

# Activation Parameters and the Catalytic Effects of Poly(3-Alkyl-1-Vinylimidazolium) Salts on the Hydrolysis of Neutral Phenyl Esters

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## Synopsis

Alkaline hydrolyses of *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl laurate (PNPL) were studied in the presence of poly(3-methyl-1-vinylimidazolium iodide) (PVII-C<sub>1</sub>), poly(3-*n*-hexadecyl-1-vinylimidazolium iodide) (PVIII-C<sub>16</sub>) and their monomeric analogs. The polysoap (PVII-C<sub>16</sub>) was a completely quaternized polyion, in contrast to other polysoap systems that have been studied. The hydrolysis of PNPA was not affected by these polyions. The hydrolysis of PNPL was instead enhanced by the addition of these cationic polyions. The magnitudes of the enhancement were in the order of PVII-C<sub>16</sub> > PVII-C<sub>1</sub>, which is explained in terms of the hydrophobicity of these polyions. Values of  $k_2$ , the rate constant of the polymer substrate complex, indicated that the esters bound to the polymer were more reactive than the free esters. Binding or association constants ( $K$ ) obtained also increased in the order PVII-C<sub>16</sub> > PVII-C<sub>1</sub>. Inhibitory results were observed for the hydrolysis of PNPL in presence of 3-*n*-hexadecyl-1-vinylimidazolium iodide (VII-C<sub>16</sub>). The activation parameters for these reactions were also investigated.

## INTRODUCTION

It is now well recognized that both micelles<sup>1</sup> and synthetic polymers<sup>2</sup> are effective catalysts for many organic reactions. These micellar and synthetic polymeric systems are of particular interest because they exhibit many features observed in enzyme reactions.<sup>1,2</sup> These features include reactivities higher than those of the corresponding monomeric systems, substrate specificity, competitive inhibition, bifunctional interactions of functional groups and substrate, and saturation by low and high molecular weight substrates.<sup>1,2</sup> The catalytic effects of micelles and synthetic polyelectrolytes on ester hydrolysis are of two different types. In the first case where no nucleophilic groups are present in either the micelle or the polyelectrolyte, the micelle or polyelectrolyte will normally tend to accumulate and/or repel the low molecular weight ionic reagents in its environment, thus changing their reaction rates. This effect would be primarily electrostatic, and either catalysis or inhibition would occur, depending upon the relative charges of the reactants and those of the micelle or polyelectrolyte. In the second case where the micelle or polyelectrolyte contains nucleophilic groups, the catalytic action will be dependent on the active substituents in addition to ionic binding sites.

Many hydrolytic studies have been reported utilizing micellar or synthetic polymeric systems. Cordes and co-workers<sup>3</sup> and Okubo and Ise<sup>4</sup> have reported

systems that incorporate both the novel features of micelles and polyelectrolytes, i.e., catalyst systems that have binding sites available for both strong hydrophobic and electrostatic interactions with suitable substrates. Such hydrophobic polyelectrolyte systems have been prepared and have been termed "polysoaps."<sup>5-8</sup> The catalytic properties of these polysoaps remain largely unexplored.

We have initiated a series of investigations to study the catalytic effects of cationic polyelectrolytes, ranging in solution behavior from "normal" polyions to polysoaps, upon the alkaline hydrolysis of neutral and anionic phenyl esters of varying chain lengths. Employing these catalysts of varying hydrophilic-hydrophobic character in conjunction with the neutral and anionic substrates of varied hydrophilic-hydrophobic character, it should be possible to illustrate the novel combination of hydrophobic and electrostatic features into a single catalytic system.

The first of these studies dealing with the hydrolysis of *p*-nitrophenyl acetate (PNPA), and *p*-nitrophenyl laurate (PNPL) is described in this paper.

## EXPERIMENTAL

### Substrates

*p*-Nitrophenyl acetate (PNPA) was synthesized from *p*-nitrophenol and acetic anhydride according to the general method of Bender and Nakamura.<sup>9</sup> The ester was recrystallized four times from petroleum ether giving a melting point of 78–79°C (lit. 81–82°C).<sup>9</sup>

*p*-Nitrophenyl laurate (PNPL) was prepared by a slight modification of the procedure reported by Zahn and Schade<sup>10</sup>: 0.125 mol of *p*-nitrophenol, 0.10 mol of lauroyl chloride, and 0.10 mol of pyridine were dissolved in 80 mL of dry toluene and refluxed for about 1 h. The solution was neutralized with saturated NaHCO<sub>3</sub> and washed with water, 5% NaOH, 0.1*N* HCl, and finally with water. The toluene solution was dried over anhydrous MgSO<sub>4</sub>, filtered, and then evaporated. The obtained light yellow waxy solid was recrystallized four times from absolute ethanol, gave a melting point of 46–47°C (lit. 45°C),<sup>10</sup> and a carbonyl stretching frequency at 1755 cm<sup>-1</sup>.

### Catalysts

#### *Monomers*

3-Methyl-1-vinylimidazolium iodide (VII-C<sub>1</sub>) and 3-*n*-hexadecyl-1-vinylimidazolium iodide (VII-C<sub>16</sub>) were obtained by the quaternization of 1-vinylimidazole with the corresponding *n*-alkyl iodides, according to the method reported by Salamone and co-workers described below.

