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Thermodynamics of Aggregation between the Cationic Surfactant and Polymer Based on Biodegradable Poly(vinyl Alcohol)

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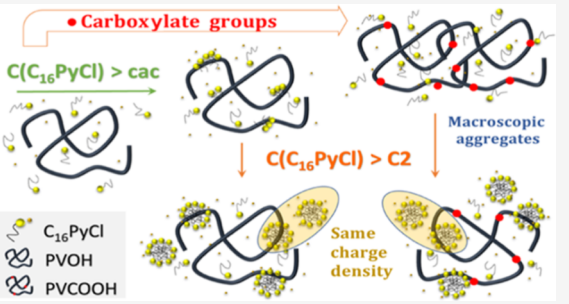
ABSTRACT: The formation of aggregates between carboxylated (PVCOOH) or neutral hydrolyzed (PVOH) poly(vinyl alcohol) and hexadecylpyridinium chloride (C_{16}PyCl) was examined by conductimetry, turbidimetry, and isothermal titration calorimetry (ITC) in the presence of different NaCl concentrations. The interaction between the polymers and C_{16}PyCl in pure water showed a critical aggregation concentration (cac = 0.8 mmol L^{-1}) only for the neutral polymer. PVCOOH interacted with the surfactant through electrostatic attraction, forming macroscopic aggregates. Integral enthalpy changes for aggregate formation (ΔH_{agg}) obtained from ITC curves varied from −0.61 (for the PVOH system in pure water) to −4.14 kJ mol^{-1} (for PVOH in the presence of 10.0 mmol L^{-1} NaCl), indicating that the formation of the aggregates was enthalpically favored. However, hydrophobic interactions drove the process for low surfactant concentration for both polymers. Saturation concentrations (C2) obtained from conductimetry were smaller than those from ITC, revealing that the binding of C_{16}PyCl on the chain of the polymers at higher surfactant concentrations shows the same electric properties as that of free micelles on the solution. Increase of the ionic strength favored the aggregation and decreased the complexity of the ITC curves, suggesting that the reorganization of the surfactant monomers on the polymeric chain with the increase in their concentration was suppressed.



1. INTRODUCTION

Surfactant and water-soluble polymers can be mixed to form complex aqueous systems with a wide range of applications. The combination of these classes of chemicals forms polymer−surfactant aggregates that have been explored for removal processes of metallic ions from water,[1] oil recovery in petroleum industries,[2] and dispersion of water-insoluble mats, such as graphene,[3] drugs,[4] and plastics.[5] Beyond environmental and industrial applications, the versatility of applications of these systems has been spread to self-care products development,[6−8] in which the low irritation potential of the human skin by the polymer−surfactant aqueous formulation is mandatory.[9] In this context, the polymer−surfactant systems comprising biocompatible compounds have attracted attention.

Poly(vinyl alcohol) (PVOH) is a promising biocompatible and biodegradable polymer obtained from hydrolysis of polyvinyl acetate. It has an outstanding performance suitable for the development of surgical devices, packaging area, biomedical fields, and additives for foods.[10,11] Due to its high water solubility, systems comprising PVOH and different surfactants in aqueous solutions have been evaluated in the last 5 decades using different techniques.[12−16]

Among the studied surfactants, cationic ones, including alkylpyridinium halides, have received some attention. Alkylpyridinium halides are unsaturated heterocyclic compounds considered effective germicides, interacting with both nonionic and ionic polymers. Shirahama et al.[17] evaluated the binding of tetradecylpyridinium chloride and bromide (C_{14}PyCl and C_{14}PyBr) and dodecylpyridinium chloride (C_{12}PyCl) to 10% acetylated PVOH using potentiometry and equilibrium dialysis. They showed an intimate connection between the ordinary micellization of the surfactants and the formation of a surfactant−polymer complex. Shirahama and Nagao[18] evaluated the effect of the acetylation degree of PVOH on its interaction with C_{14}PyBr, showing an increase in the bounded surfactant amount with the increase in the acetyl group content, without changing the binding constant. Interactions between C_{14}PyBr or hexadecyltrimethylammonium bromide (C_{16}TAB) and their mixtures with nonionic polymers [PVOH, poly(ethylene oxide) and (vinyl acetate-ethylene) copolymer] were investigated by Ghoreishi et al.[19] using electromotive force (EMF) measurements. EMF curves

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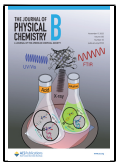

indicated a critical aggregation concentration (cac) in which the surfactants began interacting with the polymers. For C_{14}PyBr and C_{16}TAB mixtures, the presence of the polymers did not affect the formation of mixed micelles of C_{14}PyBr and C_{16}TAB that were bound to the polymers at higher surfactant concentrations.

Hexadecylpyridinium chloride (C_{16}PyCl), an alkylpyridinium halide with antimicrobial and anti-inflammatory properties, could be strategically used for the development of biocompatible formulations with PVOH.[20,21] However, to the best of our knowledge, binding of C_{16}PyCl to PVOH in aqueous systems has not been investigated yet. We believe that this knowledge could provide valuable information for the design of new biocompatible polymer−surfactant formulations. Additionally, the range of application of PVOH in formulations with surfactants can be broadened by chemical modification of its structure with carboxyl groups. The presence of carboxylic groups in the macromolecule could be suitable for charge modulation of the polymer, providing new interaction sites for cationic surfactants, favoring the formation of polymer−surfactant aggregates with new applications.

Herein, we evaluated the interaction between C_{16}PyCl and commercial PVOH and PVOH modified with carboxyl groups (PVCOOH) (Figure S1), both with a high degree of hydrolysis, using specific conductimetry, turbidimetry, and isothermal titration calorimetry (ITC) measurements. The effect of sodium chloride on the thermodynamic parameters of micellization and binding interaction between C_{16}PyCl and the polymers was also examined to determine the contributions of electrostatic interaction for the aggregation processes.

