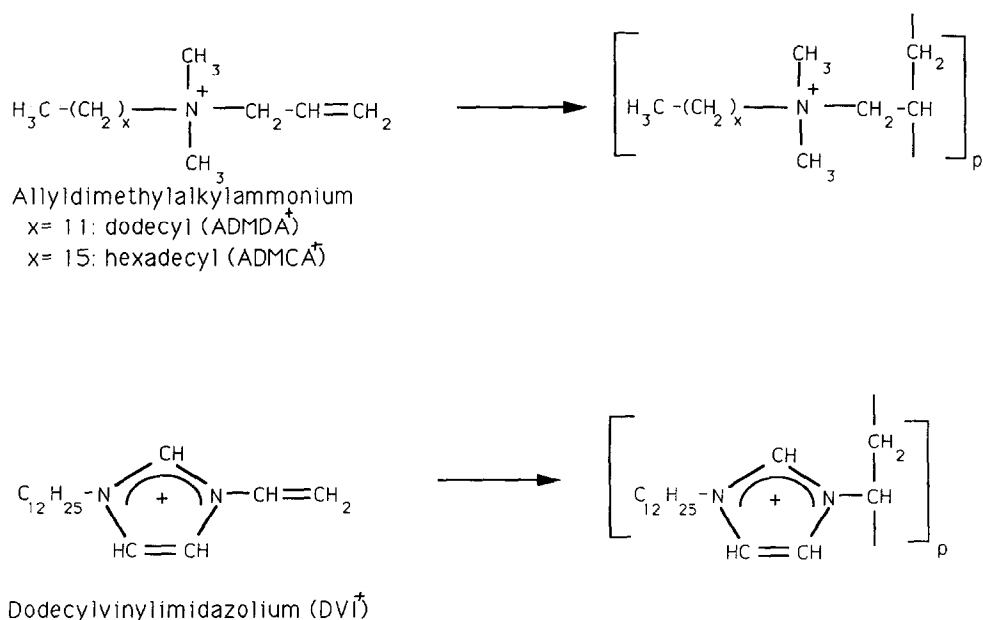


Fig. 1. Monomeric unsaturated surfactants and the corresponding polymers studied.

taining to micellar aggregates [14] and we have recently described a simple model enabling these parameters to be derived from a well chosen set of ITP experiments [15].

The purpose of this work was to show that ITP is also a useful technique for analytical studies of polysurfactants in water–organic media. More precisely, our goal is to illustrate two complementary facets of ITP through the study of a few polymerization reactions of surfactants (Fig. 1): ITP will serve first as an analytical method for the quantitative monitoring of compounds taking part in such polymerization reactions and second for physico-chemical purposes for the comparison of polysurfactants with monomeric micelles from the viewpoint of charge and mobility.

## EXPERIMENTAL

### *Monomer and polymer synthesis*

Allyldimethyldodecylammonium (ADMDA<sup>+</sup>) bromide and dodecylvinylimidazolium (DVI<sup>+</sup>) iodide were synthesized as described [9,10] by allowing *n*-dodecyldimethylamine or 1-vinylimidazole to react with allyl bromide or *n*-dodecyl iodide, respectively. Allyldimethylcetylammmonium (ADMCA<sup>+</sup>) bromide was obtained in the same way as ADMDA<sup>+</sup> bromide, using *n*-hexadecylamine in place of *n*-dodecylamine. The monomers were triply recrystallized in ethyl acetate. Their purities were confirmed by <sup>1</sup>H NMR.

Ion permutation on an anionic resin (Amberlite IRA 400AG; Rohm and Haas, Philadelphia, PA, USA) in its hydroxide form was carried out to obtain ADMDA<sup>+</sup> hydroxide. Apart from ADMDA<sup>+</sup> iodide, which was formed from ADMDA<sup>+</sup> hydroxide by a second ion-exchange process, the other salts result from the neutralization of ADMDA<sup>+</sup> hydroxide with the stoichiometric amount of the appropriate acid solution (hydrochloric, acetic or benzoic acid).

The polymerization reactions were performed in aqueous solutions of surfactant monomers at various concentrations, all well above the CMCs. The solutions were carefully degassed by submitting them to four freeze–pump–thaw cycles. The flasks were sealed and then submitted to  $\gamma$ -irradiation at a constant intensity of 2.4 krad/min for 4–30 hours. With ADMDA<sup>+</sup> ions, reactions were conducted

with various counter ions: hydroxide, acetate, chloride, bromide, benzoate and iodide.

### *Isotachophoresis*

ITP was performed with an LKB (Bromma, Sweden) 2127 Tachophor apparatus and a laboratory-made pilot unit allowing step changes in current intensity and external control of the strip-chart recorder. More details of the experimental set-up were given in a previous paper [13]. The composition of the operating electrolytes and the current intensities used for separation and detection are given in Table I.

