



Hydrolysis of benzoic anhydride mediated by ionenes and micelles

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ABSTRACT

Micelle-mediated catalysis was compared to that of ionene polymers. Hexadecyltrimethylammonium bromide (CTABr) and benzyldimethylhexadecylammonium chloride (BDHA) were the surfactants employed and 2-hydroxy-3-ionene chloride (2-OH-33R) and poly[(dipropyliminium)-1,3-propanediyl bromide], 33R33, the tested ionenes. A modified Michaelis–Menten equation described the kinetics of ionene-mediated hydrolysis. The cationic polymer 2-hydroxy-3-ionene chloride proved to be the most efficient catalyst and a detailed mechanism is proposed for the reaction with benzoic anhydride (Bz₂O) based on the kinetic evidence obtained. The catalytic efficiency follows the order 2-OH-33R > BDHA > 33R33 > CTABr.

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1. Introduction

The effect of macromolecules such as polymers on reaction rates has been widely studied and polymers bearing catalytic sites, such as hydroxamic acid [1], hydroxyl [2], pyridine [3], guanidinium [2,4] pyridoxamine [5] among other groups effectively accelerate hydrolysis of anhydrides either by nucleophilic or intramolecular catalysis, mimicking naturally occurring enzymes. For example, transamination by pyridoxamine groups attached to a modified polyethyleneimine converted pyruvic acid into the corresponding amino acid, alanine, with up to 6700-fold acceleration [5]. However, ionic polymers without reactive groups also affect reaction rates because they can concentrate reactants in their environment approximating the ionic species with opposite charge and in this way enhancing the collision rate with each other [6,7]. Furthermore, polyelectrolytes can also accelerate hydrolyses of neutral substrates. For example, Kitano and co-workers showed that polyelectrolytes containing highly hydrophobic groups accelerate hydrolysis of the neutral anhydride *p*-nitrophenyl acetate (PNPA) and this is because of the hydrophobic interactions between the anhydrides and polymers, and to the electrostatic attractive forces between OH[−] and the cationic polymers.

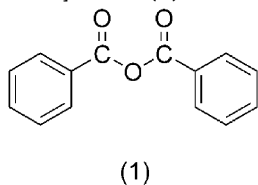
The catalytic effects of micelles are well established and depend on their ability to compartmentalize reagents [8–12]. However, this catalysis is usually less effective than by polyelectrolytes due to the considerably higher structural mobility of micelles [6]. Polyions and nonmicellizing amphiphiles can form domains with micelle-like characteristics, including solubilization and ion-binding capacity [13].

Ionenes are cationic polymers with dimethylammonium charged centers on the polymer main chain and different numbers (*x,y*) of methylene groups between quaternized nitrogens, expressed as *x,y*-ionene. Although they do not have reactive functional groups ionenes with longer interconnecting segments (3,16- and 3,22-ionene) accelerate the alkaline hydrolysis of *p*-nitrophenyl octanoate [14]. However, this rate increase is similar to that of the same reaction by hexadecyltrimethylammonium bromide (CTABr), indicating that the hydrophobically dependent ionene conformation is extended or rodlike for hydrophilic ionenes and globular or micelle-like for more hydrophobic ionenes. The latter form compact aggregates that can bind and exchange counterions and also solubilize organic molecules, thus accelerating bimolecular nucleophilic reactions [14,15].

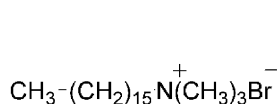
In the present study, we use the alkaline hydrolysis of benzoic anhydride (Bz₂O, **1**) to compare micellar effects of the surfactants CTABr (**2**) and benzyldimethylhexadecylammonium chloride (**3**) (BDHA) with those of the ionene polymers 2-hydroxy-3-ionene chloride (2-OH-33R) (**4**) and poly[(dipropyliminium)-1,3-

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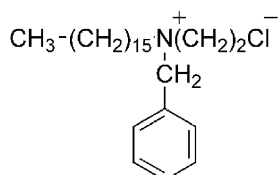
propanediyl bromide], 33R33 (5).