2. EXPERIMENTAL SECTION

2.1. Materials. Super hydrolyzed polyvinyl alcohol (PVOH), with a hydrolysis percentage higher than 99.0% [polymerization degree (DP) equal to 1000 and MM = 45000 g mol^{-1}], and polyvinyl alcohol containing carboxylic groups (PVCOOH), with a hydrolysis percentage higher than 95.0% (DP = 1700, MM = 77,000 g mol^{-1}, and the fraction of carboxylic groups equal to 1.5% mol/mol in relation to the hydroxyl groups), were supplied by Kuraray (Brazil). Hexadecylpyridinium chloride monohydrate (99.0%) and sodium chloride (higher than 99%) were all manufactured by Sigma-Aldrich (St. Loius, Missouri, USA). All chemicals were used without further purification. Deionized water was used for preparing all solutions.

2.2. Preparation of Solutions. Stock solutions of the polymers were prepared by a previous solubilization of each polymer under magnetic stirring at 358 ± 5 K. Then, the mixture was left to rest until room temperature and transferred to a volumetric flask to obtain the desired concentration. Concentrations of the polymer solutions were expressed in percentage of mass of the polymer (g) per volume of solution (mL). Surfactant and NaCl stock solutions were prepared under manual stirring at room temperature. Mixtures of the polymer (or surfactant) and NaCl stock solutions were performed in volumetric flasks to dilute each component to a desired concentration. This procedure was necessary due to the heating during the preparation of the polymeric solutions. Before carrying out the titration experiments, polymeric solutions were left to rest for at least 12 h.

All titrated and titrant solutions were used without prior pH adjustment. pH values of the systems in the titration experiments were measured and remained around 5.9 for all experiments, which is a value slightly lower than the estimated point of zero charge of PVCOOH. A polymer concentration of 0.200% (w/v) was chosen because at this concentration the polymer solution is in the dilute regime where polymer chains interact mainly with solvent molecules.

2.3. Conductivity Measurements. Aqueous solutions of 0.200% (w/v) PVOH (or PVCOOH) and 65.0 mmol L^{-1} C_{16}PyCl titrant solutions were prepared at different concentrations of NaCl (0, 1.00, 2.00, 4.00, 10.0, or 100 mmol L^{-1}). An initial volume of the polymer solution (35.0 mL) was introduced into the water-jacketed cell and titrated with the surfactant solution using a micropipette. The time between two consecutive injections was chosen considering that the conductivity value changes less than 2% after the homogenization of the system. The volumes of the additions were 25.0, 50.0, 75.0, or 100.0 μL, depending on the investigated surfactant concentration range. Similar experiments were also performed in the absence of the polymers. The cac and C2 values were calculated based on the intercept between the adjacent straight lines obtained from the linear fit (Table S1) in the conductivity versus $C_{C16PyCl}$ curves. Electrical conductivities were measured at 298.2 ± 0.1 K by using a digital conductivity meter (Tecnopon mca-150) with a conductivity cell containing a platinized platinum electrode. Prior to the measurements, the cell was calibrated with a 0.010 mol L^{-1} KCl standard aqueous solution. Conductance of the system was measured while mixing after each addition of the surfactant titrant solution.

2.4. Turbidimetric Titration. Turbidity measures were performed in a digital turbidimeter (NETLAB—TB2000 - Brazil). Aqueous solutions of 0.200% (w/v) PVOH (or PVCOOH) and 26.0 mmol L^{-1} C_{16}PyCl were prepared in the presence of NaCl (0, 1.00, 2.00, 4.00, 10.0, or 100 mmol L^{-1}). An initial volume of 15.0 mL of the polymer solution was introduced into the turbidimeter cell and titrated with the concentrate surfactant solution. A magnetic stirrer was inserted in the cell to facilitate homogenization during the titration. Prior to each turbidity measurement, the system was left in a thermostatic bath at 298.2 ± 0.5 K, and stirring was interrupted. A similar experiment was carried out in which a solution containing 0.200% (w/v) PVCOOH and 0.600 mmol L^{-1} C_{16}PyCl was titrated with a 1000 mmol L^{-1} NaCl aqueous solution.

2.5. Isothermal Titration Calorimetry. Enthalpy changes associated with C_{16}PyCl-PVOH (or PVCOOH) interaction or C_{16}PyCl micellization in the presence of different concentrations of NaCl (0, 2.00, 4.00, 10.0, or 100 mmol L^{-1}) were obtained in a thermal activity monitor system (TA Instruments, TAM III - USA) controlled using TAM assistant dedicated software. Experiments consisted of 50 consecutive 10.0 μL injections of 25.0 mmol L^{-1} C_{16}PyCl solution, using a Hamilton syringe (500 μL) controlled using a 3810 syringe pump, into the sample calorimetric reaction cell containing 2.70 mL of the solvent (pure water or NaCl + water mixture) with or without 0.200% (w/v) PVOH (or PVCOOH) at 298.15 ± 0.01 K. The reference cell was fixed with 2.70 mL of the same solvent as that present in the sample cell. Regarding the C_{16}PyCl−polymer interaction, data were prepared for analysis by subtracting the heat of dilution (titration of the solvent with the C_{16}PyCl solution) from the interaction heat [titration of the PVOH (or PVCOOH) solution with the C_{16}PyCl solution]. Titration of the PVOH (or PVCOOH) solution with the solvent produced negligible thermal effects.

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The solutions inside the syringe, sample, and reference cells were degassed, and the cannula was immersed into the sample cell 120 min before starting the titration. The interval between injections was 900 s (time required for the stabilization of the heat flow and regeneration of the baseline), and the solution in the sample cell was stirred at 180 rpm (3 s^{-1}) using a gold helix stirrer.

2.6. Point of Zero Charge. The point of zero charge (PZC) of PVCOOH was estimated using the methodology adapted from the solid addition method.[22] For this, the polymer was dissolved in aqueous solutions of 0.100 mol L^{-1} NaCl with the initial pH previously adjusted to generate a solution with concentration of 0.200% (w/v). Different initial pH values between 2.0 and 11.0 were used by adding either 0.10 mol L^{-1} HCl or 0.10 mol L^{-1} NaOH. Each system was stirred at 298.15 ± 0.01 K, and the final pH values (pH_f) of the solutions were measured after 24 h. The difference between the initial and final pH values ($\Delta pH = pH_i - pH_f$) was calculated and plotted against pHi. The pH_{PZC} was defined as the intercept of the ΔpH versus pHi curve with the abscissa.