3-Methyl-1-vinylimidazolium iodide (VII-C<sub>1</sub>): To 9.41 g (0.10 mol) of freshly distilled 1-vinylimidazole was added 85.20 g (0.60 mol) of reagent grade methyl iodide in 100 mL of dry ethyl acetate at -10°C. The reaction mixture was stirred for 1 h and then brought to room temperature overnight, during which time off-white crystals formed. The mixture was cooled and filtered, and the monomeric salt was washed three times with anhydrous diethyl ether,

followed by three recrystallizations from *n*-propanol giving off-white needles, mp 77.5–78.0°C.

**3-*n*-Hexadecyl-1-vinylimidazolium iodide (VII-C<sub>16</sub>):** To 4.23 g (0.012 mol) of *n*-hexadecyl iodide in 100 mL of dry ethyl acetate was added 1.00 g (0.0106 mol) of 1-vinylimidazole. After stirring the mixture for 48 h at room temperature, the solution was cooled to 0°C, and crystallization of the quaternary salt rapidly occurred. The crystals were filtered, washed with diethyl ether, and recrystallized three times from ethyl acetate. Off-white needles were obtained, mp 68.0–68.5°C.

### *Polymers*

**Polyvinylimidazolium Iodides.** The above monomeric salts were homopolymerized to their corresponding polyvinylimidazolium iodides, i.e., poly(3-methyl-1-vinylimidazolium iodide) (PVII-C<sub>1</sub>) and poly(3-*n*-hexadecyl-1-vinylimidazolium) iodide (PVII-C<sub>16</sub>) according to Salamone's method presented as follows<sup>11</sup>: To a heavy walled polymerization tube was added 10 mL of a 0.45*M* aqueous solution of a monomeric salt (VII-C<sub>1</sub> or VII-C<sub>16</sub>) which contained 1 mol % of 4,4'-azobiscyanovaleric acid. The contents of the tube were flushed with nitrogen and sealed in vacuum after utilization of the freeze-thaw technique. The tubes were then placed in a constant temperature bath thermostated at 60°C for 20 h. In the case of the completely water-soluble, short chain length polymer (PVII-C<sub>1</sub>), the polymeric salt solution was exhaustively dialyzed against deionized water and the product was obtained by lyophilization. In the formation of the long side-chain polymer (PVII-C<sub>16</sub>) the solution turned opaque during the reaction and approximately 30% water-insoluble polymer formed with the remainder existing in an emulsified solution. This solution was dialyzed against deionized water, and then isolated in aqueous solution. Sufficient quantity of absolute ethanol was added to this solution in order to obtain a 20 mol % ethanol-water solution. This solution was then employed in the kinetic studies. The concentration of the original solution was determined by solid content analysis.

### **Kinetic Measurements**

#### *Preparation of Solution for Kinetics*

Catalyst solutions were prepared in 20 mol % ethanol-water buffered to the proper pH. Sufficient potassium chloride was added to adjust the ionic strength to 0.002*M*. To 20 mL of the buffered catalyst solution placed in a volumetric flask thermostated at the proper temperature, 3 mL of an ethanol solution of the substrate was added. The concentrations of substrate and catalyst reported are of the final reaction mixture.

#### *Kinetic Measurements*

The rate of hydrolysis of substrate was measured both in the presence and absence of polymer or monomer utilizing a Beckman Model 25 spectrophotometer equipped with a sipper cell. The absorbance ( $A_t$ ) of the nitrophenolate anion was measured as a function of time at 406 nm, utilizing the sipper

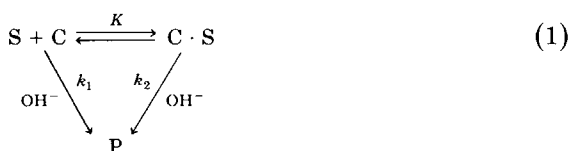
cell. Absorbance at infinite time ( $A_\infty$ ) was taken after at least 10 half-lives. Representative samples demonstrated that the pH did not change during the reactions (Fisher, Accumet, Model 220 pH meter). The reaction mixtures were thermostated in a constant temperature bath at the proper temperature. The determination of  $\lambda_{\max}$  for nitrophenolate anion as well as the shift in  $\lambda_{\max}$  for methyl orange in presence of the catalysts was obtained with the utilization of a Perkin-Elmer Hitachi 200 spectrophotometer.

### Data Treatment

The collected data were found to obey pseudo-first-order kinetics by plotting  $\ln(A_\infty - A_t)$  vs. time ( $t$ ). Generally, the plots were straight lines for more than 50% reaction. The slopes of these plots were taken as the observed first-order rate constant ( $k_{\text{obs}}$ ). Plots of  $k_{\text{obs}}$  vs. catalyst resulted in straight lines, indicating a first-order dependence on catalyst for some systems. The slope of the line was the second-order catalytic rate constant ( $k_{\text{cat}}$ ). The intercept corresponded to the first-order buffer rate constant ( $k_{\text{blank}}$ ). For the poly(*n*-alkyl-1-vinylimidazolium) systems, plots of  $k_{\text{obs}}$  vs. [catalyst] indicated saturation phenomena according to the kinetic scheme presented in eq. (1). In these systems  $k_{\text{obs}}$  is the measured first-order rate constant. By plotting  $1/(k_{\text{obs}} - k_1)$  vs.  $1/[C]$ , the kinetic constants can be obtained.

