Polyethyleneimine + Cationic Surfactant Systems: Self-Organization and Reactivity Study

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The aggregation behavior and catalytic activity toward nucleophilic substitution in *p*-nitrophenyl acetate of the polyethyleneimine (PEI) + cationic surfactant systems is studied. The values of the critical aggregation concentrations are shown to be much lower as compared to critical micelle concentrations of single solutions. A decrease in the self-diffusion coefficient of surface-active ions is observed within the concentration range limited by the tensiometry critical points. The data obtained provide evidence for mixed aggregation in the PEI + cationic surfactant systems. Due to the contribution of specific interactions, surfactants with hydroxyethylated head groups cetyldimethyl(2-hydroxyethyl)ammonium bromide and cetylmethylbis(2-hydroxyethyl)ammonium bromide demonstrate a higher affinity toward PEI as compared to cetyltrimethylammonium bromide. The systems studied show catalytic activity toward the cleavage of *p*-nitrophenyl acetate, which increasees with the number of hydroxyethyl fragments in their head groups and reaches more than 2 orders of magnitude.

Introduction

Supramolecular systems based on surfactants and polymers attract wide attention from researchers in the fields of colloid and polymer chemistry, catalysis, ecology, biology, etc.[1−4] Polyethyleneimines (PEIs) attract particular interest due to their application in the oil industry, genetic engineering, analytic chemistry, pharmacology, medicine, etc.[5−8] There are a number of publications on the surface and solution behavior of the PEI-based systems.[9−14] In the PEI + surfactant systems aggregation is found to occur in a different way depending on the solution pH, the surfactant type, and the molecular mass and architecture of PEI. In the case of cationic surfactants (CSs) only their complexes with polyanions have been intensively studied,[3,15,16] while interactions with uncharged polymers and the more so with cationic polyelectrolytes have been scarcely explored, with the exception of a few studies[17−19] focused on the formation of mesostructured thin films at the water/PEI + CTAB solution interface. In the PEI + CS pairs, unfavorable electrostatic interactions are assumed to occur, which usually prevents mixed aggregation. Nevertheless, there are some points encouraging further investigations of these systems. (i) Unbuffered aqueous PEI solution are characterized by a pH of around 10 to 11 depending on the PEI concentration and molecular mass. Under these conditions PEIs behave as weak polyelectrolytes, e.g., 0.05 $\mathrm{mol \cdot L^{-1}}$ PEI contains ≤ 5 % protonated amino groups.[20−22] Thus, the low degree of protonation of the unbuffered PEI is responsible for its likeness with the neutral polymer. (ii) Along with the typical CS cetyltrimethylammonium bromide (CTAB), surfactants with hydroxyethylated head groups are explored in our works,[23,24] which provide specific interactions the opportunity to contribute additionally to the PEI + CS mixed aggregation. The solution behavior of the uncharged polymer + surfactant systems is well documented and clearly understood.[3,25−27] The current view is that self-organization in these systems occurs cooperatively and is characterized by two critical points at the surface tension isotherms and the conductivity versus concentration plots. The first break point is the critical aggregation concentration (cac), and the second one is the concentration of polymer saturation (cps). Small micelles are formed within the interval between the cac and the cps, which are peripherally bound with macromolecules, while above the cps there exist regular polymer-free micelles. Since under a spontaneous solution pH (pH > 10) PEI demonstrates behavior analogous to that of a neutral polymer, self-organization through the above model is probable. To avoid unwarranted simplification, it should however be mentioned that according to a couple studies[28,29] the solution behavior of PEI + surfactant systems is much more complicated as compared to that of neutral polymer + surfactant systems and strongly depends on the nature of both components and the experimental conditions. The PEI + SDS system is shown to demonstrate a complex pattern of surface tension behavior with SDS concentration. The higher SDS adsorption and a transition from a monolayer to a multilayer adsorption at the interface occur when the solution pH is high and when the polymer architecture is branched rather than linear. It is of particular importance that the enhancement of PEI + SDS interactions is probably observed with a decrease in the charge density of PEI, indicating that intermolecular bonds different from electrostatic interactions are involved in the PEI + SDS assembly. This is in line with results obtained for PEI + CTAB systems[17−19] supporting the contribution of dipole−cation interactions to the mixed assembly. The formation of mesostructured thin films at the interface templated by surfactants is documented.[17−19] Rodlike aggregates are shown to be formed at the interface, while elliptic micelles occur in the PEI + CTAB bulk solution unlike spherical aggregates formed in a single CTAB solution.[17] The difference in the morphology of the aggregates in mixed PEI + CTAB versus single CTAB

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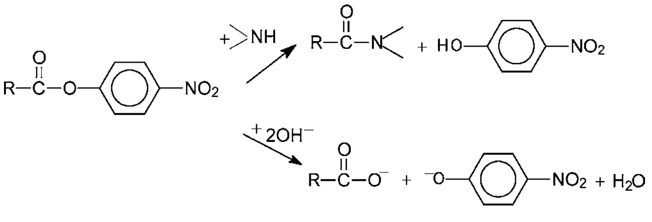
Scheme 1



solution may be considered as an argument in favor of the fact that mixed aggregation does occur. On the basis of the conductometry, tensiometry, and X-ray-reflectometry studies, the authors concluded[17] that under diluted conditions (these are maintained in our earlier and present studies) two critical points, i.e., cac and critical micelle concentration (cmc) (= cps) characterize the surface and solution behavior of the PEI + CTAB system, with the latter strongly depending on the polyelectrolyte character of PEI.