### *CMC determinations*

The CMCs were determined from electrical conductivity measurements of aqueous monomer surfactant solutions at various concentrations, using a Tacussel (Villeurbanne, France) CD 60 numerical resistivimeter. The CMC is the concentration at which the plot of conductivity *versus* concentration changes its slope. The results are given in Table II.

### *Ultrafiltration*

Filtron Novacell 150 devices (Pharmacia, Les Ulis, France) with a 5000 g/mol molecular weight cut-off were used to perform the batch ultrafiltrations. Volumes of 20 ml of the sample solution were introduced into the cell and submitted to ultrafiltration under a pressure of  $0.5 \cdot 10^5$  Pa.

## RESULTS AND DISCUSSION

### *ITP analysis of crude irradiated reaction mixtures*

In previous work on the ITP determination of ionic surfactant mixtures, the influence of the composition of the leading electrolyte was studied in detail [13]. It was shown that the three parameters playing a prominent part were the methanol content in water, the leading ion concentration and the leading electrolyte pH.

Methanol was used as an organic modifier in order mainly to suppress the micellization phenomenon. This solvent was selected among other water-miscible solvents as the one maintaining the best resolution between surfactant homologues, although an increased tendency for drifting was generally observed for analyte conductivity steps with contents above 50%. The minimum methanol content

TABLE I  
TYPICAL COMPOSITIONS OF OPERATING ELECTROLYTE SYSTEMS

All solutions were prepared in water–methanol (80:20).

| Parameter                                | Operating electrolyte system |                           |                        |                            |
|--|------------------------------|---------------------------|------------------------|----------------------------|
|  | L <sub>1</sub>               | L <sub>2</sub>            | L <sub>3</sub>         | L <sub>4</sub>             |
| Leading electrolyte:                     |                              |                           |                        |                            |
| Leading ion                              | K <sup>+</sup> , 10 mM       | K <sup>+</sup> , 10 mM    | K <sup>+</sup> , 2 mM  | K <sup>+</sup> , 2 mM      |
| Buffer                                   | Acetate, 13.2 mM             | $\beta$ -Alaninate, 12 mM | Acetate, 2.64 mM       | $\beta$ -Alaninate, 2.4 mM |
| pH <sup>a</sup>                          | 5.5                          | 10.6                      | 5.5                    | 10.6                       |
| Additive                                 | TEG <sup>b</sup> , 2% (v/v)  | TEG, 2% (v/v)             | –                      | –                          |
| Terminating electrolyte                  | $\beta$ -Alanine, 10 mM      | Ethanolamine, 10 mM       | $\beta$ -Alanine, 2 mM | Ethanolamine, 2 mM         |
| Current ( $\mu$ A): separation/detection | 130/30                       | 130/30                    | 70/20                  | 70/20                      |

<sup>a</sup> pH values obtained with electrodes filled with aqueous electrolytes.

<sup>b</sup> TEG = tetraethylene glycol.

required for suppressing polymer aggregation should therefore be employed. As the concentration in any analyte zone remains proportional to that of the leading ion in the leading electrolyte, the latter concentration is another key parameter to be set in keeping with aggregation suppression. The leading ion concentration should therefore be kept below the CMC values in the solvent mixtures considered. Most of the following experiments reported here were performed with 10 mM leading electrolytes, but analysis of long-chain surfactants (*e.g.*, more than sixteen carbon atoms in the main chain) are favoured by lower concentrations. However, in practice, the range of accessible concentrations will be limited if both the correct buffering capacity and

low H<sup>+</sup> and OH<sup>-</sup> contributions to the total zone conductivity are to be maintained. Therefore, no attempt was made to work with leading electrolytes below 2 mM concentration. The pH of the leading electrolyte also remains a major parameter in such separations, even if the main constituents to be determined are strong electrolytes. As will be shown later, a proper choice of pH enables one to either detect or ignore degradation products such as fatty amines. Eventually, four different electrolyte systems were employed, the compositions of which are given in Table I.

Fig. 2 shows an isotachopherogram of a crude polyADMDA<sup>+</sup> sample, obtained with a water–methanol (50:50, v/v) acidic leading electrolyte. By enrichment of the crude polymer sample with known amounts of monomer, the monomer step was first identified as the lowest conductivity step produced by the sample components, while it can reasonably be accepted that the drifting sample step of highest conductivity corresponds to the polymer. Hence, a large separation between the polymer and the monomer was obtained. Figs. 2 and 3A allow the influence of the methanol content in the operating electrolytes to be evaluated and a careful examination of the isotachopherograms shows that a higher methanol content results in more step drifting, probably owing to poorer heat dissipation. It should

TABLE II  
CMC VALUES OF ADMDA<sup>+</sup> IN WATER ASSOCIATED WITH VARIOUS COUNTER-IONS

Determination: see Experimental.