## RESULTS AND DISCUSSION

The kinetic scheme employed in the hydrolyses of neutral nitrophenyl esters catalyzed by poly(*n*-alkyl-1-vinylimidazolium) iodides of varying hydrophobic-hydrophilic character, is shown in eq. (1). The rate constants were evaluated from the plots of  $1/(k_{\text{obs}} - k_1)$  vs.  $1/[C]$  according to eq. (2):



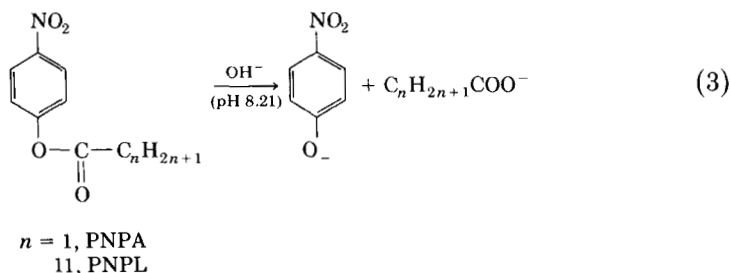
$$\frac{1}{k_{\text{obs}} - k_1} = \frac{1}{k_2 - k_1} + \frac{1}{K(k_2 - k_1)} \cdot \frac{1}{[C]} \quad (2)$$

Here S, C, C · S, and P denote the substrate, polymer or monomer catalyst, substrate polymer complex, and product, respectively, and  $k_{\text{obs}}$  is the measured first-order rate constant,  $k_1$  the first-order rate constant for the hydrolysis reaction of the substrate, and  $k_2$  the first-order rate constant for the hydrolysis reaction of the complex. Equation (2) predicts a linear relationship between  $1/(k_{\text{obs}} - k_1)$  and  $1/[C]$  in its graphical representation with  $1/(k_2 - k_1)K$  being the slope of the line and  $1/(k_2 - k_1)$  being the intercept. According to this relation, the kinetic parameters of eq. (1) can be evaluated graphically.

### Hydrolysis of PNPA and PNPL Catalyzed by Poly(*n*-Alkyl-1-Vinylimidazolium) Iodides

The catalytic activities of poly(3-methyl-1-vinylimidazolium iodide) (PVII-C<sub>1</sub>) and poly(3-*n*-hexadecyl-1-vinylimidazolium iodide) (PVII-C<sub>16</sub>) of

varying hydrophilic-hydrophobic character and their respective monomeric compounds 3-methyl-1-vinylimidazolium iodide (VII-C<sub>1</sub>) and 3-*n*-hexadecyl-1-vinylimidazolium iodide (VII-C<sub>16</sub>) were investigated by surveying the hydrolysis of a series of neutral nitrophenyl esters presented in eq. (3). The kinetic experiments were performed at 30°C in aqueous buffer media containing 20% mol ethanol, [tris(hydroxymethyl)aminomethane (TRIS) = 0.002M],  $\mu = 0.002$ , and pH = 8.21.



The rates of hydrolysis of these esters catalyzed by the above polymers and their low molecular weight analogs were found to be pseudo-first-order kinetics. Plots of  $\ln(A_\infty - A_t)$  vs. time were straight lines for 50–80% conversion or more, as shown in Figure 1. The rate constants were evaluated from the plots of  $1/(k_{\text{obs}} - k_1)$  vs.  $1/[C]$  according to the kinetic scheme of eq. (1).

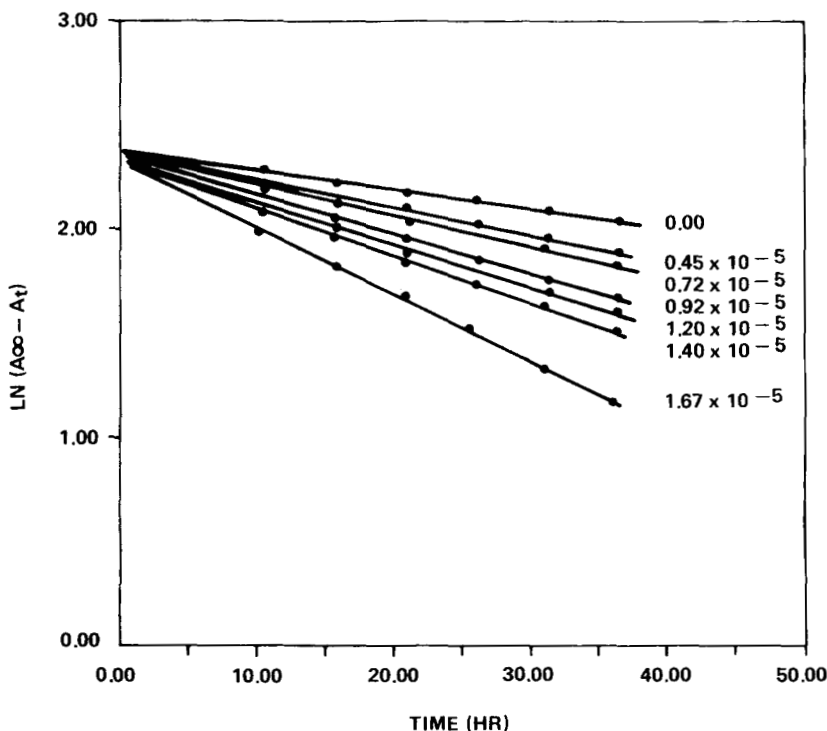


Fig. 1. Variation of  $\ln(A_\infty - A_t)$  with time for the hydrolysis of PNPL in the presence of PVII-C<sub>16</sub>. [PNPL] =  $1.66 \times 10^{-5}M$ , pH 8.21, 20% EtOH-H<sub>2</sub>O.