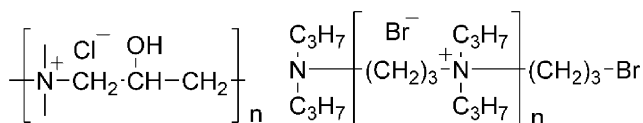
(1)



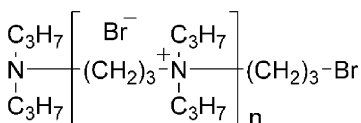
(2)



(3)



(4)



(5)

2. Experimental details

2.1. Materials

2-OH-33R (4) was prepared as previously described [16] and 33R33, 5, was synthesized from *N,N,N',N'*-tetrapropylpropane diamine prepared by the method reported by Knapick and co-workers [17]. The polymerization followed the procedure of Rembaum [18] and Knapick et al. [17]. Bz₂O was prepared and purified as described [19]. The surfactants CTABr and BDHA (Sigma) were used as received. Other reactants and solvents, of analytical grade were used without further purification.

2.2. Potentiometric titrations

Concentrations of both polymers in the stock solution were determined by titration of the bromide or chloride counterion by the Mohr method. Standard solutions were 0.1-M silver nitrate and silver chromate was the indicator. The concentration of polymer, expressed as monomeric units, was 77.6 and 93.5 mM for 33R33 ionene and 2-OH-33R, respectively.

2.3. Kinetics

Reactions were followed in aqueous solution at constant pH with a Hewlett-Packard 8452A spectrometer at 244 nm for Bz₂O. All reactions were followed in 0.01 M borate buffer and it has been shown that under these conditions first-order rate constants, k_{obs} , are not affected by this dilute buffer [20]. The reaction was in quartz cuvettes, a final volume of 2.0 mL and 50 μM Bz₂O. Temperature was controlled with a thermostated water-jacketed cell holder. First-order rate constants, k_{obs} , were calculated from linear plots of $\ln(A_{\infty} - A_t)$ against time for at least 90% reaction using an iterative least-squares program; Correlation coefficients were >0.999 for all kinetic runs. Surfactant and polymer

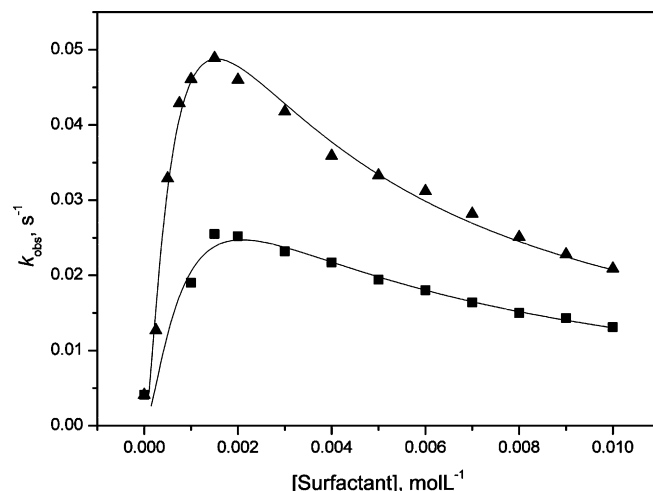


Fig. 1. First-order rate constants for the alkaline hydrolysis of Bz₂O vs. surfactant concentration for CTABr (■) and BDHA (▲), in the presence of 0.01 M borate buffer, pH 9.0, 25 °C.

solutions were prepared with deionized H₂O (Milli-Q system, Millipore).

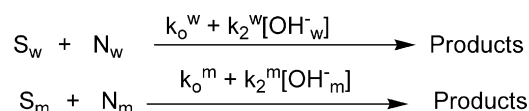
3. Results and discussion

3.1. Reactions in micelles

The reactions of Bz₂O with hydroxide ion were studied in water as a function of surfactant concentration at pH 9.0 with 0.01 M borate buffer. Fig. 1 shows the micellar-mediated reactions with k_{obs} going through maxima with increasing micelle concentration, typical of bimolecular ion-molecule reactions [21].