The sphere of our interest is the design of supramolecular catalytic systems for reactions of the transfer of the acyl and phosphoryl groups.[4,30−32] These reactions are of significance in organic chemistry and play a key role in biology.[33] Catalytic effects of the single surfactant and the PEI systems on the nucleophilic substitution at carbon and phosphorus atoms are widely documented in the literature, our publications included.[34−38] Meanwhile the design of polymer + surfactant catalytic systems is a relatively novel field covered by only a few works, including our recent studies.[20,21,39,40] The catalytic effects of the PEI + cationic surfactant systems on the hydrolytic reactions have been poorly studied,[41−43] and it remains unclear whether the catalysis observed is due to the mixed PEI + surfactant aggregates or results from the effects of individual components, i.e., polymer-free micelles and single PEI molecules. This work focuses on the aggregation behavior and catalytic activity toward nucleophilic substitution in *p*-nitrophenyl acetate (PNPA) (Scheme 1) of the PEI + cationic surfactant systems. CTAB and its substituted analogues bearing one or two hydroxyethyl fragments in the head groups, i.e., cetyldimethyl(2-hydroxyethyl)ammonium bromide (CHAB) and cetylmethylbis(2-hydroxyethyl)ammonium bromide (CDHAB), were used as surfactants. Branched PEI with a molar mass of 25 000 g·mol^{-1} was used as the polymer.

Experimental Section

CHAB and CDHAB were prepared according to the published procedure.[23] CTAB was purchased from Sigma. Commercial PNPA, ethylenediamine (EDA), and PEI, average molar mass 25 000 g·mol^{-1}, were from Aldrich (polyethyleneimine chains are branched, with primary, secondary, and tertiary nitrogen in the ratio 1:2:1). To simplify the analysis of the data, the solution concentrations of PEI are given as molar concentrations on a monomer basis (moles of monomer per liter of solution). Aqueous solutions were prepared using bidistilled water. The fraction of nonprotonated amino group was estimated on the basis of potentiometric titration. The pH-metric measurements were carried out in a thermostatically controlled cell at (25 ± 0.1) °C by using an I-130 ionomer pH meter with an uncertainty of less than 0.05 pH unit. HCl (0.01 mol·L^{-1}) solution was used as a titrant. The pH meter was calibrated using the certified Hanna buffer solutions made of potassium dihydrogen phosphate and disodium hydrogen phosphate with pH 4.01, 7.01, and 10.01.

Conductivity measurements were performed using an inoLab Cond level 1 instrument. Surface tension measurements were performed using the du Nouy ring detachment methods. The experimental details are described elsewhere.[44]

Dynamic light scattering (DLS) measurements were performed by means of the PhotoCor complex and the Malvern Instruments Zetasizer Nano. The measured autocorrelation functions were analyzed by Malvern DTS software, the DynaLS program, and the second-order cumulant expansion methods. The diffusion coefficient was measured at least three times for each sample. The average error in these experiments was approximately 4 %. The solutions were filtered with Millipore filters to remove dust particles from the scattering volume. The experimental details are described elsewhere.[20]

All NMR experiments were performed on a Bruker AVANCE-600 spectrometer operating at 600.13 MHz for ^{1}H. The spectrometer was equipped with a Bruker multinuclear *z*-gradient inverse probe head capable of producing gradients with a strength of 50 G·cm^{-1}. All experiments were carried out at (30 ± 0.2) °C. Chemical shifts were reported relative to the peak for HDO (4.7 ppm) as an internal standard (Figures 3S, 4S, and 5S, Supporting Information). The Fourier transform pulsed-gradient spin−echo (FT-PGSE)[45−47] experiments were performed by the BPP−STE−LED (bipolar pulse pair−stimulated echo−longitudinal eddy current delay) sequence.[45] Data were acquired with a (50.0 or 120.0) ms diffusion delay, with the bipolar gradient pulse duration from (2.2 to 6.0) ms (depending on the system under investigation), a 1.1 ms spoil gradient pulse (30 %), and a 5.0 ms eddy current delay. The bipolar pulse gradient strength was varied incrementally from (0.01 to 0.32) T/m in 32 steps.

The diffusion experiments were performed at least three times, and only the data with correlation coefficients of a natural logarithm of the normalized signal attenuation ($\ln(I/I_0)$) as a function of the gradient amplitude $b = \gamma^2 \cdot \delta^2 \cdot g^2 \cdot (\Delta - \delta/3)$ (γ is the gyromagnetic ratio, g is the pulsed gradient strength, Δ is the time separation between the pulsed gradients, and δ is the duration of the pulse) higher than 0.999 were included. All separated peaks were analyzed, and the average values are presented. The temperature was set and controlled at (30 ± 0.2) °C with a 535 L/h air flow rate to avoid any temperature fluctuations owing to sample heating by the magnetic field pulse gradients. The uncertainty of the determination of self-diffusion coefficients did not exceed 5 %.

After Fourier transformation and baseline correction, the diffusion dimension was processed with the Bruker Xwinnmr software package (version 3.5). The diffusion constants were calculated by exponential fitting of the data belonging to individual columns of the pseudo-2D matrix. Single components have been assumed for the fitting routine. The pulse programs for all NMR experiments were taken from the Bruker software library.