3. RESULTS AND DISCUSSION

3.1. Interaction between PVOH (or PVCOOH) and C_{16}PyCl in Pure Water. Intermolecular interaction between ionic surfactants and polymers in aqueous solution can be evaluated considering the surfactant concentration increase in the presence of a polymer by monitoring a physicochemical property that is sensitive to the changes in those weak interactions. One of these properties is the electrical conductivity, which enables obtaining parameters such as cmc, cac, and C2 with accuracy. The mobility and concentration of ions in the bulk solution are strongly dependent on the aggregation processes that take place at these specific concentrations ranges.[23] Figure 1 shows the conductivity curves obtained from the titration of pure water or 0.200% (w/v) PVOH with C_{16}PyCl aqueous solutions, at 298.2 K.

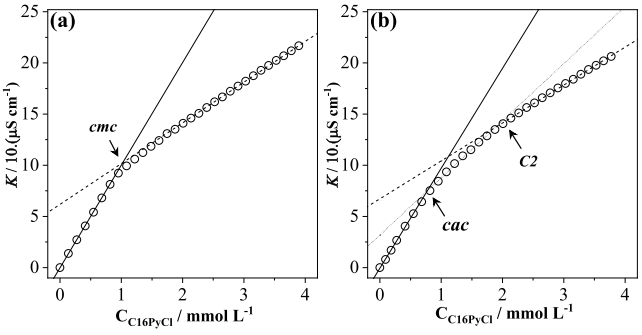

Figure 1. Conductivity (K) vs $C_{C16PyCl}$ obtained in (a) pure water and (b) 0.200% (w/v) PVOH, at 298.2 K. For all measurements, the specific conductivity of the solvent was discounted. Lines (solid, dashed, and dotted) represent the linear fit for each region of the curve.

Titration of pure water with the surfactant solution (Figure 1a) showed two linear regions with an abrupt change in the slope of the K versus $C_{C16PyCl}$ curve at the concentration of 1.04 ± 0.02 mmol L^{-1}, named the critical micelle concentration (cmc). The cmc characterizes the aggregation process and was determined by the intersection between the fitted linear curves in the pre- and postmicellar regions. The slope $(\partial K/\partial C_{C16PyCl})_T$ in the second region (40.4 ± 0.1 μS L cm^{-1} $mmol^{-1}$) was smaller than in the first (97.9 ± 0.8 μS L cm^{-1} $mmol^{-1}$). This behavior is due to the decrease of the mobility of a great number of chloride ions that moved from the bulk to the double electric layer of the micelles formed when the surfactant monomers aggregated.

The ratio between the slope of the fitted curves in the post- and premicellar regions gives the counterion dissociation degree (α_{mic}). The α_{mic} value obtained was 0.412 ± 0.005, indicating that nearly 40% of chloride ions are free in the bulk, in which the mobility in the solution due to the interaction with the micelle is not changed.[24,25] The cmc and α_{mic} values reported here are consistent with those obtained by González-Pérez et al.[26] (cmc = 0.97055 mmol kg^{-1} and α_{mic} = 0.417, at 298.15 K).

In the presence of PVOH (Figure 1b), the conductivity curve differed from that in pure water, presenting three linear regions. The first change in the slope of the curve in the presence of PVOH from 97 ± 1 to 56 ± 2 μS L cm^{-1} $mmol^{-1}$ occurred at 0.8 ± 0.1 mmol L^{-1}, a smaller value than the cmc obtained in pure water. This result shows that PVOH changed the aggregation process of the surfactant and the concentration in which the surfactant aggregation took place in the presence of the polymer is the cac. The first region in Figure 1b ($C_{C16PyCl} \leq 0.8$ mmol L^{-1}) had the same slope as that observed in the premicellar region of the titration curve of pure water with the surfactant solution, indicating that the same molecular events occurred in both systems in these surfactant concentration ranges. Slopes and equations of all linear fitted curves are shown in Table S1 in the Supporting Information.

A second change in the slope of the conductivity curve in the presence of 0.200% (w/v) PVOH was observed at 1.9 ± 0.4 mmol L^{-1}. Beyond this concentration, named C2, the slope of the K versus $C_{C16PyCl}$ curve (37.0 ± 0.3 μS L cm^{-1} $mmol^{-1}$) was close to that in the postmicellar region of the curve obtained in Figure 1a. This indicates that C_{16}PyCl aggregate formation is similar to those in pure water that were formed at this critical concentration.

Previous studies have proposed that in the region between cac and C2, the surfactant spontaneously interacts with the polymer, forming surfactant−polymer aggregates in the solution.[27−30] Considering the processes occurring in the PVOH aqueous solution for lower surfactant concentrations, as the C_{16}PyCl concentration increased, the addition of monomers of C_{16}PyCl in the system concentrated in the bulk solution and in the air−solution interface up to the concentration reaching the cac, in which the surfactant−PVOH aggregates began to be formed. The amount of the surfactant bound to the polymer increased as $C_{C16PyCl}$ increased until C2 was reached, in which the energetic saturation of PVOH macromolecules occurred, forming free micelles of C_{16}PyCl in the solution. Therefore, above C2, free monomers and micelles of the surfactant coexist with the PVOH−surfactant nanoaggregates in the system. However, it should be highlighted that this assumption is based on the hypothesis that the ionization degree of the free C_{16}PyCl micelles in the solution is different from that of the aggregates formed on the polymeric chain, which will be better evaluated in Section 3.3.

Conductivity experiments were carried out by changing PVOH by PVCOOH to evaluate the effect of the polymer structure on the surfactant−polymer interaction. Figure 2

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shows the conductivity curve obtained from the titration of 0.200% (w/v) PVCOOH aqueous solution with an aqueous solution of C_{16}PyCl, at 298.2 K.

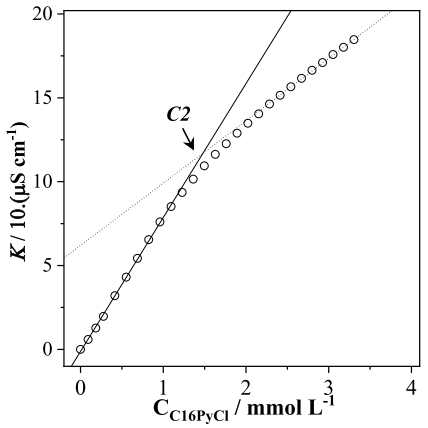

Figure 2. Conductivity (K) vs $C_{C16PyCl}$ obtained in 0.200% (w/v) PVCOOH, at 298.2 K. For all measurements, the specific conductivity of the solvent was discounted. The lines (solid and dashed) represent the linear fit applied.