The quantitative treatment used to fit the data was based on the widely used pseudophase model which considers partitioning of the reagents between the aqueous and micellar pseudophases and simultaneous reactions in both regions (Scheme 1) [10,22].

In Scheme 1, k_0^w and k_0^m correspond to the rate constants for the spontaneous water reaction, k_2^w and k_2^m are second-order rate constants for the hydroxide ion reactions and subscripts w and m indicate micellar and aqueous pseudophases, respectively. It is important to remark that the reaction in aqueous solvents have been studied in considerable detail and, as shown in the scheme, the rate constant is a function of both the second-order rate constant for the hydroxide ion reaction in the aqueous phase, k_2^w , and the contribution of the spontaneous water reaction (k_0^w) and a similar dependence is observed in micellar media [20,22]. In order to simplify the data treatment, we neglect the contribution of the spontaneous reaction in water because, at pH 9.0, the second-order term is responsible for more than 94% of the reaction. Similarly, in the micellar pseudophase, k_0^m can also be neglected because k_0^m is in the range of 30 times slower than the rate constant for the spontaneous reaction in the aqueous phase and since hydroxide ion is concentrated in the surface of the cationic surfactant, the contribution of k_2^m [OH_m^-] should be much larger than that of the spontaneous water reaction.



Scheme 1. Reactions in the aqueous and micellar pseudophases.

Table 1
Kinetic parameters obtained from Eq. (1)

Constants	CTABr	BDHA
K_{xy}	0.09	0.25
α	0.25	0.35
V_m (M ⁻¹)	0.37	0.37
K_s (M ⁻¹)	721.2	680.3
k_2^w (M ⁻¹ s ⁻¹)	427	427
CMC (M)	0.00035	0.00025
pH	9.0	9.0
k_2^m (M ⁻¹ s ⁻¹)	42.6 ± 0.97	65.3 ± 0.88

With these simplifications, the observed rate constants can be described using the pseudophase model for ionic reactions, which involves competition between reactive and inert counterions, by means of Eq. (1).

$$k_{\text{obs}} = \frac{k_2^w [\text{OH}_w^-] + (k_2^m/V)([\text{OH}_m^-]/[\text{OH}_w^-])K_s}{(1 + K_s[C_d])(1 + [\text{OH}_m^-]/[\text{OH}_w^-])} \quad (1)$$

Here k_2^w and k_2^m are second-order rate constants for reactions in the aqueous and micellar pseudophases, respectively. V is the molar volume of the surfactant reaction region, K_s , the binding constant of substrate to the micelle, in terms of concentration of micellized surfactant, $[C_d]$, which is assumed to be $[S]$ -cmc, where $[S]$ is the total surfactant concentration. $[\text{OH}_w^-]$ is the total hydroxide concentration, and $[\text{OH}_m^-]$, the hydroxide ion concentration in the micellar pseudophase, in terms of the total solvent volume, that was calculated from Eqs. (2)–(4).

$$[\text{OH}_m^-] = \frac{-A_2 + \sqrt{(A_2)^2 + 4K_{xy}[\text{OH}_w^-]C_d(1 - \alpha)}}{2} \quad (2)$$

$$A_2 = \alpha C_d + \text{CMC} + K_{xy}[\text{OH}_w^-] \quad (3)$$

$$K_{xy} = \frac{[\text{OH}_m^-][X_w]}{[\text{OH}_w^-][X_m]} \quad (4)$$

In these equations, K_{xy} is the ion-exchange constant for hydroxide and the micelle counterion, α describes the fractional micellar dissociation and CMC is the critical micelle concentration in the reaction conditions. Fig. 1 shows the treatment of the data by using Eq. (1). Table 1 summarizes the kinetic parameters for Bz₂O base hydrolysis in solutions of cationic surfactants.