The reaction was controlled by monitoring the *p*-nitrophenolate anion absorption at 400 nm. A Specord M-400 spectrophotometer with temperature-controlled cell holders was employed. All runs were performed at a substrate concentration of $5 \cdot 10^{-5}$ mol·L^{-1}. The observed rate constants (k_{obsd}) were determined from the equation $\ln(A_\infty - A) = -k_{\text{obsd}} \cdot t + \text{const}$, where A and A_∞ are the absorbances of the micellar solutions at point t during and after completion of the reaction, respectively. The k_{obsd} values were calculated using the weighed least-squares computing methods. Each value of k_{obsd} is the average of at least three independent determinations differing by no more than 4 %.

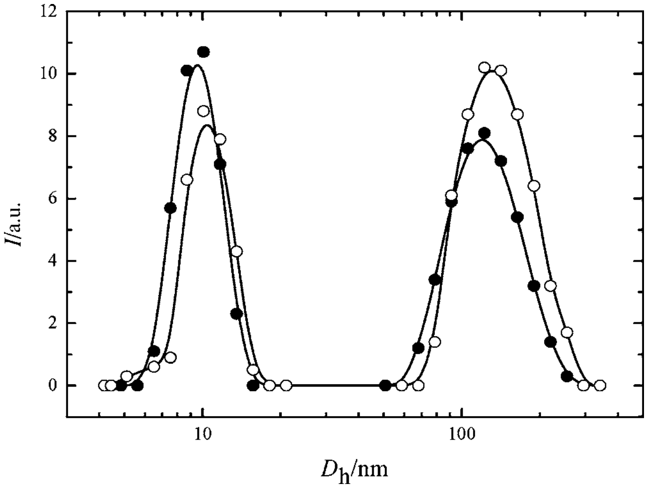


Figure 1. Size distribution analysis (by the intensity parameter) of the 0.02 mol·L^{-1} (●) and 0.05 mol·L^{-1} (○) PEI aqueous solutions, 25 °C, pH 10 (D_h is the hydrodynamic diameter).

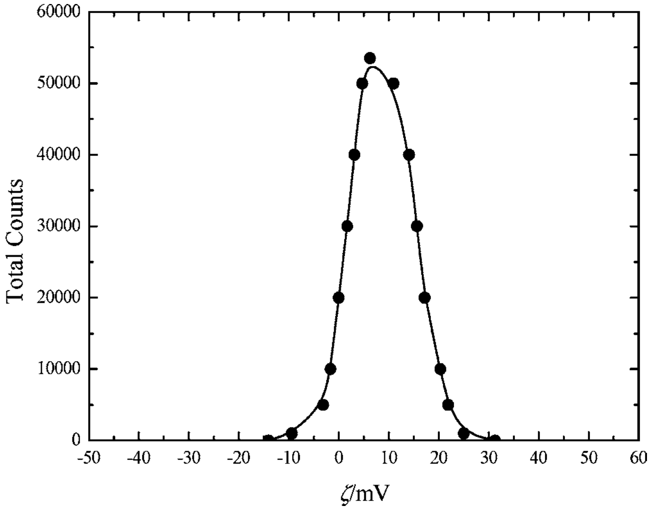


Figure 2. ζ-potential data for the 0.02 mol·L^{-1} PEI aqueous solution, 25 °C, pH 10.

Results and Discussion

Aggregation Study. Single PEI System. The aggregation in single and mixed systems based on PEI and surfactants has been investigated by tensiometry, conductometry, H^1 NMR spectroscopy, and dynamic light scattering. The tensiometry study reveals no surface activity of PEI. Meanwhile, conductivity measurements show a break point in the conductivity χ versus concentration plot (Figure 1S, Supporting Information), which can be attributed to the association of the PEI macromolecules. Association of PEI is supported by the DLS data. As can be seen in Figure 1, different types of particles are observed in the PEI solutions, i.e., small particles with a hydrodynamic diameter (D_h) of ca. 10 nm and larger ones with a D_h beyond 100 nm. The comparison of the distribution analysis (by the intensity and number parameters) reveals that the contribution of large particles is much less than that of the smaller ones. The rough estimation of the size of the PEI particles within the framework of the model of statistic coils for flexible polymer (eqs 1 and 2, where R_{e-e} is the mean end-to-end distance (nm), M is the molar mass, and R_g is the radius of gyration of a polymer (nm))[48] yields a value of R_g equal to 5 nm. Taking into account the fact that for branched polymers the radius of gyration is the most correct characteristic of a statistic coil, small particles can be attributed to the individual PEI molecules, while large ones are probably the aggregated polymer. The PEI association is probably contributed by electrostatic interactions (dipole−dipole and ion−dipole) and hydrogen bonds.

$$R_{e-e}{}^2 = 0.006 \cdot M \tag{1}$$

$$R_g{}^2 = R_{e-e}{}^2/6 \tag{2}$$

As mentioned above, the fraction of protonated amino groups for unbuffered PEI does not exceed 5 %. This is in line with the data in Figure 2 showing the electrokinetic potential for 0.05 mol·L^{-1} PEI solution. The value of $\zeta = +8.5$ mV provides evidence that under these conditions PEI manifests properties of a weak polyelectrolyte.