Similar to the curve obtained in pure water, the conductivity curve profile in the presence of PVCOOH showed two linear regions. However, the concentration in which the fitted linear curves intercepted each other was equal to 1.48 ± 0.08 mmol L^{-1}, a concentration higher than the cmc, suggesting that a different mechanism of interaction occurred. Furthermore, the slope of the first fitted linear curve in the presence of PVCOOH (87 ± 1 μS L cm^{-1} $mmol^{-1}$) was nearly 10 units smaller than that obtained in pure water (97.9 ± 0.8 μS L cm^{-1} $mmol^{-1}$).

The decreased slope of the first fitted linear curve in the K versus $C_{C16PyCl}$ curve in the presence of PVCOOH indicated a reduction of the free ion concentration in the system compared with that in pure water, in which surfactant monomers were free and dissociated from the chloride anions (see α_{agg} in Table 1 for systems containing PVCOOH). Probably, an aggregation process between the surfactant and the PVCOOH macromolecules occurred without attaining a critical concentration. This process was due to the formation of PVCOOH−surfactant aggregates that were more favorably formed than PVOH−surfactants. These results suggest that the formation of the first aggregates involved the formation of specific interactions, whereas the formation of the latter depended on a cooperative process.

Table 1. Aggregation Parameters of C_{16}PyCl in the Presence and Absence of 0.200% (w/v) PVOH (or PVCOOH) at Different NaCl Concentrations and 298.2 K, Obtained from Conductimetric Measurements[a]

system	C_{16}PyCl			C_{16}PyCl + PVOH			C_{16}PyCl + PVCOOH	
[NaCl]	cmc	α_{mic}	ΔG°_{mic}	cac	C2	α_{agg}	C2	α_{agg}
0	1.04	0.41	−27.1	0.8	1.9	0.57	1.5	0.9
1.00	0.70	0.37	−29.4	0.6	1.8	0.51	1.2	0.7
2.00	0.55	0.35	−30.7	0.5	1.8	0.47	1.2	0.7
4.00	0.39	0.28	−33.5	0.3	1.0	0.42	1.3	0.6
10.0	0.23	0.15	−38.4	0.2	0.7	0.37	0.6	0.8

[a]The error associated with the aggregation parameters is lower than 5%. The units of concentration and energy are millimoles per liter and kilojoules per mole, respectively.

For surfactant concentrations higher than 1.48 ± 0.08 mmol L^{-1}, the interaction between PVCOOH and C_{16}PyCl probably ceased, and surfactant free micelles were formed in the solution. Furthermore, aggregates of PVCOOH−C_{16}PyCl with the same ionization degree as that of the free C_{16}PyCl micelles in the solution were generated, similarly to that formed for the PVOH system at C2. Thus, C2 was ascribed to the intersection point between the linear fit in Figure 2.

The difference in the types of aggregates formed between C_{16}PyCl and each polymer was corroborated with turbidimetry measurements of PVOH and PVCOOH aqueous solutions in the presence of the surfactant. Specifically, turbidity of polymer solutions in the presence of surfactants can provide information about the presence of macroscopic aggregates involving polymer−surfactant interactions.[31] Figure 3 shows the turbidity of 0.200% (w/v) PVOH (or PVCOOH) in different concentrations of C_{16}PyCl.

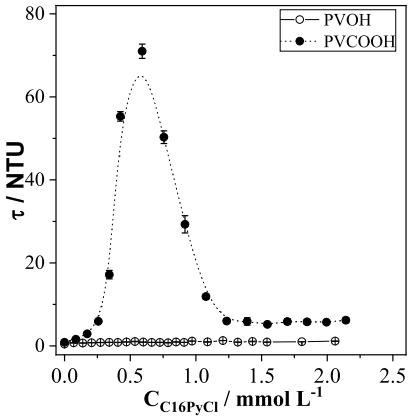

Figure 3. Turbidity (τ) vs $C_{C16PyCl}$ obtained in 0.200% (w/v) polymer aqueous solution, at 298.2 K. The dashed line represents the tendency of the physical phenomenon.

Turbidity of the PVOH aqueous solutions did not change in the presence of the surfactant. However, as the C_{16}PyCl concentration increased in the presence of PVCOOH, the turbidity of the system started increasing, indicating the formation of macroscopic PVCOOH−surfactant aggregates. Experimental τ values reached a maximum at 0.59 mmol L^{-1}. Then, they decreased when the surfactant concentration increased up to 1.22 mmol L^{-1}, becoming constant beyond this concentration. It should be highlighted that beyond this concentration, the turbidity of the system was slightly higher than that observed in the absence of the surfactant. This profile of the turbidimetry curve shows that the formed macroscopic aggregate structure depended on the PVCOOH/C_{16}PyCl concentration ratio in the solution.

The concentration range in which τ changed with the surfactant concentration, that is, $C_{C16PyCl}$ < 1.22 mmol L^{-1}, is within the range observed in the first linear region of the K versus $C_{C16PyCl}$ curve in Figure 2 ($C_{C16PyCl}$ < 1.48 mmol L^{-1}). This result confirms that the decrease in the slope in the first region of the conductimetric curve (Figure 2) when compared with that in pure water resulted from the formation of PVCOOH−surfactant aggregates without the need of a critical concentration.