The good agreement of the experimental and calculated values shows the validity of the pseudophase ion-exchange model under the conditions studied. Values of K_{xy} obtained are similar to those found in the literature [23]. The CMC values in water of 9.4×10^{-4} M for CTABr and 4.7×10^{-4} M for BDHA [24] were lower in the reaction conditions, as is generally observed [25]. The CMC values did not affect the predicted rate profile except in very dilute surfactant. The assumption of constant degree of micelle ionization is valid because with the low K_{xy} , α depends largely on the halide ion concentration in the aqueous pseudophase [25].

In both conditions, $k_2^w > k_2^m$, as is typical of anhydride and anhydride hydrolyses in aqueous micelles. The difference between the k_2^m values studied is consistent with the different head group effects. Second-order constants for reactions of anionic nucleophiles with nonionic substrates typically increase with decreasing medium polarity, and head group polarity of BDHA is lower than of CTABr. The k_2^m/k_2^w ratio for the hydrolysis of the Bz₂O was 0.1 in CTABr and 0.16 in BDHA solutions. Although the binding constant K_s is lower for BDHA due to its higher hydrophobicity, the ion-exchange constant is higher for BDHA. Thus, the observed kinetic effect of cationic surfactants is mostly due to the concentration of hydroxide ion and substrate in the micellar pseudophase.

The first-order rate constant for the hydrolysis of Bz₂O at pH ~ 9, where the hydroxide ion reaction is predominant, extrapolated to

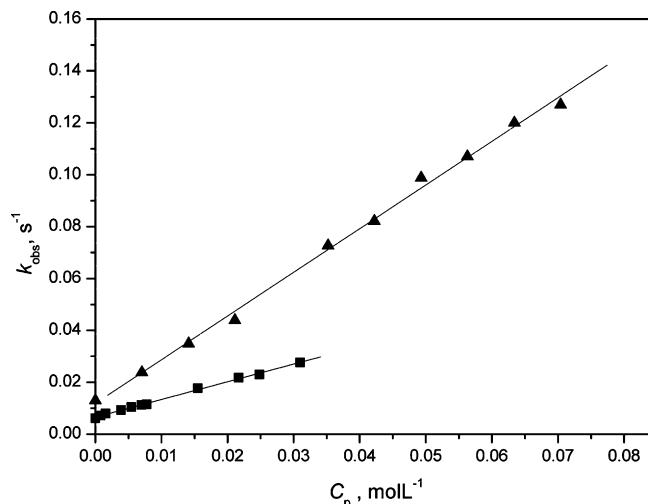


Fig. 2. Dependence of the hydrolysis reaction rate of Bz₂O on the presence of 33R33 (■) and 2-OH-33R (▲), pH 9.0, 25 °C.

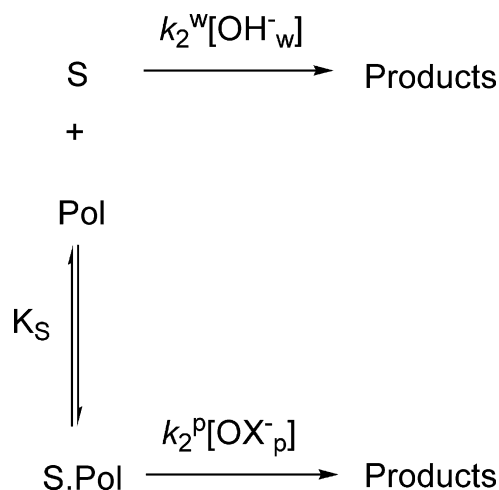
zero buffer, is $4.33 \times 10^{-3} \text{ s}^{-1}$ at 25 °C [26], and as shown in Fig. 1, micellar solutions of BDHA and CTABr effectively speed the reaction by factors of about 12-fold and 6-fold, respectively. The acceleration of Bz₂O hydrolysis by cationic surfactants, is in agreement with previous results [26], and the values of the rate constants in Table 1 show that the observed catalytic effect is not due to an effective increase of the rate constant in the micellar phase, but to increase in the concentration of hydroxide ion in the micellar phase.