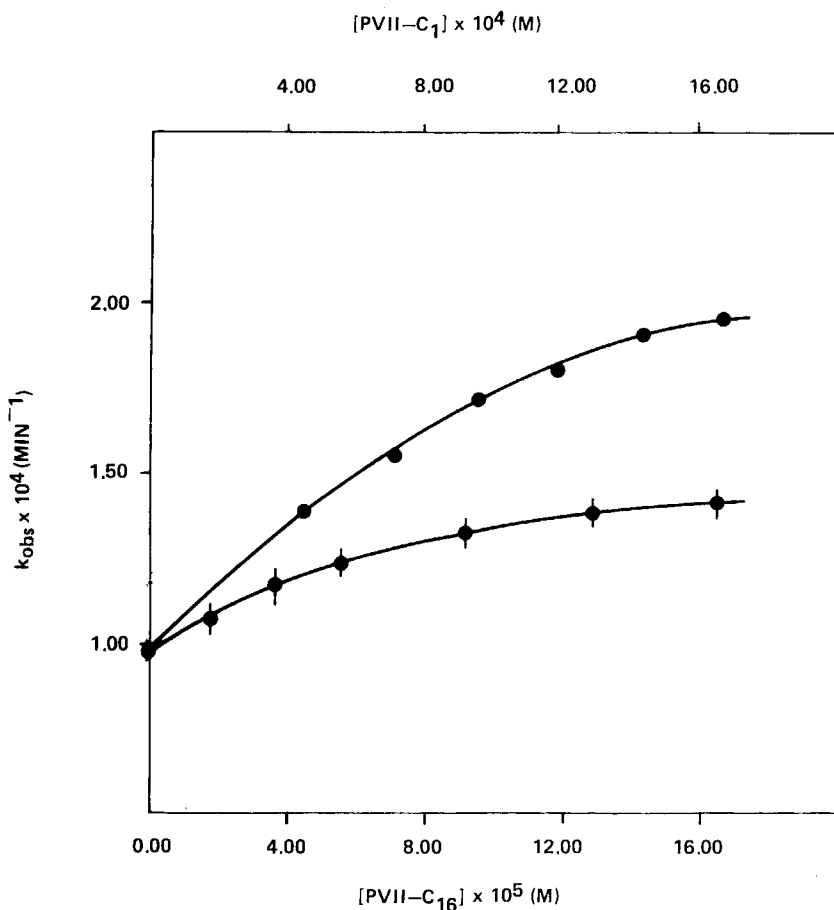


Fig. 2. Variation of observed rate constants for the hydrolysis of PNPL with varying concentrations of PVII-C<sub>1</sub> (●) and PVII-C<sub>16</sub> (●) at 30°C. [PNPL] =  $1.66 \times 10^{-5}M$ , pH 8.21, 20% EtOH-H<sub>2</sub>O.

The observed rate constants for the hydrolysis of PNPL with varying concentrations of PVII-C<sub>1</sub> and PVII-C<sub>16</sub> at 30.0°C are presented in Figure 2. Plots of  $1/(k_{obs} - k_1)$  vs.  $1/[C]$  for the hydrolysis of PNPL are shown in Figure 3. The kinetic parameters of eq. (2) for the hydrolysis of PNPA and PNPL in the presence of these polyions are compiled in Table I. As can be seen from Figure 2, the alkaline hydrolysis reactions of PNPL were enhanced by the addition of cationic polyelectrolyte and polysoap and the magnitudes of the enhancement were in the order of PVII-C<sub>16</sub> > PVII-C<sub>1</sub>.

Saturation type kinetics are observed, strongly suggesting the formation of a complex between polymer and ester. This complexation phenomenon implied the validity of the kinetic scheme employed [eq. (1)]. In these systems, both  $K$  and  $k_2$  increased according to the hydrophobicity of the polyion or the ester.

Values of  $k_2$  are seen to be greater than  $k_1$  values. Thus, the esters bound to polyions are more reactive than the esters themselves. Values of  $k_2$  increased in the order PVII-C<sub>16</sub> > PVII-C<sub>1</sub>. This indicates that the reactivity