Binary PEI + CS Systems. The target systems in this study are the binary PEI + CS assemblies. Figure 3 shows tensiometry data for three pairs, i.e., PEI + CTAB, PEI + CHAB, and PEI + CDHAB, with two break points being observed for each system. With reservations mentioned in the Introduction, this can be interpreted as follows. The first critical point, C_{cr1}, probably indicates an onset of mixed aggregation in the systems and corresponds to the cac, while the second critical point, C_{cr2}, corresponds to the formation of the polymer-free micelles. It is noteworthy that the C_{cr1} values for all the pairs studied, (0.1 to 0.2) mmol·L^{-1}, are much lower than the corresponding cmc's for single surfactant solutions (Table 1). This can be considered as proof of the fact that mixed aggregation in the PEI + CS systems does occur. The second critical concentrations, C_{cr2}, lie in the range of (0.001 to 0.002) mol·L^{-1} (Figure 3, Table 1). Polymer-bound cationic micelles are formed within the concentration interval between C_{cr1} and C_{cr2}. An increase in the polymer concentration to 0.05 mol·L^{-1} is exemplified by the CTAB + PEI system to result in the widening of the interval between the critical points (Figure 3b). Low molar mass amine EDA of the same concentration exerts no effect on the CTAB micellization (Figure 3b).

Size distribution analysis is in good agreement with the above considerations. Two or three types of particles are revealed in the binary PEI + CS solutions (Figure 4). The smallest particles (D_h = (1 to 2.5) nm) can be attributed to the micelles, regardless of whether they are polymer-bound or polymer-free. Large particles are probably aggregated polymer species, irrelative to those based on macromolecules only or polymer + CS complexes. It should be noted that even though small particles of nonaggregated PEI exist in the PEI + CHAB solution, their contribution is low, unlike the PEI + CTAB system. Instead, the growth of large particles occurs, which can be due to the increased contribution of the mixed PEI + CHAB species associated through hydrogen bonds.

To obtain further information on the aggregative behavior of PEI + CS systems, self-diffusion coefficients (D_S) of components in the single and mixed systems were measured. Two surfactants, CTAB and CHAB, were explored to elucidate the influence of specific interactions (Figures 5 and 6). In single CTAB solution, a decrease in D_S occurs from (3.86·10^{-10} (dilute solution) to 0.86·10^{-10} (10 mmol·L^{-1})) m^2·s^{-1}, indicating the aggregation of the surfactant. A slight but obvious decrease in the D_S values of the surfactant species occurs in the PEI + CTAB systems. Meanwhile, the changes are valid within the concentration range between critical points extracted from the tensiometry study. For example, D_S decreases from (3.44·10^{-10} to 2.19·10^{-10}) m^2·s^{-1} when transferred from the single 1 mM

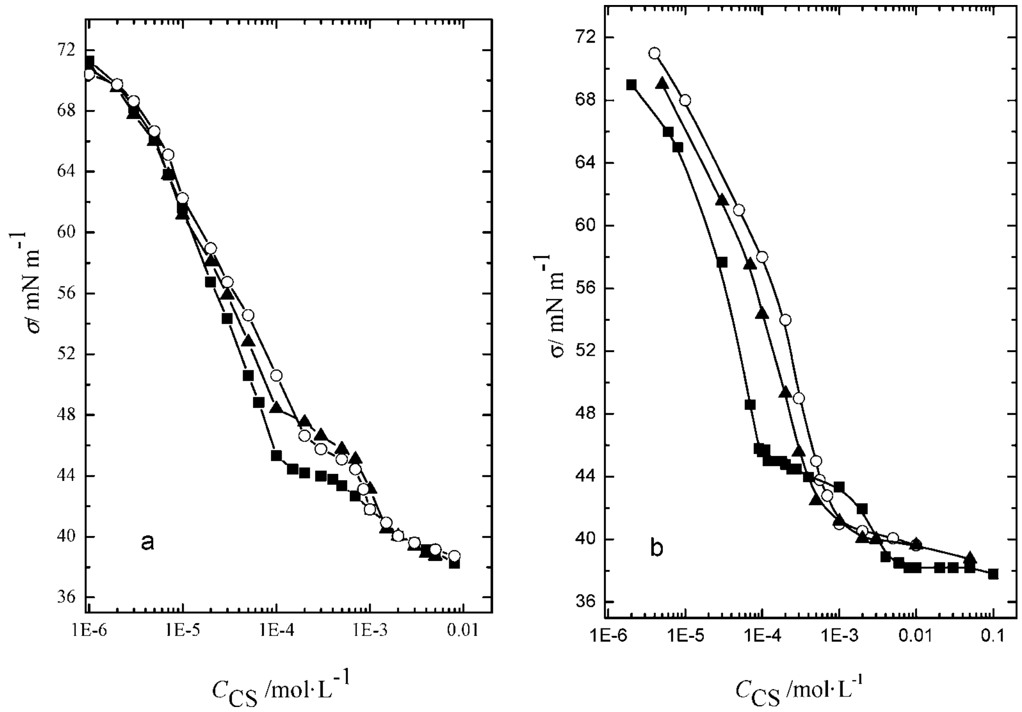


Figure 3. (a) Surface tension isotherms for PEI + CS systems, 0.02 mol·L^{-1} PEI: ▲, PEI + CTAB; ○, PEI + CHAB; ■, PEI + CDHAB. (b) Surface tension isotherms: 0.05 mol·L^{-1} amine: ▲, CTAB + ED system; ■, CTAB + PEI system; ○, CTAB single solution; 25 °C; pH 10.

