

Microgels with trialkylammonio side chains function as catalysts for the alkaline hydrolysis of substituted phenyl laurate esters

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Abstract

Microgels incorporating 2-(tetradecyldimethylammonio)ethyl methacrylate bromide have been prepared by emulsion polymerisation with methyl methacrylate, 2-ethoxyethyl methacrylate and ethylene glycol dimethacrylate in the molar ratio 0.15:0.45:0.30:0.10 respectively. The microgel solubilises aryl laurate esters in aqueous solution and catalyses the alkaline hydrolysis of these esters; the variation of rate constant with microgel concentration indicates a complexation phenomenon with the 4-nitrophenyl ester. The reactivity of the microgel sol with the laurate esters is similar to that of the analogous micellar system from cetyltrimethylammonium bromide (CTAB) described by Al-Awadi and Williams (*J. Org. Chem.*, 55 (1990) 2001).

The rate constant for the microgel-catalysed reaction of hydroxide ion with the substituted phenyl laurate esters obeys the Brønsted correlation:

$$\log k_{\text{OH}}^{\text{cat}} = -0.53\text{p}K_{\text{a}} + 4.49$$

The value of the Brønsted β_{g} (–0.53) is similar to that observed for CTAB-catalysis and for uncatalysed alkaline hydrolysis; it indicates that the catalytic site of ester hydrolysis resides in an aqueous-like region of the microgel.

Keywords: Alkaline hydrolysis; Cationic surfactant; Microgels; Phenyl esters; Polysoap

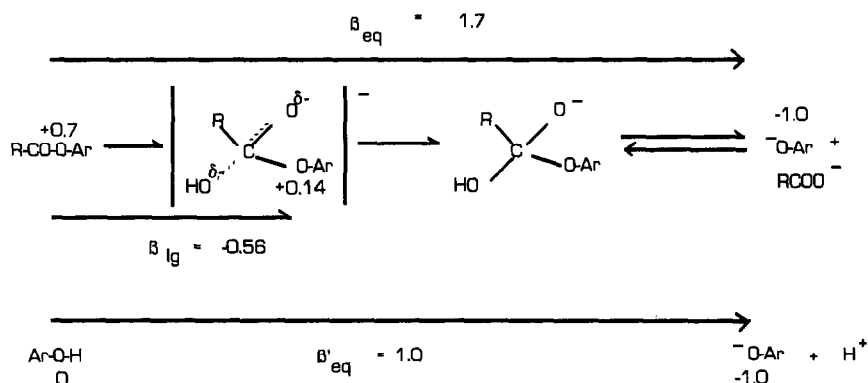
1. Introduction

Cationic micelles such as those from aqueous sols of cetyltrimethylammonium bromide (CTAB) catalyse the reaction of anions with neutral species possessing long chain aliphatic groups [1,2]. The increased concentration of the reactants in the pseudo phase of the micellar particle caused by partitioning of reactant from the bulk

solvent has been recognised as one of the main contributors to the catalytic efficiency of these systems [2].

The components of micelles exchange rapidly between micellar particles and if the enhanced catalytic activity of micelles is to be exploited some means is necessary to ‘fix’ the components of the micelle particle. Micelle-like particles where the components are prevented from exchange are well documented [3] but there have been few kinetic studies of systems in aqueous solution possessing ‘fixed’ surfactant-like com-

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Scheme 1. Effective charge map for reaction of esters with hydroxide ion [1].

ponents which have the potential for commercial exploitation.

The present report is of an investigation of the catalytic action of a microgel preparation possessing surfactant-like comonomers. Microgels are internally cross-linked spherical latex particles formed in emulsion polymerisation when the monomer feed possesses divalent monomer units [4]. The diameter of microgels may range from 40 to 3000 nm and is regulated by the composition of the monomer feed. The microgel in this study is from oil-in-water emulsion polymerisation of a methacrylate comonomer feed containing 2-(tetradecyldimethylammonio)ethyl methacrylate bromide and a cross-linking comonomer. The catalytic action of the microgel sol is compared with that of CTAB sols for the reaction of hydroxide ion with substituted phenyl laurate esters [1]. The microgel particle is similar to a polysoap particle except that the latter does not usually possess cross-linking functions; there is no gross exchange of the components of the polysoap although its structure is substantially fluxional.

Brønsted-type plots of the logarithms of rate or equilibrium constants versus the pK_a of the leaving group have slopes (β) which compare the selectivity of the reaction to polar substituents with that of the standard ionisation equilibrium. Scheme 1 illustrates the comparison of β values for attack of hydroxide ion on aryl esters.