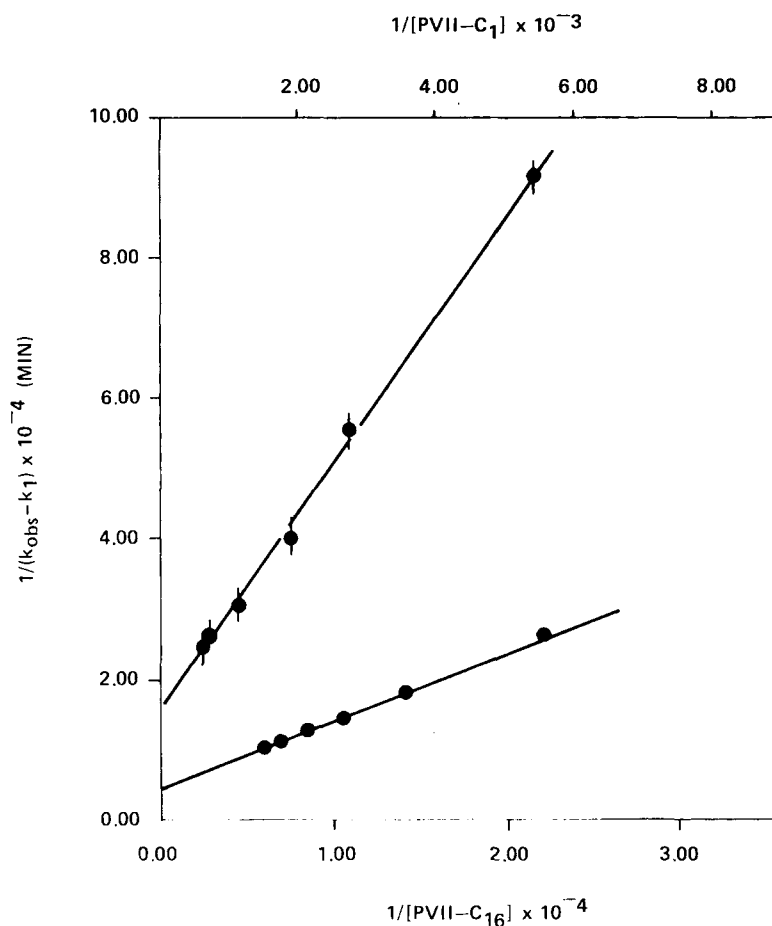


Fig. 3. Variation of  $(k_{\text{obs}} - k_1)^{-1}$  with  $[\text{PVII-C}_1]^{-1}$  (●) and  $[\text{PVII-C}_{16}]^{-1}$  (●) for the hydrolysis of PNPL at 30°C.  $[\text{PNPL}] = 1.66 \times 10^{-5} M$ , pH 8.21, 20% EtOH-H<sub>2</sub>O.

TABLE I  
Kinetic Parameters of Eq. (1) for the Hydrolysis of PNPA and PNPL  
in the Presence of Polyions and Micelles<sup>a</sup>

Ester	Catalyst	pH	$K$	$k_1$ (min <sup>-1</sup> )	$k_2$ (min <sup>-1</sup> )
PNPA	VII-C <sub>16</sub>	8.21	—	$1.71 \times 10^{-2}$	—
	PVII-C <sub>16</sub>	8.21	—	$1.71 \times 10^{-2}$	—
PNPL	PVII-C <sub>1</sub>	8.21	1080	$0.98 \times 10^{-4}$	$1.64 \times 10^{-4}$
	PVII-C <sub>16</sub>	8.21	5530	$0.98 \times 10^{-4}$	$2.99 \times 10^{-4}$
	PVII-C <sub>16</sub>	10.4	4560	$6.12 \times 10^{-2}$	$14.40 \times 10^{-2}$

<sup>a</sup>At 30°C, pH 8.21, 20% EtOH-H<sub>2</sub>O.

of the complex increases as the hydrophobic character of the complex increases.

This phenomenon does indeed agree with the finding of several workers,<sup>3,4,12,13</sup> who have reported that the order of the strength of the hydrophobicity is the same as the order of the  $k_2$  values. The association constants ( $K$ ), calculated from the kinetic measurements, increased in the order  $PVII-C_{16} > PVII-C_1$ . This order does indeed correspond to that of hydrophobicity.

It was found in this study that the polycation ( $PVII-C_{16}$ ) and its monomeric analog ( $VII-C_{16}$ ) had no effect on the neutral ester PNPA at 20% ethanol-water, pH = 8.21, and very low ionic strength. The results are presented in Table II. Previous results<sup>14</sup> have shown that when the solvolytic rates of *p*-nitrophenyl acetate and *p*-nitrophenyl hexanoate were studied in the presence of poly(3-methyl-1-vinylimidazolium iodide), the shortest side-chain polycation in 28.5% ethanol-water and pH = 9 showed no enhanced solvolytic rates. These results were not unexpected, since there were no suitable sites available on this short-chain polycation for hydrophobic interactions. Even with the long-chain polyion these hydrophobic interactions were not sufficient enough to concentrate the substrate around the hydroxyl species and thus enhance the catalysis.

For these reactions, it was concluded that no significant hydrophobic interactions occurred between the polyions and the neutral short-chain ester. It could be anticipated that hydrophobic interactions could occur between the short-chain polycations with the long alkyl ester *p*-nitrophenyl dodecanoate, and to the greatest extent between the long-chain polycations and the long alkyl ester *p*-nitrophenyl dodecanoate. This indeed can be seen from the experimental findings.

Catalysis by polysoaps for alkaline ester hydrolysis must be attributed in part at least to electrostatic stabilization of the complex compared to the ground state, by the cationic polysoap. A similar explanation has been provided for catalysis of *p*-nitrophenyl hexanoate by cationic micelles.<sup>15</sup> However, hydrophobic interactions appear important to catalytic efficiency as well. The increasing slope of rate versus concentration profiles (Fig. 2) with increasing polyion hydrophobicity can be accounted for in terms of stronger binding of ester polyion. However, the observations that the maximal rate constants achieved are also increased by increasing polyion hydrophobicity indicates that hydrophobic interactions contribute either directly or indirectly

TABLE II  
 $k_{obs}$  for the Hydrolysis of *p*-Nitrophenyl Acetate (PNPA) in the Presence and in the Absence of  $PVII-C_{16}$  and Its Monomeric Analog  $VII-C_{16}$ , at Various Concentrations of Each Polymer and Monomer<sup>a</sup>