Table 1. Critical Concentrations Obtained from Surface Tension Isotherms for the Single Surfactant Solutions and Binary PEI + Surfactant Systems

C_{PEI} / mol·L^{-1}	C_{cr1}/C_{cr2} / mmol·L^{-1} CTAB	CHAB	CDHAB
0	0.80	0.75	0.65
0.02	0.10/1.50	0.22/1.20	0.11/2.0
0.05	0.09/5.5		

CTAB solution to the PEI + CTAB sample. These data are in agreement with the surface tension results. It seems of interest to compare the effect of PEI with that of a low molar mass amine, e.g., EDA. D_S of CTAB has been found to change as ($0.86\cdot10^{-10}$, $0.78\cdot10^{-10}$, and $0.86\cdot10^{-10}$) m^2·s^{-1} in the following series of a single CTAB solution and PEI + CTAB and EDA + CTAB systems at a fixed CTAB concentration of 10 mmol·L^{-1}. These findings taken one after another provide evidence of the effect of PEI on the CTAB aggregation and contribute to the fact that the PEI + CTAB interactions are probably observed.

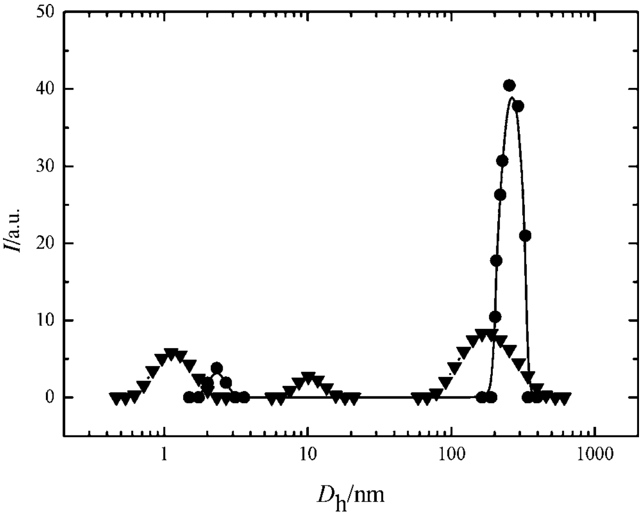


Figure 4. Size distribution analysis (by the intensity) for the PEI + CTAB (▼) and PEI + CHAB (●) systems, 25 °C, pH 10.

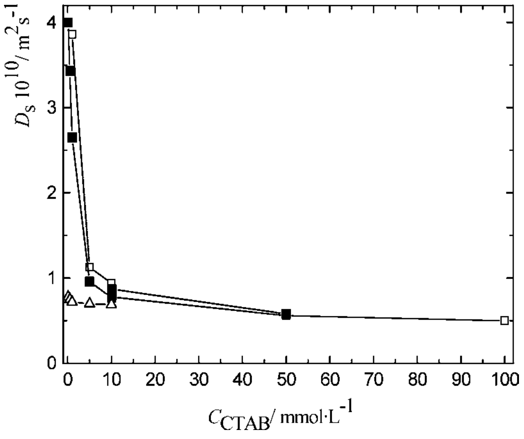


Figure 5. Dependence of self-diffusion coefficients on the CTAB concentration for a surfactant ion in the single CTAB solution (□) and for both components, i.e., surfactant ion (■) and PEI (Δ), in the PEI + CTAB system, 0.05 mol·L^{-1} PEI, D_2O, 30 °C, pH 10.

For the PEI + CHAB system a considerable decrease in the D_S values occurs in a definite concentration range, with D_S changing more abruptly than in the case of the PEI + CTAB system (Figure 6). For example, D_S decreases from ($3.44\cdot10^{-10}$ to $2.19\cdot10^{-10}$) m^2·s^{-1} in the 1 mmol·L^{-1} solutions, which clearly indicates that in this case specific interactions are involved in the polymer + surfactant aggregation.

Thus, tensiometry and NMR self-diffusion data provide evidence of the changes in the aggregative behavior of cationic surfactants in the presence of PEI. Although we failed to obtain direct proof in favor of the fact that interactions between PEI and CSs do occur (e.g., intermolecular cross-peaks cannot be observed in NOESY spectra due to experimental problems), the

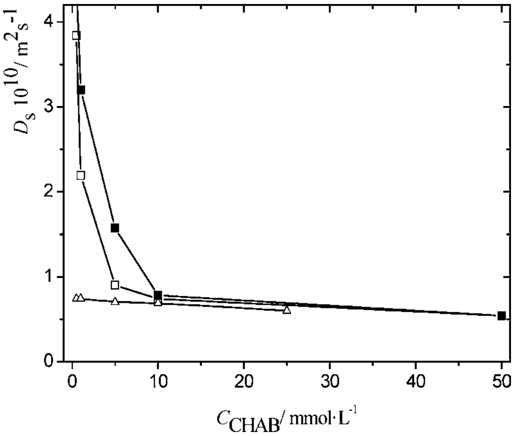


Figure 6. Dependence of self-diffusion coefficients on the CHAB concentration for a surfactant ion in the single CHAB solution (■) and for both components, i.e., surfactant ion (□) and PEI (Δ), in the PEI + CHAB system, 0.05 mol·L^{-1} PEI, D_2O, 30 °C, pH 10.