| Counter ion                      | CMC (mmol/l) | Counter ion                                    | CMC (mmol/l) |
|----------------------------------|--------------|--|--------------|
| OH <sup>-</sup>                  | 29           | Br <sup>-</sup>                                | 13           |
| CH <sub>3</sub> COO <sup>-</sup> | 20           | I <sup>-</sup>                                 | 5            |
| Cl <sup>-</sup>                  | 16           | C <sub>6</sub> H <sub>5</sub> COO <sup>-</sup> | 7            |

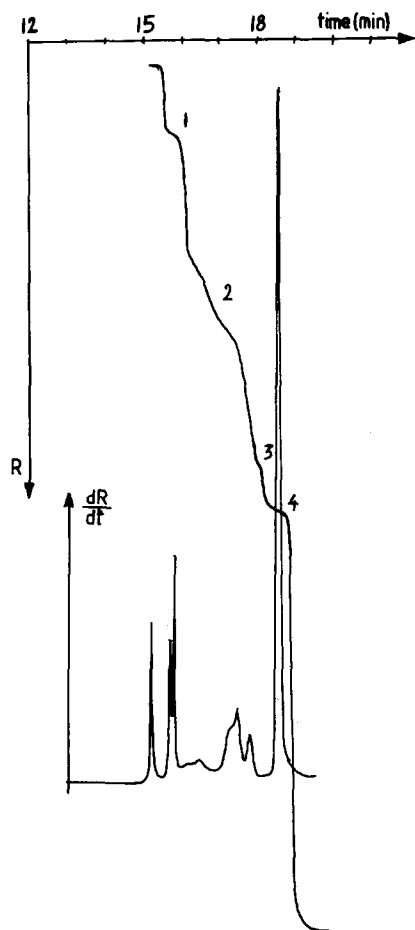


Fig. 2. Isotachopherogram of a 25-h-irradiated 100 mM solution of ADMDA<sup>+</sup> bromide. Operating electrolytes: L<sub>1</sub> (see Table I) except for the water–methanol composition (50:50, v/v). Numerals on the steps: 1 = electrolyte impurity; 2 = polymer; 3 = fatty amine (oxide) degradation product; 4 = monomer. Sample injected: 5  $\mu$ l of the 10 mM diluted solution. R axis, electrical resistance; dR/dt axis, electrical resistance derivative.

be noted that the leading electrolyte L<sub>1</sub> employed in Fig. 3A sets the analyte concentrations in all zones below the CMC of the monomer in water (20 mM for ADMDA<sup>+</sup> acetate; Table II). Hence, monomer aggregation cannot be observed. The separation conditions in Fig. 3A are good enough to distinguish clearly several species (especially from the differential trace) between the polymer and monomer steps. By submitting the same solution to basic electrolyte conditions (leading electrolyte L<sub>2</sub>, Table I), most of

these intermediate steps disappear (Fig. 3B). The corresponding species could be tentatively recognized as amine or amino oxide degradation products. Moreover, the lack of intermediate steps between those of the polymer and the monomer, under basic conditions, suggests that no, if any, oligomer was obtained. In addition, the flatness of the polymer step suggests that a fairly monodisperse polymer was also obtained in this manner.

The polymerizations of the other two surfactants studied (ADMCA<sup>+</sup> bromide and DVI<sup>+</sup> iodide) were followed isotachophoretically in a similar fashion. However, satisfactory separations between monomer and polymer can only be obtained if the leading ion concentration is lowered to 2 mM. With ADMCA<sup>+</sup>, the longer hexadecyl chain results in a very low CMC value (0.8 mM in its bromide form) and it can be inferred that the monomer micellizes at a 10 mM concentration level, even with a leading electrolyte containing 20% methanol. As for DVI<sup>+</sup>, it was mentioned in a previous paper [16] that an interaction between the monomer and the polymer is likely to occur with concentrations in excess of 2–4 mM in aqueous medium.

In an attempt to establish the best polymerization conditions, the amounts of unreacted monomer and degradation products were studied more systematically in terms of several adjustable parameters.

#### Assessment of the best polymerization conditions

A major interest of the ITP technique is that it enables one to follow quantitatively the remaining monomer and degradation products according to reaction time, counter-ion nature and initial monomer concentration. To this end, a mere standardization of the step lengths by injections of pure monomer is needed, as the response coefficients,  $k$ , defined as the ratio of the step length on the isotachopherogram ( $l$ ) to the molecular amount injected ( $n$ ) do not vary significantly for analytes of close mobilities bearing the same charge. Accordingly, it can be assumed that the response coefficients for a monomer and its major degradation product, whose conductivity step is close (Fig. 3A), are not basically different from each other.