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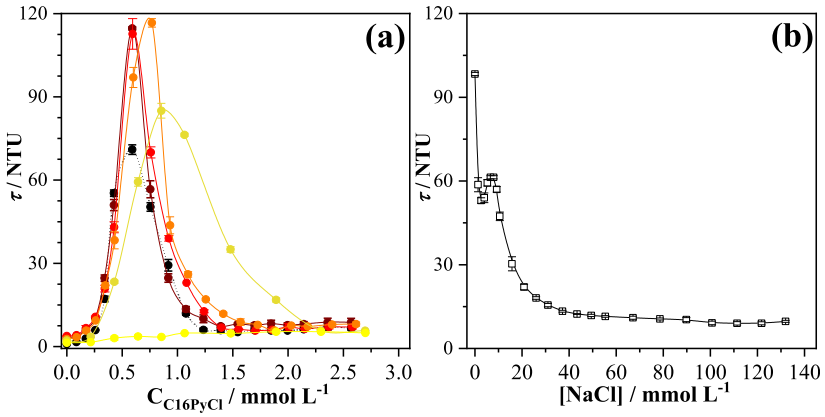

Figure 4. Turbidity (τ) vs (a) $C_{C16PyCl}$ obtained in 0.200% (w/v) PVCOOH + (●)black 0 mmol L^{-1}, (●)brown 1 mmol L^{-1}, (●)red 2 mmol L^{-1}, (●)orange 4 mmol L^{-1}, (●)mustard 10 mmol L^{-1}, and (●)yellow 100 mmol L^{-1} NaCl aqueous solution, and (b) [NaCl] obtained in 0.200% (w/v) PVCOOH + 0.600 mmol L^{-1} C_{16}PyCl aqueous solution, at 298.2 K.

In fact, PVOH and PVCOOH interacted differently with C_{16}PyCl, mainly because of the net charge of the polymers in solution. Whereas PVOH is a neutral polymer in aqueous solution in a broad range of pH values, carboxylic groups in PVCOOH can be easily charged by changing the pH of the system because of their low pK_a values.[32] The pH_{PZC} of PVCOOH was estimated, being equal to 5.98 (Figure S2). Therefore, at pH around 5.90, which is the pH of the solutions used in the experiments, some carboxylic groups were deprotonated and PVCOOH was slightly negatively charged, favoring the formation of electrostatic interactions with the $C_{16}Py^+$ cation.

As the surfactant concentration increased, the number of surfactant monomers interacting with the PVCOOH macromolecules also increased, changing the magnitude or the sign of the PVCOOH−surfactant aggregate charge. In the range of concentration from 0 to 0.59 mmol L^{-1}, as more surfactants were bound to the polymer, the negative charge of the aggregates was reduced, favoring the formation of macroaggregates (aggregates formed by various macromolecules), probably through hydrophobic interactions between the PVCOOH−surfactant aggregates. This phenomenon is reflected in the increase of the τ values (Figure 3).

The increase of the surfactant concentration above 0.59 mmol L^{-1} disadvantaged the formation of macroaggregates, as shown by the decrease of the τ values. Probably, beyond that concentration, the charge of the PVCOOH−surfactant aggregates became enough positive due to the incorporation of surfactant cations to the macromolecule. It promoted an electrostatic repulsion between them, which overcame other forces that were maintaining them interacting with each other in the macroaggregate. Thus, their sizes are decreased and the τ values are reduced. Despite that, some PVCOOH−surfactant aggregates interacted with each other even at higher surfactant concentrations. Otherwise, the τ values would be approximately zero beyond 1.48 mmol L^{-1}, such as in the system formed with PVOH. This result suggests that a delicate balance of weak intermolecular interactions determines the binding process of the surfactant with PVCOOH and the formation of the macroaggregates.

3.2. Interaction between PVOH (or PVCOOH) and C_{16}PyCl in NaCl Aqueous Solutions. A balance of the weak intermolecular interactions, such as electrostatic, hydrophobic, hydrogen bond, and van der Waals, is involved as the surfactant−polymer aggregation occurs.[33,34] This delicate balance of interactions can be affected in the presence of salts, changing the relative stability between the surfactant micelles and the polymer−surfactant aggregate, which could affect the aggregation parameters. This happens because the increase of ionic concentration in the solution increases its electric permittivity, shielding contributions of electrostatic interactions, which can reveal more clearly the role of the hydrophobic interactions on that aggregation process.

To access more information about the driving forces determining the aggregation process involving the polymers (PVOH and PVCOOH) and C_{16}PyCl, aggregation parameters were obtained in the presence of sodium chloride. Table 1 summarizes the parameters for the aggregation of C_{16}PyCl at different NaCl concentrations in the presence and absence of the polymers, obtained from conductivity measurements. All conductimetric curves details are shown in Figures S3 and S5 and Table S1.

The Gibbs free energy change of micellization (ΔG^{o}_{mic}) was obtained from eq 1,[35]

$$\Delta G^{o}_{mic} = (2 - \alpha_{mic})RT \ln(\mathrm{cmc}) \quad (1)$$

in which R and T are the gas constant and the absolute temperature, respectively.

The effects of salts on micellization of alkylpyridinium surfactants are already well known in the literature,[36,37] and a brief discussion is presented in the Supporting Information. Regarding the interaction between PVOH and C_{16}PyCl, the increase of the NaCl concentration up to 10.0 mmol L^{-1} decreased both cac and C2 values. Reduction of the cac values suggests that a higher ionic strength favored the surfactant−polymer complexes in relation to the free surfactant monomers in the bulk. At lower concentrations, NaCl acts as a structure-maker for the three-dimensional network of water molecules (kosmotropic agent[38−40]). This strengthening of the hydrogen bonds between the water molecules in the bulk of the solution decreased the number of these molecules available to interact with macromolecules and surfactant monomers, promoting a salting-out effect. This favors weak molecular interactions in the system, such as the hydrophobic interaction between the surfactant and the polymer, causing the decrease of the cac values.

Nevertheless, the reduction in the C2 values, which was also observed for the PVCOOH−C_{16}PyCl systems, disagrees with

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the formation of more favorable surfactant−polymer aggregates in the presence of NaCl. In fact, smaller C2 values in the presence of salts, generally attributed to the saturation of the macromolecule with a lower amount of surfactant monomers, are not a general result observed in studies involving other polymers.[41] Thus, these results should be carefully checked, and other technics could help confirm them.

The ability of the PVCOOH system to form macroscopic aggregates with C_{16}PyCl was used as the first approach to evaluate the extension of binding of the surfactant to that polymer. Figure 4a presents the turbidity measurements for PVCOOH and surfactant systems obtained as a function of the surfactant concentration at different NaCl concentrations.