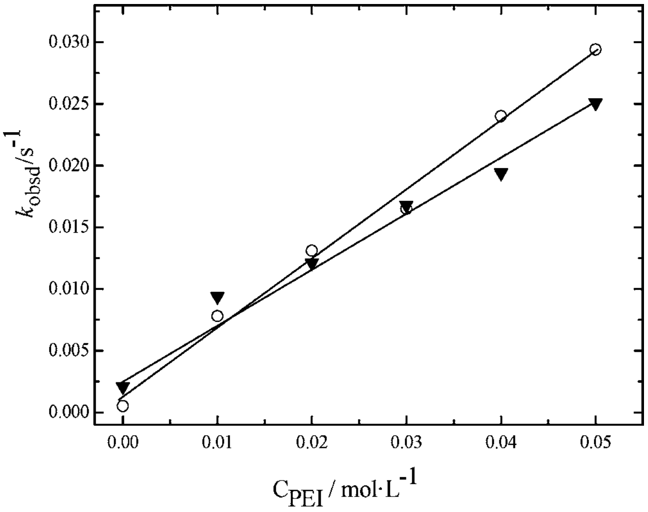


Figure 7. Observed rate constant of the cleavage of PNPA as a function of the PEI concentration, pH 9.2, 25 °C: ○, without surfactant; ▼, in the presence of 0.01 mol·L^{-1} CTAB.

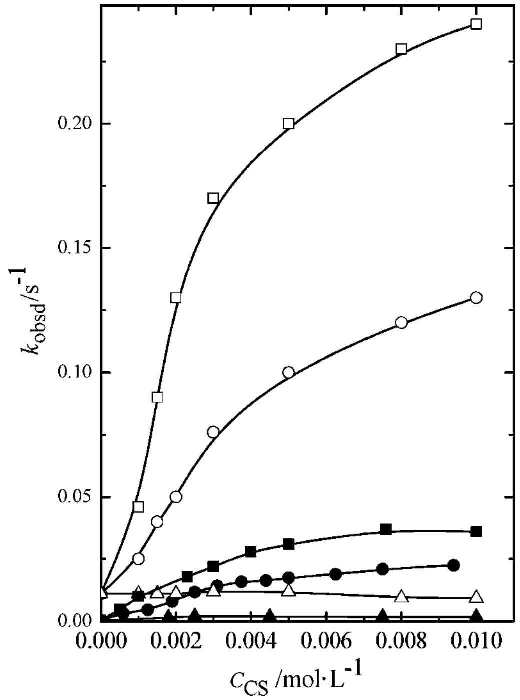
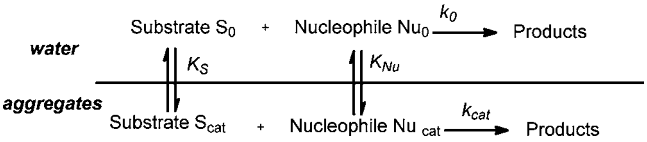


Figure 8. Observed rate constant versus surfactant concentration dependences for the cleavage of PNPA in micellar solutions of CDHAB (□, ■), CHAB (○, ●), and CTAB (Δ, ▲) in the absence (■, ●, ▲) and in the presence (□, ○, Δ) of 0.01 mol·L^{-1} PEI, pH 9.2, 25 °C.

Scheme 2. Schematic Representation of the Reaction under Study in the Micellar Solutions



data obtained can be considered as confirmations of such interactions. Hydroxyalkylated CSs demonstrate a more marked change in the characteristics measured when PEI is added due to their capacity for interacting with amino groups of the polymer via hydrogen bonds.

Catalytic Activity. The catalytic effect of the PEI + CS systems on nucleophilic substitution in PNPA was studied. Two reaction routes are assumed to occur. The basic direction is aminolysis of PNPA, which is contributed by interactions of the substrate with primary amino groups of the side chains of branched PEI along with secondary groups of the main chains. Besides, basic and spontaneous hydrolyses of PNPA probably contribute to the reaction rate. In the absence of surfactants (pH 9.2), the observed rate constant increases almost linearly with the PEI concentration (Figure 7).

The intercept of this dependence characterizes the contribution of the hydrolysis of the substrate at the corresponding pH to the observed rate constant. Micellar solutions of cationic surfactants are known to accelerate both hydrolysis and aminolysis of the substrate, with the reaction routes depending on the pH and the structure of the surfactant and polymer.[4,34−36] A decrease in the solution pH makes it possible to suppress basic hydrolysis. The investigation of the reactivity of the substrate with and without PEI provides the possibility for estimating the contributions of different reaction routes. In strong alkali solution, surfactants with a hydroxyalkyl fragment in the head group show acidic properties (pK_a = 12.4 to 12.6). Therefore, they behave as zwitterions[49] and can manifest nucleophilic activity toward the substrate. However, under the experimental conditions used in this work they are typical cationic surfactants, which reveal no nucleophilic properties. Therefore, there is no contribution of the reaction of the substrate with terminal OH groups of the surfactants to the observed rate constant.