The polymerization kinetics were first monitored for 100 mM ADMDA<sup>+</sup> bromide solution (CMC 13 mM, Table II). Fig. 4 shows that the reaction is almost completed after *ca.* 20–25 h of irradiation. By

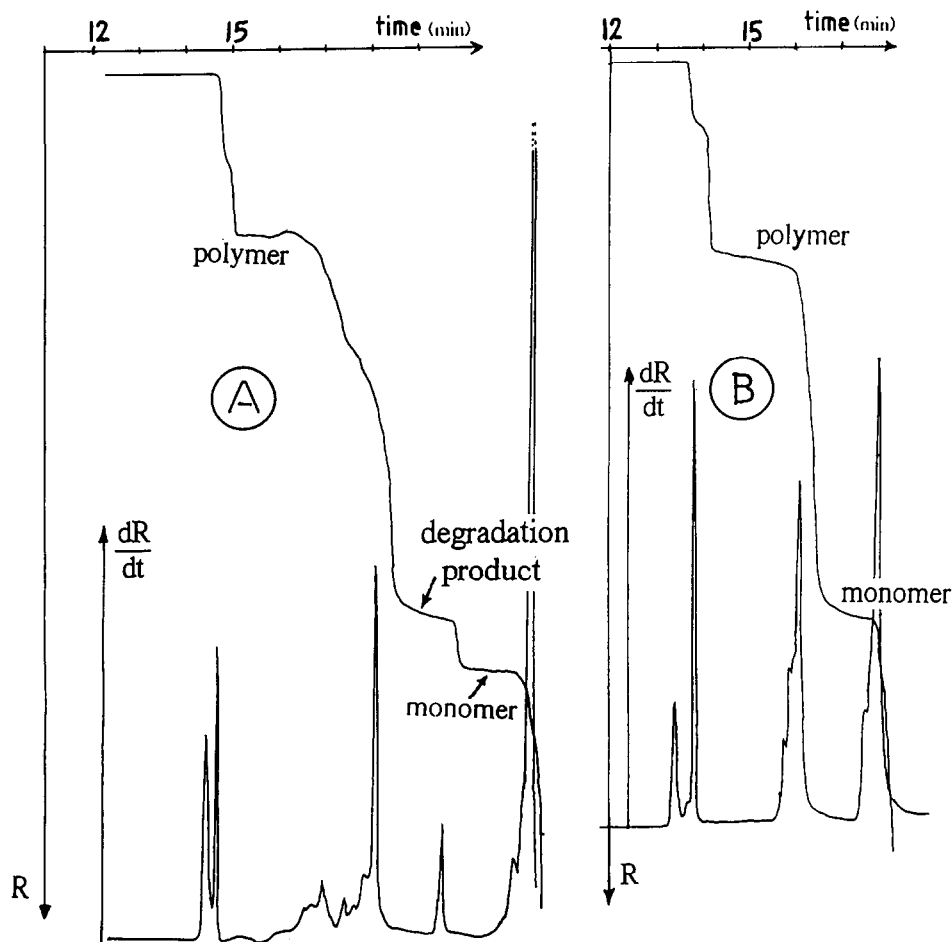


Fig. 3. Isotachopherograms of a crude polyADMDA<sup>+</sup> solution (badly degassed in order to enhance the amount of impurities) obtained under (A) acidic and (B) basic electrolyte conditions. Operating electrolytes: (A) L<sub>1</sub>; (B) L<sub>2</sub> (see Table I). *R* axis, electrical resistance; *dR/dt* axis, electrical resistance derivative.

this time, about 90% of the initial monomer has reacted and *ca.* 10% has been converted into the amine degradation product. Longer irradiation times (> 30 h) or the presence of small amounts of oxygen in the flask cause the amount of degradation products to increase drastically. Thus, a 25-h irradiation time seems optimum with respect to yield for flasks previously submitted to four freeze-pump-thaw cycles.

The polymerization yield was also investigated for ADMCA<sup>+</sup> bromide and DVI<sup>+</sup> iodide with the electrolyte conditions discussed above. It was observed that the monomer step had totally disappeared from

the isotachopherograms of 50 nmol of equivalent monomer amount after irradiation times of 4 h for a 45 mM DVI<sup>+</sup> iodide solution (CMC 4.3 mM) and of 25 h for a 10 mM ADMCA<sup>+</sup> bromide solution (CMC 0.8 mM). This result clearly indicates that the polymerization of ADMDA<sup>+</sup> bromide is not as fast as those of ADMCA<sup>+</sup> bromide or DVI<sup>+</sup> iodide, as a determinable amount of ADMDA<sup>+</sup> monomer is still visible on the isotachopherogram in Fig. 3 after a 25-h irradiation time. Further, a comparison between isotachopherograms obtained under acidic and basic conditions (electrolytes L<sub>3</sub> and L<sub>4</sub>, Table I) enabled us to evaluate the amine degradation prod-

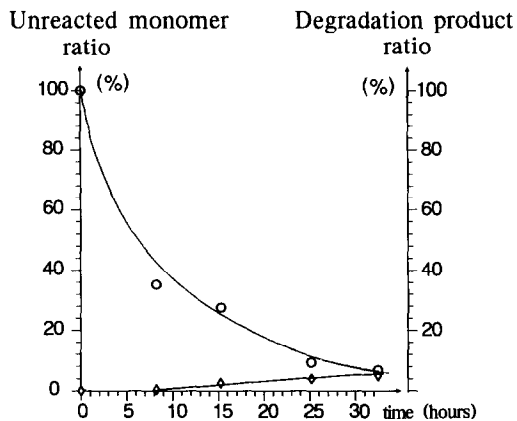


Fig. 4. Effect of irradiation time of a 100 mM ADMDA<sup>+</sup> bromide solution on (○) the unreacted monomer ratio and (◇) the degradation product ratio as determined by ITP. Operating electrolyte: L<sub>1</sub> (see Table I).

uct that had formed on completion of ADMCA<sup>+</sup> bromide polymerization as less than 10%.