Catalyst	Concentration	$k_{obs}$ (min <sup>-1</sup> )	log $k_{obs}$
—	—	$1.71 \times 10^{-2}$	-1.77
$PVII-C_{16}$	$3.10 \times 10^{-5}$	$1.72 \times 10^{-2}$	-1.76
$PVII-C_{16}$	$3.73 \times 10^{-4}$	$1.60 \times 10^{-2}$	-1.66
$VII-C_{16}$	$2.85 \times 10^{-3}$	$1.72 \times 10^{-2}$	-1.76
$VII-C_{16}$	$7.27 \times 10^{-3}$	$1.85 \times 10^{-2}$	-1.73

<sup>a</sup>20% Ethanol-water  $\mu = 0.002$ , 30°C, pH 8.0, [PNPA] =  $2.84 \times 10^{-3}$  M.



to activation energies.<sup>13</sup> Similar observations have been made for the surfactant-catalyzed hydrolysis of *p*-nitrophenyl hexanoate in that the more hydrophobic the *n*-alkyltrimethyl ammonium salt, the greater the extent of catalysis observed.<sup>15</sup> Moreover, increasingly hydrophobic polysoaps have been observed to be more effective catalysts for the fading of cationic triphenyl methyl dyes.<sup>16</sup> In related work, the hydrolysis of carboxylic and sulfate esters<sup>17-19</sup> and phenyl phosphate dianions<sup>20</sup> is enhanced by the hydrophobic character of the catalysts.

In conclusion, it should be emphasized that an increase in the esterolytic activity of the polymeric catalysts was realized by the combination of hydrophobic interactions between catalyst and substrate and that polysoaps are better catalysts for neutral nitrophenyl ester hydrolysis than their monomeric analogs.

### Binding of Methyl Orange by Polycations Containing Apolar Pendant Groups

The interactions of various water-soluble polymers with small molecules have long been studied by many authors.<sup>21</sup> It has been apparent that hydrophobic interactions, as well as electrostatic ones, are involved in binding of small molecules and play a significant role in esterolytic processes. In fact, the basis of binding ability for small molecules by synthetic macromolecules is to introduce oppositely charged moieties and hydrophobic groups to the polymer.

The nature of the microenvironment provided by quaternized polyamines has been examined by the absorption change of methyl orange.<sup>22</sup> The absorption maximum of methyl orange shifts to shorter wavelengths in less polar media: 464 nm in H<sub>2</sub>O and 420–430 nm in organic solvents. This shift has been used for characterizing the microenvironment of aqueous polymers such as lauroylpolyethylenimine<sup>23</sup> and quaternized polyvinylpyridines,<sup>24</sup> where the  $\lambda_{\max}$  value shifts to shorter wavelengths as the alkyl group on the quaternized polymers becomes longer. Shifts in  $\lambda_{\max}$  of methyl orange in presence of poly(3-*n*-alkyl-1-vinylimidazolium) salts are presented in Table III.

Visible spectra of methyl orange have been used to detect the hydrophobic domain of polysoaps<sup>25</sup> since  $\lambda_{\max}$  (near 465 nm in water) shifts to shorter wave lengths in the hydrophobic microenvironments. An appreciable shift was

TABLE III  
 $\lambda_{\max}$  Shifts of Methyl Orange<sup>a</sup> in the Presence of Polyelectrolytes  
of Varying Hydrophilic-Hydrophobic Character

Catalyst	Concentration ( <i>M</i> )	$\lambda_{\max}$ (nm)
—	—	465
VII-C <sub>1</sub>	$1.47 \times 10^{-4}$	464
VII-C <sub>16</sub>	$2.77 \times 10^{-4}$	425
PVII-C <sub>1</sub>	$2.45 \times 10^{-4}$	461
PVII-C <sub>16</sub>	$2.85 \times 10^{-5}$	394

<sup>a</sup> Methyl orange =  $5.58 \times 10^{-6} M$ , pH 8.21, 4.6% EtOH-H<sub>2</sub>O, 25 °C.

observed in the presence of PVII-C<sub>16</sub>, suggesting that this polymer possesses hydrophobic regions.

Data presented in Table III indicate the  $\lambda_{\max}$  of methyl orange is not greatly affected by PVII-C<sub>1</sub>. Relating the rates of hydrolysis for PNPL to  $\lambda_{\max}$  shifts, it is clear that the hydrophobic nature of the polysoap is the most important factor in promoting catalytic hydrolysis. In general, the hydrophobic microenvironment as given by the  $\lambda_{\max}$  shift is directly related to the rate enhancement. This is consistent with the fact that a similar relation was observed for the combination of a long-chain hydroxamate and quaternized polyvinylpyridines.<sup>22</sup>

The conformation of the polymer and therefore its esterolytic activity is largely affected by ionic strength. The effects of the ionic strength and the organic solvent on the hydrophobicity of the polyelectrolyte systems have been studied by Abe et al.<sup>26</sup> They have shown that the hydrophobicity in the domains of contracted polymer chains to be stronger than that of expanded polymer chains. Low ionic strength has been found to enhance the hydrolysis of esters. In our studies we employed polyion solutions with very low ionic strength ( $\mu = 0.002$ ). At high ionic strength the polysoaps tend to precipitate out from the solution.