Figure 8 shows the observed rate constant versus surfactant concentration plots for the cleavage of PNPA at a fixed pH of 9.2 in both the single micellar solutions of CSs and the binary PEI + CS systems. With no PEI added, the basic hydrolysis of the substrate occurs in the alkali solutions. As can be seen, hydroxyalkylated surfactants CHAB and CDHAB show a higher catalytic effect as compared to CTAB. An addition of PEI results in a considerable increase in the observed rate constants of the cleavage of PNPA (Figure 8), which can be due both to the occurrence of the reaction in the PEI + CS aggregates instead of the single surfactant micelles and to the additional contribution of the aminolysis of the substrate to the reaction rate.

The kinetic dependence in Figure 8 shows trends to reach a plateau, which is typical for the reactions with preliminary equilibrium processes, such as the formation of the catalytic complex (cat) substrate (S)−aggregate (Scheme 2).

This kind of kinetics obeys a formalism similar to the Michaelis−Menten equation for enzyme catalysis:[34]

$$k_{\text{obsd}} = \frac{k_0 + k_{\text{cat}} \cdot K_S \cdot C}{1 + K_S \cdot C} \tag{3}$$

where K_S is the binding constant of the substrate (S) related to the partition coefficient ($P_S = [S]_{\text{cat}}/[S]_0$) in the following way: $K_S = (P_S - 1) \cdot V$; indices 0 and cat refer to the water and catalytic complex, respectively; V is the molar volume of the micellar pseudophase, k_0 and k_{cat} (s^{-1}) are the pseudo-first-order rate constants in water and the catalytic complex, respectively, and C is the surfactant concentration minus cmc. The values of the effective molar volume (V) for systems based on surfactants and polymers can be calculated on the basis of their molecular weight and density.[34,44,50] According to the data,[51] the apparent molar volumes of single cationic surfactants and their complexes with polyelectrolytes average (0.3 to 0.4) $L \cdot mol^{-1}$. Taking into account the molecular weight of the surfactant and water associated with the polar groups of the polymer and surfactant, V is estimated to be about (0.9 to 1.1) $L \cdot mol^{-1}$ for the systems studied. Therefore, in crude approximation the K_S values coincide with the partition coefficients (P_S).

The results of the quantitative analysis of the kinetic dependence (Figure 8) in terms of eq 3 are summarized in Table 2. The cmc values determined as simulated parameters are close to those obtained by tensiometry (Table 1). Binding constants of the substrate by mixed PEI + CS aggregates are 2- or 3-fold higher as compared to those of the polymer-free micelles. The catalytic effect expressed as the k_{cat}/k_0 ratio increases in the CTAB, CHAB, and CDHAB single systems as 5, 80, and 160, respectively. As can be seen in Figure 8, acceleration of the aminolysis of PNPA at a fixed PEI concentration of 0.01 M occurs only in the case of hydroxyalkylated surfactants and amounts to 13- to 25-fold as compared to that of the single PEI solution. However, the summary acceleration of the cleavage of PNPA in the PEI + CS systems reaches 2 orders of magnitude when compared to the basic hydrolysis of the substrate. An additional catalytic resource can be derived from the increase in the PEI concentration. Figures 7 and 9 show k_{obsd} versus [PEI] concentration plots obtained for the cleavage of PNPA at a fixed surfactant concentration of 0.01 $mol \cdot L^{-1}$ chosen as a plateau value in Figure 8. A linear-type dependence, $k_{\text{obsd}} = k_0 + B \cdot C_{\text{PEI}}$, is revealed; calculated coefficients B and k_0 are given in Table 3. An increase in the PEI concentration at a fixed solution pH results in an increase in the summary reaction rate due to the increasing contribution of the aminolysis of the substrate. The slope values for single PEI solutions and for PEI + CTAB systems are similar, while those for PEI + CHAB and PEI + CDHAB systems are higher by ca. 1 order of magnitude. This reflects marked effects of hydroxyalkylated surfactants on the aminolysis of PNPA and supports the occurrence of strong PEI−surfactant interactions in these systems promoting the formation of the effective polymer + colloid catalytic systems.

From the viewpoint of practice it is important to study the reactivity of the substrate at mild pH. Figure 10 shows pH dependences for the cleavage of PNPA in the PEI + CS systems at a fixed PEI concentration of 0.01 $mol \cdot L^{-1}$.

In the whole pH interval the reaction rate increases in the series CTAB < CHAB < CDHAB. A decrease in pH is followed by an increase in the fraction of protonated amino groups of PEI, so that at pH < 8 PEI is markedly protonated. This results in a decrease in its ability to participate in mixed aggregation with CSs and to contribute to aminolysis of the substrate. Besides, as a consequence of a decrease in pH, a suppression of the basic hydrolysis of the substrate occurs. Therefore, the contribution of spontaneous hydrolysis becomes prevalent. This levels the k_{obsd} values of reactions in the presence and absence of PEI. Thus, the catalytic effect of the mixed PEI + CS systems is mostly expressed within the pH interval of 8.5 to 9.5.