In order to optimize the polymerization yield, irradiations were performed with various ADMDA<sup>+</sup> salts, keeping their concentration at 100 mM. The results are shown in Fig. 5, where these salts are arranged in increasing order of the counter-ion binding to micelles. Naturally, these differences in interaction between the micelle and its counter ion are also associated with variation of the CMC values (Table II), but the monomer concentration chosen, in all instances, remains far above these values. Apart from a secondary influence of the degree of counter-ion binding, it clearly appears that halide

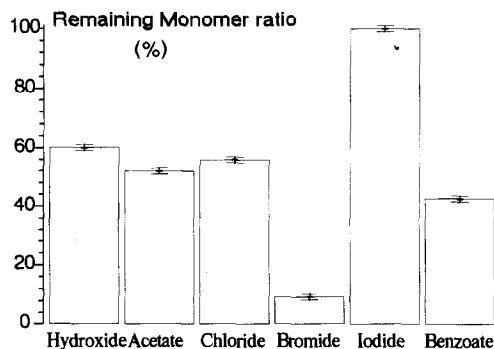


Fig. 5. Effect of counter ion associated with ADMDA<sup>+</sup> during the polymerization reaction (25 h of irradiation) of a 100 mM solution of this surfactant on the remaining monomer ratio, as determined by ITP. Operating electrolyte: L<sub>1</sub>.

counter ions play a special role in the polymerization yield. It is likely that bromide ions generate free radicals in the vicinity of the reactive double bonds, which are taking part in the polymerization reaction, hence leading to the best yield. Conversely, iodide ions might act as a shield impeding the reaction and thus leading to the poorest yield.

The last parameter studied was the initial monomer concentration. ADMCA<sup>+</sup> bromide was chosen for this series of experiments because of its low CMC value (0.8 mM) and its high solubility in water, which enabled us to vary the initial concentration over a wide range, between 8 and 100 mM, while keeping all monomers in the form of a micelle structure. Such experiments would be less easy to perform with ADMDA<sup>+</sup> halides, owing to their higher CMC values (Table II) and with DVI<sup>+</sup> iodide, which is too poorly soluble. It was ascertained (Fig. 6) that after a 25-h irradiation time the monomer conversion ratio is of the order of 90% (taking the degradation products into the account) for initial concentrations (8-10 mM) ca. ten times the CMC value, whereas it falls to only 30% for a 100 mM concentration. Undoubtedly, the initial monomer concentration plays a key role in the polymerization reactions and it turns out that it does not suffice to select any concentration above the CMC value to obtain a high yield of micelle

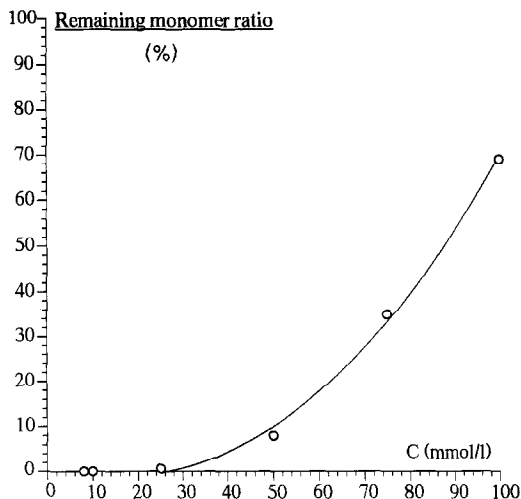


Fig. 6. Variation of the relative amount of ADMCA<sup>+</sup> remaining after a 25-h irradiation time in its bromide form as a function of the initial concentration of this surfactant. ITP operating electrolyte: L<sub>3</sub>.

polymerization. At present, the understanding of this concentration effect suffers from the lack of a kinetic model relevant to this specific reaction, so that we only set forth two putative explanations. First, it can be considered that the fixed intensity of  $\gamma$ -radiation can no longer produce the number of free radicals required with high monomer concentrations. However, this assumption does not seem consistent with the fact that, for the same radiation intensity and the same initial concentration (100 mM), 80% of the initial ADMDA<sup>+</sup> bromide amount was polymerized while an additional 10% was degraded. In addition, the sudden variation in reaction yield observed in Fig. 6 after 25 h of irradiation may originate from a change in the aggregate structure above a second critical concentration of the monomer, as recently suggested by Egorov [17] for a surfactant of similar chain length. However, this second assumption also seems questionable, as a great change in the rate of radical propagation would be related to a corresponding reduction in the fluidity of the micellar surface that has never been observed, to our knowledge. Hence, we consider that this point has not received a sound explanation.