The quantitative treatment of the data neglects pre-micellar rate effects and they are generally neglected with $[\text{surfactant}] \gg \text{cmc}$ [26]. Only one maximum is observed for the Bz₂O hydrolysis, although two maxima were observed for reactions in dilute surfactant in different conditions [27].

3.2. Reactions in polymers

The alkaline hydrolysis of Bz₂O was also studied in the presence of the ionene polymers 33R33 and 2-OH-33R using borate buffer, Fig. 2, where k_{obs} increases linearly with concentrations of 33R33 and 2-OH-33R. There is up to a 25-fold enhancement of the observed rate constant for the hydrolysis of Bz₂O with 2-OH-33R and up to a 6-fold enhancement with ionene 33R33, compared to reaction in their absence. The rate enhancement can be attributed to the substrate incorporation on the polymer domains, where the anhydride can react with the hydroxide in the solution, for the case of 33R33. But in the case of 2-OH-33R the substrate can also react with the alkoxide ion formed on the polymer chain. The secondary hydroxyl group on the polymer should have an acid dissociation constant slightly lower than that of choline ($\text{p}K_a = 12.8$) [28], and the resulting alkoxide ion will effectively react with benzoic anhydride (see below). The expected $\text{p}K_a$ is similar to that reported for CHEHAB ($\text{p}K_a = 12.4$) [29] and other polymers such as the ionenes poly[methylbutylimino 2-hydroxi propanodiyil; chloride] (2-hydroxi 33R4 chloride) and poly[methyloctylimino 2-hydroxi propanodiyil; chloride] (2-hydroxi 33R8 chloride) ($\text{p}K_a = 12.0$ and 11.99, respectively) [30].

Scheme 2, developed by Klotz [31] for nucleophilic substitutions by azide ions was used to derive Eq. (5), where C_p is the polymer concentration, expressed as monomeric units. It is assumed that the hydrolysis can occur in a non-polymeric environment, k_2^w (Eq. (5)), but the substrate can also bind to the polymer (K_s) and react



Scheme 2. Reactions in the aqueous phase and in the polymer domains.

in this region, $k_2^p[\text{OX}^-]_p$ (Eq. (5)).

$$k_{\text{obs}} = \frac{k_2^p[\text{OX}^-]_p K_s C_p + k_2^w[\text{OH}^-]_w}{1 + K_s C_p} \quad (5)$$

In Eq. (5), the term $[\text{OH}^-]_w$ is the hydroxide concentrations in water and $[\text{OX}^-]_p$ when $X = \text{H}$, corresponds to the hydroxide in the polymer domain, defined as the, molarity in the total solution and, particularly in the case of 2-OH-33R, for $X = \text{R}$, it corresponds to the sum of the equilibrium concentrations of hydroxide and alkoxide ions. Eq. (5) predicts that in dilute polymer, $1 > K_s C_p$, a plot of k_{obs} versus polymer concentration will be linear, with an angular coefficient $k_2^p[\text{OX}^-]_p K_s$ and a y-axis intercept $k_2^w[\text{OH}^-]_w$. Low values of K_s are consistent with the linear plot, reflecting the low hydrophobicity of the polymers. Indeed, a low value of $K_s < 10$ was estimated, within an error $< 10\%$, because for higher values of K_s , a saturation profile would be observed. Table 2 gives calculated values of $k_2^p[\text{OX}^-]_p K_s$ obtained from the fit of the data in Fig. 2, considering a value of k_2^w of $427 \text{ M}^{-1} \text{ s}^{-1}$ for the spontaneous alkaline hydrolysis of Bz_2O at 25°C . Values of $K_s(k_2^p/k_2^w)([\text{OX}^-]_p/[\text{OH}^-]_w)$ are presented in order to evaluate the real catalytic effect of the polymers. Reactions were also carried out at pH 8.50, as shown in Table 2.