#### The Effect of 3-*n*-Hexadecyl-1-Vinylimidazolium Iodide on the Hydrolysis of *p*-Nitrophenyl Laurate

The catalytic activity of VII-C<sub>16</sub> was investigated for the hydrolysis of PNPL, a long chain neutral substrate in 20% ethanol-water and pH 10.4. The hydrolysis of PNPL in presence of VII-C<sub>16</sub> is shown in Figure 4 where  $k_{\text{obs}}$  is plotted against the concentration of VII-C<sub>16</sub>. It is seen that the VII-C<sub>16</sub> monomer inhibits the hydrolysis of PNPL and that the rate measurements do not obey the kinetic scheme presented in eq. (1). The mechanism of this inhibition is not very well understood. The findings suggest that the inhibition could be related to a displacement of hydroxide from the surface of the monomeric micelle as a consequence of binding of other anions or that the substrate is absorbed in such a manner that its ester group is not in close proximity to the hydrolyzing hydroxyl ions.

Since these experiments were performed in the presence of constant amounts of added salt and buffer, the actual anion concentration increases with increasing surfactant concentration due to the contribution of the counterion of the surfactant itself. Since anions have proved to be potent inhibitors of the detergent-dependent processes, it is possible that the inhibition at high detergent concentrations is, in fact, a salt effect. It is reported in the literature<sup>27</sup> that the inhibition of surfactant-dependent hydrolysis of *p*-nitrophenyl hexanoate (PNPH) at high levels of the surfactants disappears if the total anion concentration is maintained constant as the concentration of the surfactant is increased. Hence, this decrease in the hydrolysis of the PNPH is almost certainly the result of increased concentration of the counterion of the surfactant. A similar explanation for the related behavior of PNPL seems appropriate here, although the hydrolysis of this substrate has not been specifically examined under conditions of constant total anion concentration. The results obtained here are in substantial agreement with previous findings.<sup>28</sup>

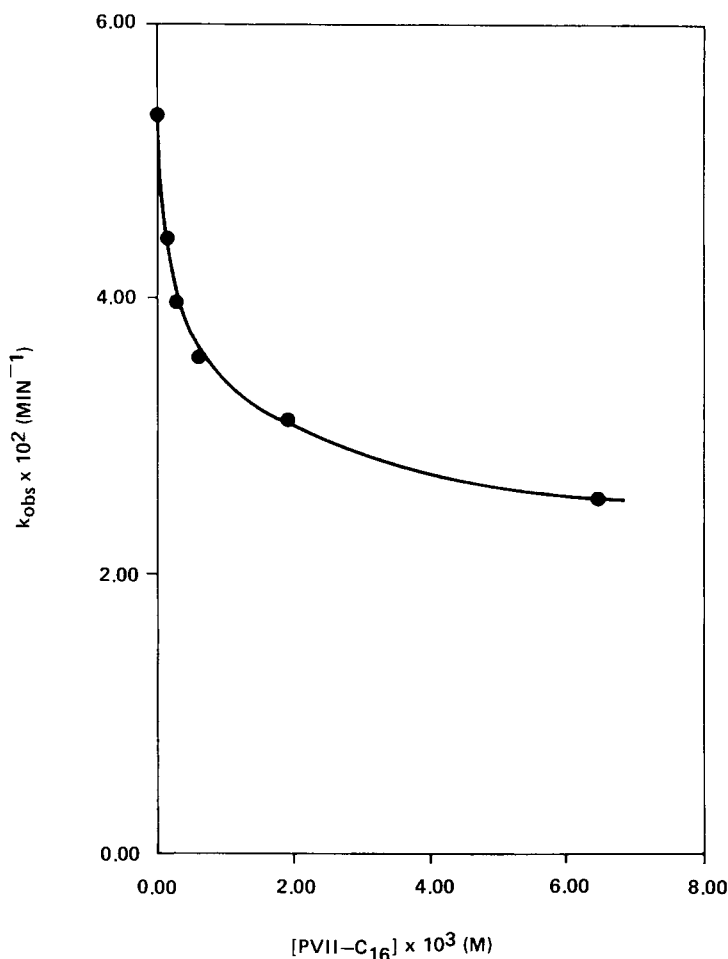


Fig. 4. Variation of  $k_{\text{obs}}$  with concentration of VII-C<sub>16</sub> for the hydrolysis of PNPL at 30°C. [PNPL] =  $4.49 \times 10^{-5} M$ , pH 10.4, 20% EtOH-H<sub>2</sub>O.

Menger and Portnoy have also reported marked inhibition of hydrolysis of PNPA and *p*-nitrophenyl octanoate by sodium lauryl sulfate,<sup>29</sup> a finding fully in agreement with the Cordes and Romsted report on the inhibition of the reactions of hydroxide ion and leucine with similar substrates.<sup>15</sup>

#### Activation Parameters for the Hydrolysis of Neutral Substrates

In order to investigate the temperature dependence of hydrolytic rates and to determine the contribution from hydrophobic and electrostatic attraction displayed by poly(*n*-alkyl-1-vinylimidazolium) iodides, the first order catalytic rate constants were determined at temperatures varying from 20° to 40°C in 20% (w) ethanol-water, pH 8.21 (at 25°C). The activation parameters for the solvolytic reaction were calculated using the following equations: (1) the activation energy from the slope of a plot of  $\ln k_2$  vs.  $1/T$  as determined by the least squares method; (2) the enthalpy of activation from  $\Delta H^* = \Delta E^* -$

TABLE IV  
 Activation Parameters for the Catalyzed Hydrolyses of PNPL<sup>a</sup>

Catalyst	$\Delta E^*$	$\Delta H^*$	$\Delta F^*$	$\Delta S^*$
—	8.14	7.56	25.93	-62.66
VII-C <sub>16</sub>	5.20	4.62	25.52	-71.29
PVII-C <sub>1</sub>	7.00	6.42	25.70	-65.77
PVII-C <sub>16</sub>	5.11	4.53	25.28	-70.78

<sup>a</sup>All values are in  $k_{\text{cat}}/\text{mol}$  except  $S(\text{eu})$ . Measurements were performed at 20°C in 20% (w) ethanol-water; pH 8.21,  $\mu = 0.002$ . [Substrate] =  $1.75 \times 10^{-5}M$ .