Anyway, the preceding ITP results enable one to choose the optimum counter ion (bromide), the optimum initial concentration of the monomer and the optimum irradiation time, to yield 80–100% polymer, depending on the monomer. We shall now concentrate on comparing these polymers with classical micelles from a physico-chemical point of view.

#### *Analogy between ionic polymers and micelles*

In this study, ITP turned out to be more than an effective and flexible technique for the determination of surfactant monomers. Owing to the absence of a stationary phase and the existence of a steady state, the ITP process is amenable to quantitative modelling, which conversely can give access to the evaluation of physico-chemical parameters, such as absolute mobilities and acidity or complex formation constants. The classical ITP equations can be easily extended to account for the migration of ionic micelles in equilibrium with their monomers, as shown previously [15]. In short, the micelle mobility can be derived from the measurement of the conductivity step height of the micelle zone using usual

procedures, while the degree of counter-ion binding is related to the corresponding step length. Defining  $\beta$  as the ratio of bound counter ion per micelle to the aggregation number and  $\alpha$  as the fraction of free counter ion, we obtained, for the case where the CMC value is negligibly small compared with the total surfactant concentration [15]:

$$\alpha = 1 - \beta = \frac{m_{\text{mic}}}{m_{\text{mic}} - m_{\text{c}}} \cdot \frac{I}{Fv} \cdot \frac{l}{n} \quad (1)$$

where  $m_{\text{mic}}$  and  $m_{\text{c}}$  are the effective mobilities of the micelle and counter ion, respectively,  $I$  is the current intensity,  $F$  the Faraday constant,  $v$  the recorder chartspeed,  $l$ , the step length and  $n$  the amount of monomer injected. The ITP behaviour of poly-surfactants can be modelled in a simpler and more usual way than that of micelles as no equilibrium between monomer and polymer need be considered. Eqn. 1 remains valid with  $n$  representing injected amounts expressed in number of moles of monomer units. On that basis, the analogy between polymers and micelles can be highlighted on isotachopherograms in comparing the step lengths and heights produced by equal amounts of a polymer and a micelle (expressed as monomer units) injected successively. The experiment was conducted with polyADMDA<sup>+</sup> as a test polymer. However, a direct comparison between polyADMDA<sup>+</sup> and micelles of ADMDA<sup>+</sup> was not tempted because the CMCs of ADMDA<sup>+</sup> are too high, even in purely aqueous media (Table II). In effect, a leading electrolyte concentration greater than ten times the CMC value should be employed so that the amount of free monomer in the micelle zone would be negligible (*i.e.*, the CMC value be negligible compared with the surfactant zone concentration). This is why a more common surfactant, *n*-hexadecyltrimethylammonium ion, C<sub>16</sub>H<sub>33</sub>Me<sub>3</sub>N<sup>+</sup> (CMC 1.6 mM), was finally chosen.

As shown in Fig. 7, the steps heights and hence the mobilities of C<sub>16</sub>H<sub>33</sub>Me<sub>3</sub>N<sup>+</sup> micelles and poly-ADMDA<sup>+</sup> are very close to each other. At this point, it is worth noting that the initial counter ion of the analytes (*i.e.*, bromide here) is rapidly eliminated towards the terminating electrode vessel and replaced in all the zones by the counter ion of the leading electrolyte (*i.e.*, acetate here) migrating in the opposite direction. This aspect is of prime importance for comparing the degrees of counter-



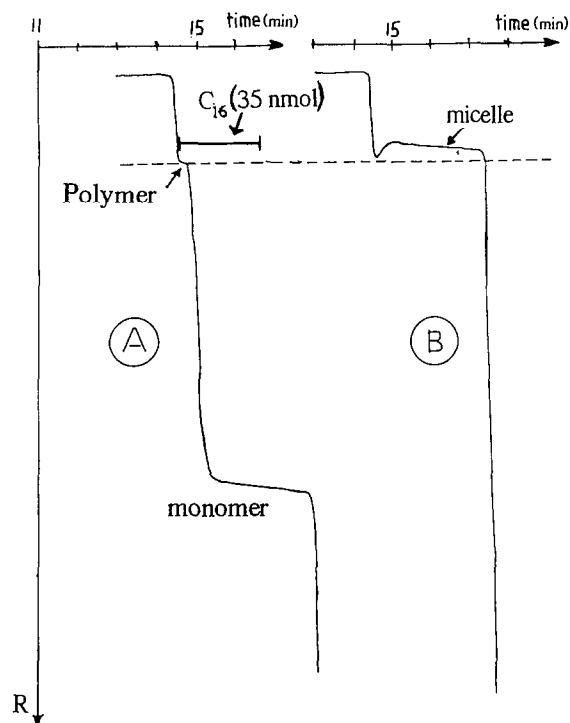


Fig. 7. Comparison of the ITP behaviours of (A) polyADMDA<sup>+</sup> as obtained after a 15-h irradiation of a 100 mM solution of ADMDA<sup>+</sup> bromide, and (B) C<sub>16</sub>H<sub>33</sub>Me<sub>3</sub>N<sup>+</sup> micelles. Operating electrolytes: L<sub>1</sub>, except for the solvent, which was water. Samples injected: 50 nmol of equivalent monomers or C<sub>16</sub>H<sub>33</sub>Me<sub>3</sub>N<sup>+</sup>. R axis, electrical resistance.