According to Table 2, 2-OH-33R is a better catalyst than 33R33 with the ratio of the $k_2^p[\text{OX}^-]_p K_s$ values between the two polymers being 2.5 and this result is consistent with the fact that 2-OH-33R behaves as a functional polymer, with the ionized hydroxyl group acting as the nucleophile. A similar behavior was observed in other reactions and, for example, in the decomposition of Dicofol (1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol), a ratio of $k_{\text{obs}}^{\text{Dicofol}}/k_{\text{obs}}^{\text{CTABr}} = 1.80$ was attributed to the contribution of the 2-hydroxyethyl group in the surfactant head group of CHEDAB, which acts as a base in the elimination reaction [21]. Since the value of K_s is rather small ($< 10 \text{ M}^{-1}$), concentration of the substrate in the polymer surface should be rather less important. Thus, the catalytic effect of the polymer, which is given by the values of

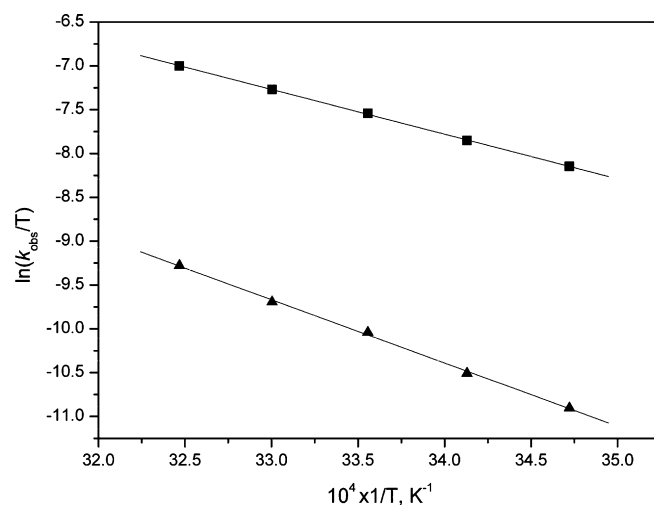


Fig. 3. Dependence of the observed rate constants for Bz_2O hydrolysis on the temperature in the presence (■) and absence (▲) of 2-OH-33R.

$K_s(k_2^p/k_2^w)([\text{OX}^-]_p/[\text{OH}^-]_w)$, seems to be related to both the (k_2^p/k_2^w) and $([\text{OX}^-]_p/[\text{OH}^-]_w)$ ratios. It is interesting to note that for compounds with structures similar to the 33R33 polymer, it has been shown that anions are indeed concentrated in analogue cationic domains. In fact, previous studies using gemini surfactant with three methylene groups between quaternized nitrogens, showed a significant incorporation of anions such as chloride, bromide and hydroxide [32]. Thus, for 2-OH-33R the observed effect could be attributed to both the ability of the polymer to pre-concentrate hydroxide ions ($[\text{OH}^-]_p$) and to the fact that the alkoxide ion of the polymer can be an effective base in the reaction.

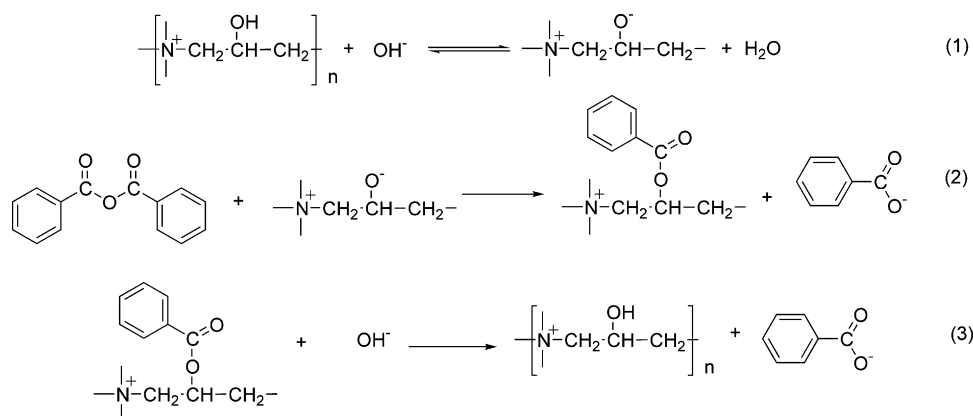
Activation parameters were also obtained for the hydrolysis of Bz_2O in the presence and absence of 2-OH-33R to give additional insight into the nature of the reactions studied. A graphical representation of the experimental results is given in Fig. 3.