The value β_{lg} measures the change in 'effective charge' [5] on the aryl oxygen from ester to transition state compared with that in the ionisation

($\beta_{eq}' = 1$). Since the overall β_{eq} for the hydrolysis of esters is known (1.7) the extent of bond fission at the aryl oxygen can be estimated simply from the ratio β_{lg}/β_{eq} . Since selectivity of reactivity to polar substituents is a function of charge change [5] effective charge may be defined as the hypothetical charge required to give the observed β value compared with unit charge defined to give a unit value of β for a standard ionisation reaction. The standard ionisation in the present case is of substituted phenols and the effective charges on the oxygens in acid and base in this system are defined as (0) and (-1) respectively; the effective charges on the aryl oxygens of the ester and transition state are respectively (+0.7) and (+0.14).

The effect on the kinetic parameters of varying the substituent of the leaving phenolate anion (β_{lg}) enables us to determine effective charges [5] on the leaving oxygen in the transition state of the microgel catalysed reaction. The effective charge may be compared with that of the micellar and uncatalysed systems and will give information about the comparative polarities of the microscopic environment of the transition states in the different systems.

2. Experimental

2.1. Materials

2-(Tetradecyldimethylammonio)ethyl methacrylate bromide was prepared from dimethylam-

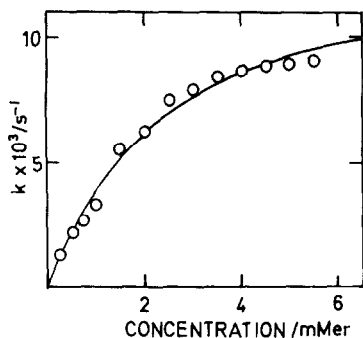


Fig. 1. Dependence on molarity of tetradecyldimethylammonio groups in the microgel sol for the hydrolysis of 4-nitrophenyl laurate at pH 11.4. Line is drawn from Eq. 2 with parameters given in the text. Conditions: 25°, 0.1 M KCl solvent, carbonate buffers.

ino methacrylate by the method of Hamid and Sherrington [6]. Other monomers were from either Aldrich or Fluka Chemical Companies and were freed from polymerisation inhibitors by extraction with dilute aqueous alkali. 4-Nitrophenyl laurate was purchased from Aldrich and the other phenyl laurates were from a previous study [1,7]. Other materials were of analytical reagent grade or were recrystallised or redistilled from bench grade reagents.

Emulsion polymerisation was carried out with monomer feed (5 ml) comprising methyl methacrylate, 2-ethoxyethyl methacrylate, ethylene glycol dimethacrylate and 2-(tetradecyldimethylammonio)ethyl methacrylate (in the molar ratios: 0.45:0.30:0.10:0.15). The quaternary ammonium monomer was dissolved in water (100 ml) in a screw-cap bottle in an oil bath set at 60°C. The remaining monomers were added and the bottle purged with nitrogen. Polymerisation was initiated with ammonium persulphate (50 mg), the bottle sealed and the contents stirred at 60°C. The tetradecyldimethylammonio species acted as the emulsifying agent for the polymerisation. After about 2 h the characteristic 'blue' opalescence had appeared; the product was then cooled and the suspension centrifuged with a small bench centrifuge to remove a small amount of coagulated material. The sol was ultrafiltered with Amicon PM30 membranes repeatedly (volume was made up with distilled water) to remove any residual low molecular weight material. A sample of the

stock solution of the microgel sol was evaporated to dryness in an oven and the weight employed to compute the microgel concentration. Elemental analysis of the dry residue gave the total nitrogen content which in turn gave the molarity of the tetradecyldimethylammonio groups in the microgel sol; an approximately theoretical yield of polymer was obtained in the polymerisation process.

2.2. Methods

Hydrolysis rates were measured by adding an aliquot (20 μ l) of an acetonitrile stock solution of the ester to a microgel solution (2.5 ml) buffered to a specified pH in a silica cell in the thermostatted cell compartment of a Hitachi 124 double beam spectrometer. The final concentrations of laurate esters were in the range of 10 μ M. The wavelength for kinetic study was determined by carrying out a separate experiment under similar conditions involving repetitive scanning of the ultraviolet-visible spectrum. Pseudo first order rate constants were calculated from the change in absorbance with time by use of a curve-fitting programme with a microcomputer. Concentrations of laurate esters larger than those possible in aqueous solution may be obtained in the microgel sol due to a partitioning phenomenon. A Radiometer PHM26 digital pH-meter was employed to determine the pH of the reactant solution in the silica cell after the reaction. The pH-meter was fitted with a Russell CMAWL CL057 combined pH probe which was calibrated with EIL standard buffer powders to ± 0.01 pH units.

Measurements of particle size were carried out by use of a Malvern Automeasure instrument (4700V4).