Table 2. Quantitative Treatment of the Kinetic Data of the Reaction of PNPA in Single Surfactant Solutions and Binary PEI + Surfactant Systems in Terms of Eq 3 (0.01 $mol \cdot L^{-1}$ PEI, pH 9.2, 25 °C)

	C(PEI)	k_{cat}	K_S	cmc	k_0	
	$mol \cdot L^{-1}$	s^{-1}	$L \cdot mol^{-1}$	$mol \cdot L^{-1}$	s^{-1}	k_{cat}/k_0[a]
CTAB	0	0.002	860	0.00056	0.0004	5
CHAB	0	0.033	240	0.00024	0.0004	82
	0.01	0.14	530	0.00082	0.011	13 350[b]
CDHAB	0	0.63	190	0.0001	0.0004	158
	0.01	0.28	630	0.00077	0.011	25 700[b]

[a] Acceleration of the reaction as compared to that of the single PEI solution. [b] Acceleration of the reaction as compared to basic hydrolysis of the substrate under a solution pH of 9.2.

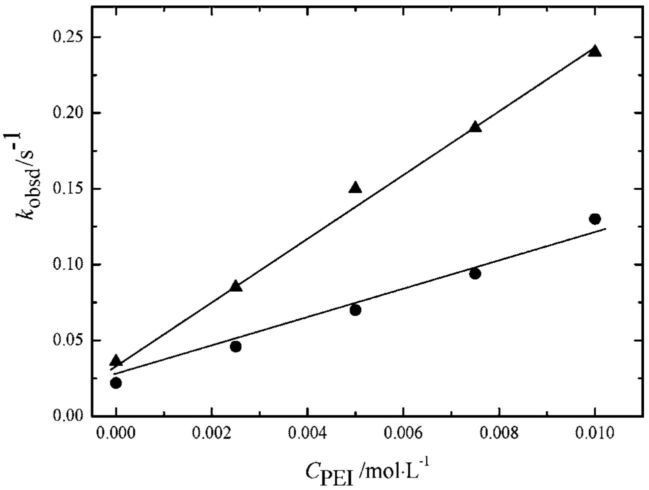


Figure 9. Observed rate constant versus PEI concentration for the cleavage of PNPA in the PEI + CS systems, pH 9.2, 25 °C, $C_{\text{CS}} = 0.01$ $mol \cdot L^{-1}$: ▲, CDHAB; ●, CHAB.

Table 3. Fraction of the Neutral Form of PEI (α) in Surfactant Solutions at pH 9.2 and Coefficients of Linear Dependence, $k_{\text{obsd}} = k_0 + B \cdot C_{\text{PEI}}$,[a] $C_{\text{CS}} = 0.01$ $mol \cdot L^{-1}$, 25 °C

	α	k_0 s^{-1}	B	R[b]
PEI[a]	0.89	0.0012 ± 0.0008	0.56 ± 0.025	0.996
PEI + CTAB[a]	0.85	0.0034 ± 0.0009	0.43 ± 0.03	0.990
PEI + CHAB	0.85	0.02 ± 0.0045	10.8 ± 0.69	0.998
PEI + CDHAB	0.89	0.036 ± 0.0015	20.4 ± 0.23	0.999

[a] [PEI] is varied from (0 to 0.05) $mol \cdot L^{-1}$. [b] R is the correlation coefficient.

Conclusions

The aggregation in the polyethyleneimine + cationic surfactant systems is studied by tensiometry, dynamic light scattering, and NMR self-diffusion. Surface tension isotherms demonstrate two break points, with the values of critical aggregation concentrations being much lower as compared to the cmc's of single surfactant solutions. A decrease in the self-diffusion coefficients of surface-active ions is observed within the concentration range between the critical points. The data obtained provide evidence of mixed aggregation in the PEI + cationic surfactant systems. Surfactants with hydroxyethylated

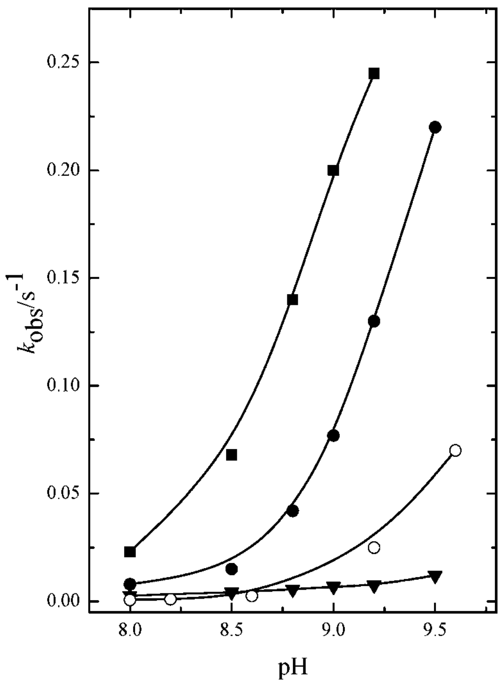


Figure 10. Observed rate constant versus pH for the cleavage of PNPA in the PEI + CS systems, pH 9.2, 25 °C, $C_{CS} = 0.01$ mol·L^{-1}, $C_{PEI} = 0.01$ mol·L^{-1}: ■, CDHAB; ●, CHAB; ▼, CTAB; ○, CHAB in the absence of PEI.

head groups demonstrate higher affinity toward PEI due to the contributions of specific interactions. The systems under study show catalytic activity toward the cleavage of *p*-nitrophenyl acetate which grows with the number of hydroxyethyl fragments in their head groups and reaches more than 2 orders of magnitude.

Supporting Information Available:

NMR spectra and characteristics of the solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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