Based on the data of Fig. 3, values of $\Delta S^\ddagger = -19.22 \text{ eu}$ and $\Delta H^\ddagger = +14.41 \text{ kcal mol}^{-1}$ were obtained for the basic hydrolysis of Bz_2O and the results are consistent with those previously reported [33]. In the presence of 2-OH-33R, values of $\Delta S^\ddagger = -28.39 \text{ eu}$ and $\Delta H^\ddagger = +10.18 \text{ kcal mol}^{-1}$ are obtained for the hydrolysis of benzoic anhydride. Clearly, the contribution of several water molecules in the ground state and in the transition state is consistent with the negative entropy values for the hydrolysis in the presence and absence of polymer. Besides, the negative entropy values are indicative of higher hydration in the transition state compared with the ground state and the effect is higher in the presence of the polymer. Thus, the catalytic effect is mostly due to the decrease in the enthalpy of activation, which more than compensates the more negative entropy of activation obtained in the presence of the polymer. The results are completely different from those reported in the cyclodextrin catalysis, where the small catalytic effect was attributed to a large increase in entropy of activation, which compensates the increase in enthalpy of activation [33]. Comparing

Table 2

Calculated values of $k_2^p[\text{OX}^-]_p K_s$ for the reactions studied with Bz_2O as substrate

Polymer	T ($^\circ\text{C}$)	pH	$10^3 \times k_2^p[\text{OX}^-]_p K_s (\text{M}^{-1} \text{ s}^{-1})$	$K_s(k_2^p/k_2^w)([\text{OX}^-]_p/[\text{OH}^-]_w) \text{M}^{-1}$
33R33	25	9.04	681	157
2-OH-33R	25	9.00	1680	387
2-OH-33R	25	8.50	924	407
2-OH-33R	20	9.00	1340	309
2-OH-33R	20	8.50	611	269



Scheme 3. Mechanism of benzoic anhydride hydrolysis in the presence of 2-hydroxy-3-ionene.

Arrhenius fits for reactions in the aqueous phase is straightforward, but reactions in the presence of the polymer are complex and the constant K_s is already incorporated in the kinetic rate constants. As a result, the differences observed in the activation parameters of cyclodextrins and polymers, may well be a result of differences in the contributions of reactivity and binding.

If the hypothesis that 2-OH-33R acts as a nucleophile is correct then it is expected that the Bz_2O hydrolysis would be consecutive with the formation of a stable intermediate. Scheme 3 presents the proposed mechanism for the hydrolysis of Bz_2O involving an intermediate, consisting in a pre-equilibrium (1), followed by a two-step reaction, (2) and (3). In the pre-equilibrium (1), the hydroxide ion deprotonates the polymer and the conjugated base of the polymer attacks benzoic anhydride in the first step (2), forming the acylated polymer intermediate (benzoyl anhydride). The second step (3) is expected to be the reaction rate-determining step, in which the intermediate is attacked by hydroxide ion, regenerating the polymer.

Indeed, the experimental results are consistent with Scheme 3, where the intermediate was detected. Two reactions were then followed, the first reaction, which is fast and the rate constants increase linearly with polymer concentration is shown in Fig. 2. The second reaction is slow, taking about 6 h and involves breakdown of an intermediate. In this second step rate constants are largely insensitive to the polymer concentration, as shown in Fig. 4.