For NaCl concentrations up to 4.00 mol L^{-1}, the concentration of the surfactant in which the macroaggregates disappeared (i.e., the surfactant concentration at which a plateau was observed in the turbidimetric curve) was similar to the C2 value obtained from the conductimetric curves (Table 1). However, at 10.0 mmol L^{-1} NaCl, this concentration was nearly 4 times higher than the C2 value obtained from the conductimetric method. This result suggests that the saturation concentration of PVCOOH was underestimated by conductivity measurements. This is a surprising result and suggests that there is a critical concentration in the formation of the PVCOOH−C_{16}PyCl aggregates, in which the molecular organization of the surfactant monomers interacting with the aggregate is similar to that of the monomers in the free micelles, generating species with similar ionization degrees (see the absence of a second break point in the conductimetric curve in Figure S5d).

This unexpected result was confirmed by evaluating the effect of NaCl on the turbidity of 0.200% (w/v) PVCOOH + 0.600 mmol L^{-1} C_{16}PyCl mixtures (Figure 4b). This chosen surfactant concentration corresponds to the C2 value obtained from the conductimetric method at 10.0 mmol L^{-1} NaCl. As observed, when the NaCl concentration increased, the turbidity of the mixture decreased until the salt concentration reached 2.66 mmol L^{-1}. Then, a further increase of the NaCl concentration increased the turbidity, reaching a local maximum in the curve at 6.62 mmol L^{-1}, indicating a favoring of the macroaggregate formation in the system at this concentration range. For concentrations higher than 6.62 mmol L^{-1} NaCl, the turbidity decreased exponentially, with a high turbidity still observed at NaCl 10.0 mmol L^{-1}, showing that at this concentration, the surfactant binding has not ceased the macroagregate formation. Only around 100 mmol L^{-1} NaCl, τ values remained almost constant, indicating the disappearance of the macroaggregates in the system.

Interestingly, at 100 mmol L^{-1} of NaCl, the turbidity of the system remained almost constant at all evaluated surfactant concentrations (Figure 4a), suggesting that at a higher salt concentration, the shielding of the electrostatic forces involved in the aggregation process disfavored the formation of the macroscopic aggregates or even prevented the aggregation process.

The complex profile of the turbidity versus [NaCl] curve and the effect of NaCl on the turbidity versus $C_{C16PyCl}$ curve indicated that the salt modulated with different intensities the electrostatic interactions between the species in the system, including surfactant/polymer, surfactant/surfactant, and polymer−surfactant aggregate/polymer−surfactant aggregate interactions. Because we could not obtain conductivity measurements at 100 mmol L^{-1} NaCl and because the systems containing PVOH did not form macroscopic aggregates, the ITC experiments represent a more sensitive approach to better understand the aggregation processes involving C_{16}PyCl and PVCOOH (and PVOH) polymers.

3.3. ITC Study for C_{16}PyCl−PVOH (or PVCOOH) Interaction. An experimental technique that can determine the energetics associated with weak molecular interactions in supramolecular systems such as those formed by the polymer and surfactants is the ITC.[42] Figure 5a shows the observed molar enthalpy change (ΔH_{obs}) for the dilution of a surfactant aqueous solution in pure water and in 0.200% (w/v) polymer (PVOH or PVCOOH) aqueous solution, at 298.15 K.

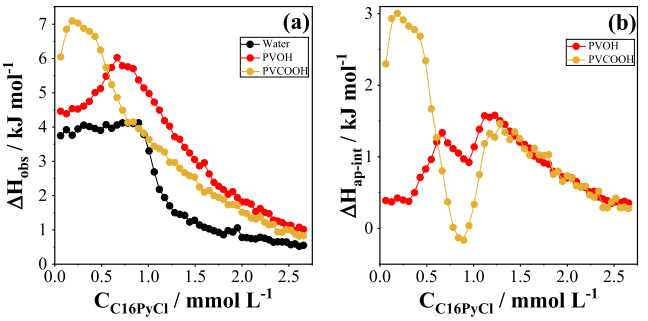

Figure 5. (a) ITC curves for titration of pure water and 0.200% (w/v) polymer with C_{16}PyCl aqueous solution, at 298.15 K, and (b) $\Delta H_{ap\text{-}int}$ vs $C_{C16PyCl}$ curves obtained from curves in (a). Figure S6 in the Supporting Information shows the thermograms used to obtain Figure 5a. Thermodynamic parameters of micellization and discussion about them can be found in Figure S7 and Table S2 in the Supporting Information.

In the presence of both polymers, ITC curves showed ΔH_{obs} values quite different from those obtained in pure water, indicating that different molecular events occurred in the systems with and without the polymers, confirming that the surfactant interacted with the macromolecules.

For the titration of PVOH solution, at C_{16}PyCl concentrations up to 0.31 mmol L^{-1}, the ITC curve was parallel to that obtained in pure water, with ΔH_{obs} just slightly higher. This suggests that in this range of concentration, no interaction between the surfactant and the polymer occurred. Beyond 0.31 mmol L^{-1}, ΔH_{obs} values began to increase, indicating the beginning of the aggregation processes (cac). Logically, this value was smaller than those obtained from other techniques (conductimetry and turbidimetry), which was associated with the higher sensibility of calorimetry to detect the interaction between C_{16}PyCl and PVOH.[28]

In the concentration range from 0.31 to 0.90 mmol L^{-1}, the more positive values of ΔH_{obs} for the curve obtained in the presence of PVOH were associated with the endothermic interaction process between the surfactant and the sites of the macromolecules, indicating that the aggregation process was driven by the entropy increase in this concentration range. For each injection, however, part of the ΔH_{obs} spent in the global process was associated with diluting the surfactant in the calorimetric cell, which corresponds to the ΔH_{obs} value obtained in the first level of the dilution curve of the surfactant. To obtain a better comparison between these curves, the apparent enthalpy change of interaction ($\Delta H_{ap\text{-}int}$) curves were obtained by subtracting the surfactant dilution curve in water from that in polymer solution (Figure 5b). The term "apparent" is used because the amount of surfactant

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monomers that interacted with the polymer at each surfactant concentration in unknown in the absence of binding isotherms. Despite this, the $\Delta H_{ap\text{-}int}$ versus $C_{C16PyCl}$ curve can provide a good qualitative analysis for comparisons between different systems.[29]

Because of the previous analysis, $\Delta H_{ap\text{-}int}$ values were positive in the investigated range of concentration, increasing with the increase of $C_{C16PyCl}$ from 0.31 to 0.67 mmol L^{-1}. Beyond this last concentration, the $\Delta H_{ap\text{-}int}$ values began to decrease abruptly up to 0.95 mmol L^{-1}, when the $\Delta H_{ap\text{-}int}$ values increased again, attaining a new local maximum at 1.23 mmol L^{-1}, characterizing two endothermic peaks in the $\Delta H_{ap\text{-}int}$ versus $C_{C16PyCl}$, that is, two concentrations range with a local maximum. Finally, around 2.50 mmol L^{-1}, the $\Delta H_{ap\text{-}int}$ became constant again, indicating that the surfactant−polymer interaction process has ceased.