ion binding,  $\beta$ , to micelles and polymers. It is well known that  $\beta$  varies markedly with the nature of the counter ion bound, going typically from *ca.* 0.4 to 0.8 on substituting benzoate for OH<sup>-</sup>. The present operating electrolyte enabled us to determine  $\beta$  values for micelles and polymers with acetate as counter ion. The  $\beta$  values with other counter ions could be obtained very simply by changing the counter ion of the leading electrolyte. Hence ITP suppresses the need to perform a tedious counter-ion permutation of the analyte samples on a resin bed on which polymer adsorption can occur.

Measuring the respective step lengths for the C<sub>16</sub>H<sub>33</sub>Me<sub>3</sub>N<sup>+</sup> micelle and polyADMDA<sup>+</sup> from Fig. 7 and using eqn. 1,  $\beta$  values of 0.56 and 0.93 were calculated for the micelle and the polymer, respectively. This result indicates that acetate ions are much more strongly bound to the polymer than

to the micelle. It can be estimated, at a glance, by comparing the length of the polymer step with the length given by an equal amount of C<sub>16</sub>H<sub>33</sub>Me<sub>3</sub>N<sup>+</sup> micellized surfactants. The amount of polymer in Fig. 7A corresponds to 35 nmol of monomer units. Clearly, the much larger zone length of the 35-nmol C<sub>16</sub>H<sub>33</sub>Me<sub>3</sub>N<sup>+</sup> step drawn just above indicates a higher degree of counter-ion binding to the polymer. Similar results were obtained with polyDVI<sup>+</sup> and polyADMCA<sup>+</sup>. Hence the polymers resulting from  $\gamma$ -irradiation of cationic unsaturated surfactants behave like dynamic micelles as far as electrical mobility is concerned, but they seem to interact with their counter ions more strongly. Moreover, as shown in Figs. 2 and 3, these physico-chemical properties are hardly modified when methanol is added to the electrolyte up to at least 50%.

In an attempt to confirm that, as illustrated in Fig. 3B, very few oligomers are formed using this synthesis procedure, and in order to provide further insight into the molecular weight of the polymers obtained, ultrafiltration experiments were performed and the resulting two phases (retentate and ultrafiltrate) were analysed by ITP. The ultrafiltration of dynamic micellar solutions is well controlled at present. In particular, it has been established that the surfactant concentration in the ultrafiltrates will remain near to the CMC if the concentration of the initial sample is higher than the CMC [5]. This means that only free surfactant monomers are allowed to pass through the ultrafiltration membrane and that the size of a micelle is larger than the pore size of the membrane, corresponding to a molecular weight cut-off of *ca.* 5000 g/mol.

In this respect, we decided to ultrafilter a polyADMDA<sup>+</sup> bromide sample resulting from irradiation of a 100 mM monomer solution for 25 h. In order to suppress the micellization of the remaining monomers (CMC 13 mM, Table II), the sample was diluted to a 10 mM monomer equivalent concentration prior to ultrafiltration. Two solvents were tested successively to make the dilution: pure water and water-methanol (40:60, v/v). The ITP analysis of the ultrafiltrates revealed that no polymer is able to cross the membrane when ultrafiltration is carried out with purely aqueous samples (Fig. 8A). This behaviour suggests that the synthesized units do have a permanent structure, independent of the monomer concentration. However, in water, some