The observed results suggest that the Bz_2O alkaline hydrolysis mediated by ionenes can occur as shown in Fig. 5, where (1) is the reaction in the absence and (2) and (3) in the presence of ionenes. The typical macroion effect is demonstrated in (2), with the macroion approximating the reactants, enhancing the hydrolysis reaction rate which can be due to hydrophobic and electrostatic

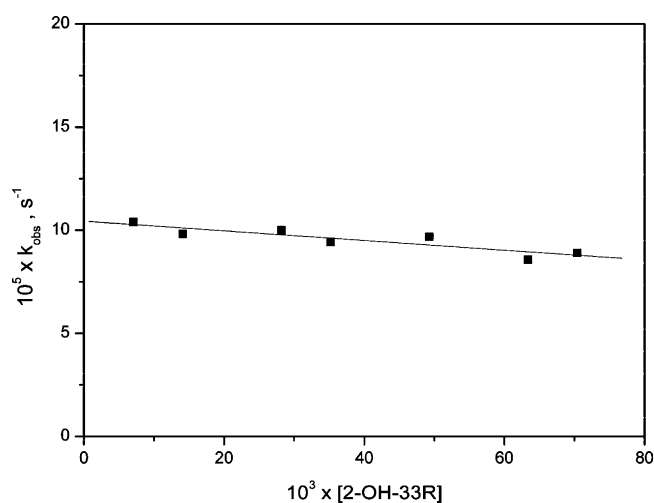


Fig. 4. Observed rate constants of the second reaction as a function of 2-OH-33R, at 25 °C, pH 9.00.

effects. In (3), not only the macroion acts a microreactor, but it can also attack the anhydride, leading to an acylated polymer intermediate, thus greater enhancements effects are observed.

Interesting is when comparing the results of the hydrolysis of Bz_2O in the presence of the ionenes and surfactants, they present at least comparable rate enhancements, even when considering the absence of hydrophobic effects in the ionenes. This is interesting because they are readily soluble in water and furthermore can be easily separated from the reagents.

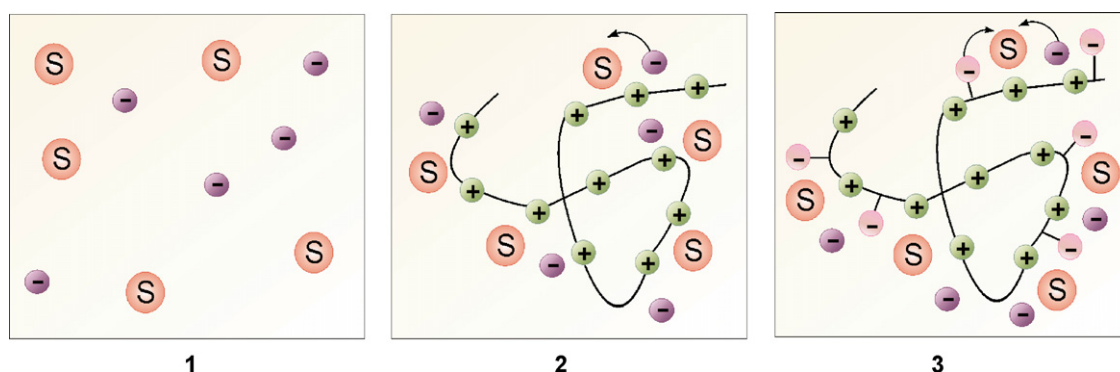


Fig. 5. Schematic description of the macroion effect on anhydride hydrolysis.

4. Conclusion

Micellar-mediated hydrolyses were compared to those of ionene polymers. Micellar effects on bimolecular reactions were treated considering the equilibrium distribution of the substrate and nucleophile between aqueous and micellar pseudophases and a modified Michaelis–Menten equation described the kinetics of ionene-mediated hydrolysis. The cationic polymer 2-hydroxy-3-ionene chloride (2-OH-33R) is the most effective catalyst and a detailed mechanism of hydrolysis involving an intermediate is proposed. Participation of alkoxy group in 2-OH-33R enhances the reactivity of this polymer as compared with the 33R33 polymer in anhydride hydrolysis, i.e., 2-OH-33R is a functional polymer, with the ionized hydroxyl group as the nucleophile. The catalytic efficiency in terms of k_{obs} follows the order 2-OH-33R > BDHA > 33R33 > CTABr.

Acknowledgements

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