The complex profile of the curve suggests the occurrence of different molecular events involving the aggregation process of the surfactant on the macromolecular chain as the C_{16}PyCl concentration increased. Probably, this profile could be associated with the reorganization of the $C_{16}Py^+$ monomers on the macromolecular chains since it has been already pointed out for other nonionic polymer−surfactant systems:[30] at low surfactant concentrations, in which the interaction occurs, the monomers are bound individually to the macromolecules. Then, as the surfactant concentration was increased, monomers of surfactant began to form small aggregates anchored on the polymer, which promoted a partial rehydration of the PVOH polymer chains, decreasing $\Delta H_{ap\text{-}int}$ (first endothermic peak). This phenomenon was favored by the electrostatic shielding between the charged groups of $C_{16}Py^+$ by the hydroxyl polar groups of the polymer, which decreased the $\Delta H_{ap\text{-}int}$ values at surfactant concentrations smaller than 0.89 mmol L^{-1}. Finally, those anchored surfactant aggregates increased their size due to the incorporation of new surfactant monomers until the saturation of the polymer chain was reached, characterizing the second endothermic peak.

When PVOH was changed by PVCOOH, a different behavior was observed in the first part of the $\Delta H_{ap\text{-}int}$ versus $C_{C16PyCl}$ curve. For the first injection of the surfactant solution in the calorimetric cell (0.063 mmol L^{-1}), the $\Delta H_{ap\text{-}int}$ was remarkably high (2.30 kJ mol^{-1}). At this surfactant concentration, the formation of macroaggregates was not observed (see Figure 4a, in which turbidity values began to increase abruptly just from 0.172 mmol L^{-1}), and the apparent enthalpy change should come mainly from the interaction between the surfactant and the interaction sites of PVCOOH. This is an interesting result, indicating that although the attractive electrostatic interactions favored the aggregation processes between C_{16}PyCl and PVCOOH, without the need of a critical concentration, they were not enough intense to become the main intermolecular interaction determining the binding of the surfactant to the polymer, but probably the hydrophobic ones. Otherwise, the $\Delta H_{ap\text{-}int}$ values would be negative. As the surfactant concentration increased up to 0.189 mmol L^{-1}, $\Delta H_{ap\text{-}int}$ increased, which was probably associated with the desolvation of the surfactant−polymer aggregates to form the macroscopic aggregates.

Since the exact amount of the surfactant bound to each polymer for each injection could not be obtained, it was not possible to directly compare the magnitude of the $\Delta H_{ap\text{-}int}$ values for the PVCOOH and PVOH systems. Despite this, it is interesting to note that some features of both curves in Figure 5b at higher surfactant concentration were similar, specially beyond 0.67 mmol L^{-1}, in which $\Delta H_{ap\text{-}int}$ values for the PVCOOH system displayed local minimum and maximum values (0.89 and 1.28 mmol L^{-1}, respectively) in similar concentrations observed for PVOH (0.89 and 1.23 mmol L^{-1}, respectively). This result suggests that some of the molecular events determining the aggregation process involved the interaction between the surfactant and similar repeating unities present in both polymers, that is, those containing the hydroxyl groups (Figure S1). This is an interesting result that confirms that the macroaggregates formed between $C_{16}Py^+$ and PVCOOH complexes are due to the neutral charge that is established as the cationic surfactant neutralizes the carboxylate groups in the polymer chain.

To better understand this aggregation energetics, the effect of NaCl on the $\Delta H_{ap\text{-}int}$ versus $C_{C16PyCl}$ curves for systems comprising PVOH and PVCOOH polymers were evaluated, and the results are present in Figure 6. The ITC curves used to obtain these results are shown in Figures S8−S10.

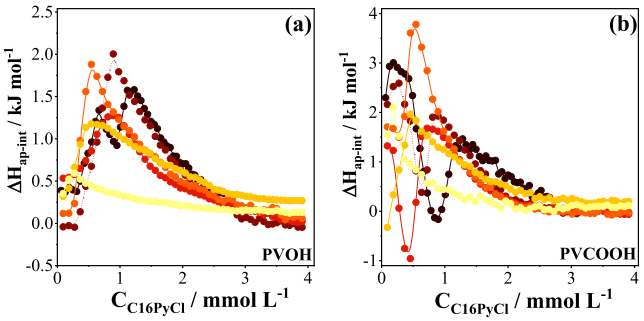

Figure 6. $\Delta H_{ap\text{-}int}$ vs $C_{C16PyCl}$ curves for (a) PVOH and (b) PVCOOH in the presence of different NaCl concentrations: (●)black 0 mmol L^{-1}, (●)brown 1 mmol L^{-1}, (●)red 2 mmol L^{-1}, (●)orange 4 mmol L^{-1}, (●)mustard 10 mmol L^{-1}, and (●)yellow 100 mmol L^{-1}.