3. Results

The fission of the aryl laurates in buffer solutions containing the microgel obeyed excellent pseudo first order kinetics to over 90% of the total reaction. The rate constants for the reaction of 4-nitrophenyl laurate exhibited a non-linear depend-

Table 1

Rate constants for alkaline hydrolysis of substituted phenyl laurate esters in the presence of microgel possessing 2-(tetradecyltrimethylammonio)ethyl side chains^a

Substituent	pK_a^{ArOH}	k_{OH}^{cat} ^b	k_{OH}^{cat}/K_{eq} ^c
4-NO ₂	7.16	5.53	2210
2-NO ₂	7.21	2.59	1040
4-CN	7.95	5.35	2140
3-NO ₂	8.37	1.24	496
3-Cl	9.02	0.486	194
4-Cl	9.38	0.344	138
H	9.95	0.134	53.6
4-CH ₃	10.2	0.161	64.4

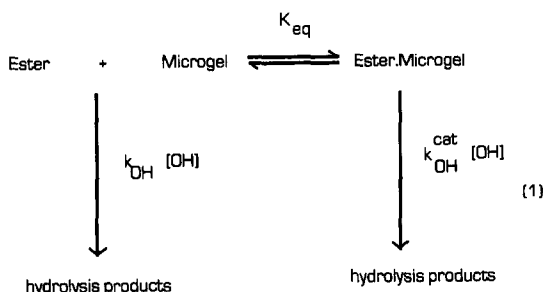
^a 25°C, carbonate buffer pH 11.40 (0.1 M), 0.1 M KCl solvent, microgel concentration at 1.24 mM in ammonio head groups.

^b From three data points divided by hydroxide ion concentration after correction for background rate without microgel. Units: M⁻¹ s⁻¹.

^c The value of K_{eq} is taken to be that for the 4-nitrophenyl ester (see Results). Units: M⁻¹ Mer⁻¹ s⁻¹.

ence on the merlarity of the ammonio residue in the microgel sol and the data are illustrated in Fig. 1. The data indicate a complexation type phenomenon (Eq. 1) and the derived equilibrium constant (2.50 ± 0.31 mMer) obtained by fitting data of Fig. 1 to Eq. 2 ($[Mic]$ = merlarity of the microgel based on ammonio head group concentration).

Eq. 1



$$k_{obs} = \frac{(k_{OH} \cdot K_{eq} + k_{OH}^{cat} [Mic]) [OH]}{(K_{eq} + [Mic])} \quad (2)$$

indicates a slightly weaker *partitioning* of ester into microgel than that observed for 4-nitrophenyl laurate by the analogous CTAB micellar particles under similar conditions (0.41 mM) [1].

The uncatalysed rate is negligible under the conditions of the experiments ($k_{OH} = 0.018$ M⁻¹ s⁻¹ for the 4-nitrophenyl ester); the second order

rate constant, k_{OH}^{cat} for the 4-nitrophenyl ester (5.53 M⁻¹ s⁻¹) is of the same order as that for the CTAB catalysis (4.8 M⁻¹ s⁻¹) [1]. The pseudo first order rate constants for fission of 4-nitrophenyl laurate at constant microgel merlarity were proportional to hydroxide ion concentration from pH's 10.5 to 11.4.

Rate constants, second order in ester and hydroxide ion concentration, are recorded in Table 1 for the catalytic action of microgel on substituted phenyl laurate esters (at a constant merlarity of ammonio residues). Experiments with CTAB and a variety of esters [1] indicate that there is no substituent effect on the equilibrium constant (K_{eq}) for complexation. By analogy, it is reasonable to assume that K_{eq} is independent of substituent for the microgel so that the values of k_{OH}^{cat} for the microgel may be computed from the observed second order rate constants (k_{OH}^{cat}/K_{eq}) (recorded in Table 1). The values of k_{OH}^{cat} may be fit to a Brønsted-type plot against the pK_a of the leaving phenol (Eq. 3) and this is illustrated in Fig. 2.

$$\log k_{OH}^{cat} = -0.53 \pm 0.07 pK_a + 4.49 \pm 0.61$$

$$(r = 0.950) \quad (3)$$

The microgel sols were essentially monodisperse as determined from the particle sizing meas-