$RT$ ; (3) the free energy of activation from  $\Delta F^* = RT \ln(kT/hk_2)$ ; and (4) the entropy of activation from  $\Delta S^* = (\Delta H^* - \Delta F^*)/T$ .

The activation parameters for the hydrolysis of long chain neutral ester PNPL catalyzed by the hydrophilic and hydrophobic polyions, PVII-C<sub>1</sub> and PVII-C<sub>16</sub>, respectively, and by the hydrophobic monomer VII-C<sub>16</sub>, are compared in Table IV. It is quite apparent from the data (Table IV) that the enhanced activity of the polymeric catalysts is due to a favorable entropy term. The three activation parameters,  $\Delta H^*$ ,  $\Delta F^*$ , and  $\Delta S^*$  decreased with polyelectrolyte addition. The decrease in  $\Delta S^*$  suggests that the acceleration is due to the enthalpic loss. This phenomenon is also attained in the hydrolysis of the charged phenyl esters in the presence of the above catalysts as described in our previous studies.<sup>30</sup>

### References

1. E. H. Cordes and R. B. Dunlap, *Accounts Chem. Res.*, **2**, 329 (1969).
2. H. Morawetz, *Adv. Catal. Relat. Subj.*, **20**, 341 (1969).
3. T. Rudolfo, J. A. Hamilton, and E. H. Cordes, *J. Org. Chem.*, **39**, 2281 (1974).
4. T. Okubo and N. Ise, *J. Org. Chem.*, **38**, 3120 (1973).
5. U. P. Strauss and N. L. Gershfeld, *J. Phys. Chem.*, **58**, 747 (1954).
6. U. P. Strauss, N. L. Gershfeld, and E. V. Crook, *J. Phys. Chem.*, **60**, 577 (1956).
7. S. K. Sinha, A. I. Medalia, and D. R. Harrington, *J. Am. Chem. Soc.*, **79**, 281 (1957).
8. H. H. Freedman, J. P. Mason, and A. I. Medalia, *J. Org. Chem.*, **23**, 76 (1958).
9. M. L. Bender and K. Nakamura, *J. Am. Chem. Soc.*, **84**, 2577 (1962).
10. H. Zahn and F. Schade, *Chem. Ber.*, **96**, 1747 (1963).
11. J. C. Salamone, S. C. Israel, P. Taylor, and B. Snider, *Polymer*, **14**, 639 (1973).
12. J. H. Fendler and E. J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic, New York, 1975.
13. J. Baumrucker, M. Calzadilla, P. Lindquist, D. Dunham, M. Price, B. Sears, and E. H. Cordes, *J. Am. Chem. Soc.*, **94**, 8164 (1972).
14. H. Morawetz, C. G. Overberger, J. C. Salamone, and S. Yaroslavsky, *J. Am. Chem. Soc.*, **90**, 651 (1968).
15. M. T. A. Behme, J. G. Fullington, R. Noel, and E. H. Cordes, *J. Am. Chem. Soc.*, **87**, 266 (1965).
16. T. Okubo and N. Ise, *J. Am. Chem. Soc.*, **95**, 2293 (1973).
17. G. P. Royer, and I. M. Klotz, *J. Am. Chem. Soc.*, **91**, 5885 (1969).
18. H. C. Kiefer, W. I. Cogdon, I. S. Scarper, and T. M. Klotz, *Proc. Natl. Acad. Sci. USA*, **69**, 2155 (1972).
19. I. M. Klotz, G. P. Royer, and I. S. Scarpa, *Proc. Nat. Acad. Sci. USA*, **68**, 263 (1971).
20. T. Ueda, S. Harada, and N. Ise, *Polym. J.*, **3**, 476 (1972).
21. T. Takagishi, Y. Nakata, and N. Kuroki, *J. Polym. Sci.*, **12**, 807 (1974).
22. Y. Okahuta and T. Kunitake, *J. Polym. Sci.*, **16**, 1865 (1978).
23. I. M. Klotz, G. P. Royer, and A. R. Sloniewsky, *Biochemistry*, **8**, 4752 (1969).
24. T. Kunitake, S. Shinkai, and S. Hirotsu, *J. Org. Chem.*, **42**, 306 (1977).

25. S. Shinkai, and T. Kunitake, *Biopolymers*, **15**, 1129 (1976).
26. K. Abe, M. Koide, and E. Tsuchida, *J. Polym. Sci.*, **15**, 2469 (1977).
27. C. H. W. Hirs, M. Halmann, and J. H. Kycia, in *Biological Structure and Function*, Academic, New York, 1962, Vol. 1, p. 41.
28. L. R. Romsted and E. H. Cordes, *J. Am. Chem. Soc.*, **90**, 4404 (1968).
29. F. M. Menger and C. E. Portney, *J. Am. Chem. Soc.*, **89**, 4698 (1967).
30. S. C. Israel, K. I. Papatomas, and J. C. Salamone, *Am. Chem. Soc. Symp. Ser.*, **212**, 75 (1983).

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