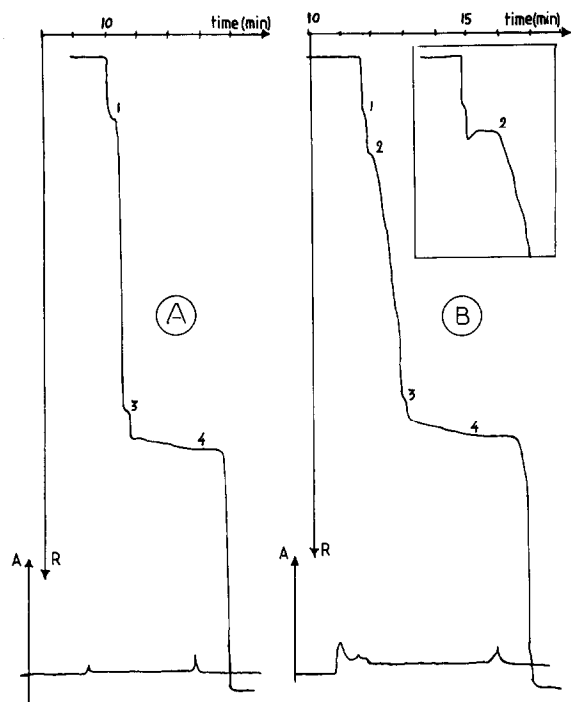


Fig. 8. Comparison of ultrafiltrates of polyADMDA<sup>+</sup> bromide solutions diluted to a 10 mM equivalent monomer concentration with (A) water and (B) water–methanol (40:60, v/v). Inset: part of the retentate isotachopherogram with the same electrolyte conditions. Numerals on the steps: 1 = electrolyte impurity; 2 = polymer; 3 = fatty amine (oxide) degradation product; 4 = monomer. Ultrafiltration membrane: Filtron Novacell 150, molecular weight cut-off 5000 g/mol. Operating electrolyte: L<sub>3</sub>. R axis, electrical resistance; A axis, UV absorbance (254 nm).

aggregates of oligomers might form, hence impeding their passage through the membrane. This is why the influence of methanol on the ultrafiltration separation was also examined. Figure 8B shows that in this instance, a small amount of products having mobilities close to that of the polymer and also some UV-absorbing degradation products are found in ultrafiltrates (the absence of these species in Fig. 8A proves that they were probably solubilized within the polymer aggregates in water). In comparing Fig. 8B with the inset retentate isotachopherogram, it clearly appears that most of the polymer remains in the retentate even in water–methanol (40:60) solution. At this stage, it can be concluded that the molecular weight of the polymer itself is higher than 5000 g/mol.

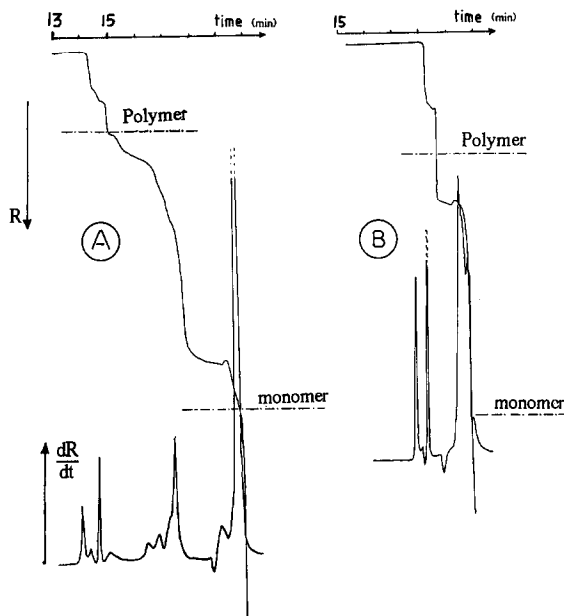


Fig. 9. Isotachopherograms of a 10 mM of a 10 mM ADMDA<sup>+</sup> bromide solution after a 25-h irradiation time. (A) Acidic electrolyte conditions (L<sub>1</sub>); (B) basic electrolyte conditions (L<sub>2</sub>). Volume injected, 5  $\mu$ l. R axis, electrical resistance; dR/dt axis, electrical resistance derivative.

In order to stress further the analogy between dynamic micelles and those of ionic polymers, a 10 mM solution of ADMDA<sup>+</sup> bromide, *i.e.*, at a concentration below the CMC value, was irradiated for 25 h. The ITP analysis of the resulting reaction mixture showed that, under these conditions, the high-mobility polymer described previously was not formed at all (Fig. 9A and B). Instead, a large amount of degradation compounds is produced. This last experiment indicates that polymerization only progresses in the core of the micelle and is likely to stop rapidly in a purely aqueous medium. This can also be seen as a hint that the polymers and the micelles are close in size.

## CONCLUSIONS

The ITP monitoring of reaction mixtures of ionic surfactants submitted to  $\gamma$ -irradiation has been shown to be an efficient means for the optimization of operational parameters such as the initial surfactant concentration, the nature of its associated

counter ion and the time of irradiation. Once optimized, these reactions lead to polymeric surfactants with yields in excess of 80%, and it has been shown that these ionic polymers behave like polymerized micelles. In effect, their mobility was determined to be close to that of a classical dynamic micelle and it can be expected from ultrafiltration experiments that their degree of polymerization is of the same order of magnitude as the aggregation number of the corresponding dynamic micelles. Further, ITP provides an original means of evaluating the degree of counter-ion binding to the surfactant aggregates that will be more systematically used in our laboratory in the future.

ITP has turned to be an invaluable method allowing the identification and determination of the major ionic or ionizable compounds present in reaction mixtures. Among other advantages are the absence of a background electrolyte and stationary phase, the control of the analyte concentration in its own zone by the leading ion concentration, the relative ease of modelling, the versatility of conductivity detection and the overall simplicity of implementation and result interpretation.

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