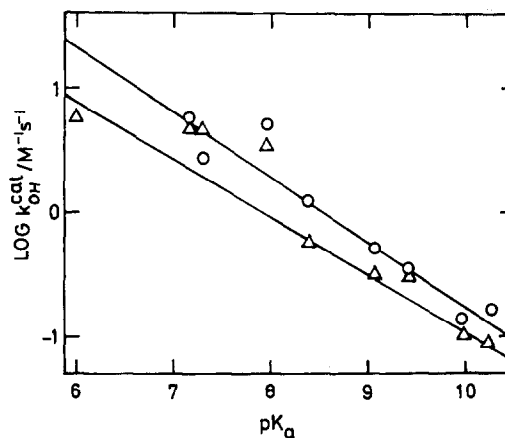
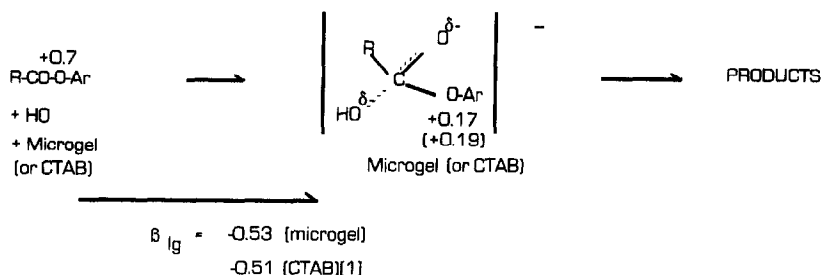


Fig. 2. Brønsted dependence of k_{OH}^{cat} on the pK_a of the leaving phenol for microgel-catalysed reaction of hydroxide ion with substituted phenyl laurate esters. Microgel: open circles; CTAB: open triangles; lines are respectively from Eq. 3 with parameters from Table 1 and from Ref. [1]. Conditions: 25°C, pH 11.4, concentration of microgel = 1.24 mM, 0.1 M KCl solvent, carbonate buffers.



Scheme 2. Effective charge map for the alkaline hydrolysis of esters catalysed by microgel or CTAB.

urements and the particles had diameters of 337, 289 and 306 nm respectively in methanol, pH 10.02 and pH 5.00 buffers (carbonate and acetate, respectively).

4. Discussion

Kinetics of the ammonio residues in the microgel sols obey a phenomenon involving partition of ester to the microgel particle (Eq. 1). The microgel has about one fifth of the (third order) reactivity compared with CTAB against ester hydrolysis measured against the molarity of ammonio side chain or molarity of CTAB surfactant molecule. The combined rate parameter (k_{OH}^{cat}/K_{eq}) refers to the overall energy jump from the 'non-partitioned' ground-state to the transition-state of the rate limiting step in the partitioned environment (Scheme 2).

The reactivity of the ester when it is in its 'partitioned' state is almost the same as that in CTAB catalysis (the 4-nitrophenyl ester has $k_{OH}^{cat} = 4.8 \text{ M}^{-1} \text{ s}^{-1}$ for CTAB and $5.53 \text{ M}^{-1} \text{ s}^{-1}$ for microgel). The slightly greater overall reactivity of CTAB (as measured by the combined parameter) is accounted for by the better partitioning factor (K_{eq}) of the micelle compared with that of the microgel. The weaker partitioning of the microgel is attributed to the dilution of the trialkylammonio side chains by the ethoxyethylcarbonyl and methoxycarbonyl residues from the ethoxyethyl methacrylate and methyl methacrylate comonomers. Only some 15% of the molecules in the microgel particle possess an ammonio head whereas the total surface of the micellar particle is composed of the ammonio head. The percentage composi-

tion compares with the partitioning ability of the microgels being 20% of that for the CTAB micelles. Presumably the association of ester with microgel occurs in regions possessing the ammonio head. The low concentration of substituted phenyl laurates (ca. $10 \mu\text{M}$) was never sufficient compared with the amount of microgel to saturate the surface of the microgel; under the prevailing conditions there is no possibility of any interactions between esters in the partitioned phase.

Fig. 2 illustrates the Brønsted-dependence for the alkaline hydrolysis rate constant for the ester partitioned into the pseudo-phase for the CTAB micellar system and that for the microgel system. The slopes (β_{lg}) of the two lines are similar and moreover are similar to that for the uncatalysed reaction of hydroxide ion with the ester. The similar slopes indicate that similar changes in effective charges occur on the aryl oxygen from ground state (free ester, hydroxide ion and surfactant) to the transition state of the respective reaction system. The simplest explanation of this result is that the microscopic medium of the ester moiety in the transition state in the 'partitioned' state (Scheme 2) has a similar polarity to that in pure water and also to that in the CTAB micelle wherein similar catalysis occurs. It is likely that the tetradecylammonio side chain provides hydrophobic attraction to the lauryl side chain of the ester leaving the ester function (CO-OAr) in the part of the interfacial region which has bulk solvent-like character. The slightly greater (non-random) scatter in the Brønsted plot for both microgel and micellar systems compared with that of the uncatalysed reaction is consistent with the ester's being parti-

tioned into a pseudo-phase possessing a different overall structure from that of water.

We conclude that the fixation of the ammonio surfactant side chains in a microgel does not alter the mechanism or catalytic advantage of the system significantly from that in the CTAB micelle. The ammonio microgels, unlike micelles, may be attached without structural alteration to solid supports and thus have potential for application in continuous reactors.

Acknowledgements

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