The presence of the salt changed the profile of the $\Delta H_{ap\text{-}int}$ versus $C_{C16PyCl}$ curves, indicating that the electrostatic interactions contributed to the aggregation process of the surfactant with both polymers. For the PVOH system, all NaCl concentrations suppressed one of the endothermic peaks (local maximum value in the $\Delta H_{ap\text{-}int}$ versus $C_{C16PyCl}$ curve), suggesting that the aggregation processes had a smaller complexity in the presence of the salt. Probably, the electrostatic shielding of the charged groups of $C_{16}Py^+$ promoted by Cl^- anions favored the formation of surfactant aggregates anchored on the polymer, even at small surfactant concentrations. It prevented $C_{16}Py^+$ monomers from forming interactions with the macromolecular chain, avoiding the rehydration processes that induce the appearance of the second endothermic peak. This is also corroborated by the displacement of the maximum of the endothermic peak in the $\Delta H_{ap\text{-}int}$ versus $C_{C16PyCl}$ curves for smaller surfactant concentrations with a decrease in the magnitude of the $\Delta H_{ap\text{-}int}$ value in the maximum of the curve, as the salt concentration increased. The interaction between micelles of the surfactant and the polymer in the presence of NaCl involved dehydration of the PVOH chain in a smaller extension than that in pure water since the polymeric chain is recognized to be localized in the micellar surface, decreasing the electrostatic repulsion between the head groups of the surfactant.[28] The higher the micelle stabilization (at a higher NaCl concentration) is, the

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smaller the extension of the dehydration process per mole of surfactant added in the system is, which decreased the intensity of the endothermic peak.

For the PVCOOH systems (Figure 6b), different salt concentrations promoted different effects on the profile of the $\Delta H_{ap\text{-}int}$ versus $C_{C16PyCl}$ curves. Whereas at 1.00 mmol L^{-1} NaCl, the curve only changed the positions of the maximum and minimum values of the $\Delta H_{ap\text{-}int}$, as well as their magnitude, retaining the curve profile, an abrupt change was observed at 2.00 mmol L^{-1} NaCl, in which the curve first displayed a minimum at 0.45 mmol L^{-1} and then a local maximum appeared at 0.71 mmol L^{-1}. Surprisingly, the $\Delta H_{ap\text{-}int}$ attained values around −1.0 kJ mol^{-1} at 0.5 mmol L^{-1}, suggesting that the aggregation process was enthalpically favored in the smaller surfactant concentration range at this salt concentration.

At NaCl concentrations higher than 4.00 mmol L^{-1}, the curves displayed a similar profile to that observed for the PVOH systems in the presence of the salt (Figure 6a), with only an endothermic peak observed, even at 100 mmol L^{-1} of NaCl, in which the formation of macroscopic PVCOOH−surfactant aggregates were not observed (Figure 4a). This result suggests that this higher salt concentration shielded the electrostatic attractions between the surfactant and $-COO^-$ groups of PVCOOH as well as the interactions between the polymer−surfactant aggregates that form the macroaggregates. Thus, at 100 mmol L^{-1} NaCl, the aggregation process mainly occurred in the $-CH_2(OH)CH_2$-unities of the macromolecules of PVCOOH.

To systematize some of the information observed in the complex profiles of the $\Delta H_{ap\text{-}int}$ versus $C_{C16PyCl}$ curves and to compare the aggregation process in the different evaluated solvents, cac, C2, the decrease in the Gibbs free energy change for C_{16}PyCl aggregation in the presence of PVOH (or PVCOOH) when compared with its aggregation in the solvent ($\Delta\Delta G_{agg}$), and the integral enthalpy change for aggregate formation (ΔH_{agg}) were determined from ITC results. The number of monomers of the surfactant bound by unit of mass of each polymer (N_{agg}) was also estimated and are presented and discussed in the Supporting Information (Figure S11).

The $\Delta\Delta G_{agg}$ was obtained from the following equation:

$$\Delta\Delta G_{agg} = (2 - \alpha_{mic})RT \ln \frac{cac}{cmc} \quad (2)$$

in which R is the universal gas constant and T is the absolute temperature. The cac and cmc values were obtained from the calorimetric experiments. α_{mic} was obtained from conductimetry. The ΔH_{agg} parameter was estimated using eq 3, proposed by Olofsson and Loh:[42]

$$\Delta H_{agg} = \left[\frac{\sum q_{obs} - Yq_{demic+dil}}{Yn_{inj} - V_Y cmc} \right] \quad (3)$$

in which it was assumed that C2 was achieved in the Yth injection of n_{inj} moles of C_{16}PyCl, giving a total volume V_y. At C2, the concentration of free monomers was equal to the cmc of the surfactant, with a total amount of the surfactant added equal to Yn_{inj}. Then, $V_y$cmc is the amount of the surfactant that did not interact with the polymer at C2; Σq_{obs} is the energy measured in the interaction process; and $Yq_{demic + dil}$ is the energy of demicellization and dilution. Under this condition, the ΔH_{agg} value indicates the enthalpy change for the formation of the surfactant−polymer aggregates from 1 mol of surfactant monomers in the concentration range from cac to C2. All thermodynamic parameters obtained from the ITC experiments are shown in Table 2. $\Delta\Delta G_{agg}$ values were not calculated for PVCOOH systems because cac is not present. As for PVOH, at 100 mmol L^{-1} NaCl, it was not possible to determine cac for the evaluated techniques. In this last condition, ΔH_{agg} could not also be obtained because it was not possible to obtain the values of $q_{demic + dil}$.

Table 2. Thermodynamic Parameters of Aggregation Obtained from Calorimetry for C_{16}PyCl Aggregation in the Presence of 0.200% (w/v) PVOH (or PVCOOH) in Different NaCl + Water Mixtures, at 298.15 K[a]

system	C_{16}PyCl + PVOH				C_{16}PyCl + PVCOOH	
[NaCl]	cac	C2	$\Delta\Delta G_{agg}$	ΔH_{agg}	C2	ΔH_{agg}
0	0.54	2.52	−2.56	−1.10	2.38	−1.18
1	0.45	3.37	−1.90	−3.70	2.50	−2.79
2	0.45	3.43	−1.11	−3.76	2.42	−3.01
4	0.36	3.57	−0.66	−3.10	2.35	−3.18
10	0.18	3.37	−3.55	−4.12	2.57	−3.91

[a]The error associated with the aggregation parameters is lower than 5%. The units of concentration and energy are millimoles per liter and kilojoules per mole, respectively.

The effect of NaCl concentrations on the cac values obtained by ITC followed the same tendency as that observed in the results obtained from conductimetry. However, C2 values obtained by ITC values were higher than those obtained from conductimetry, especially at 10.0 mmol L^{-1} NaCl, in which the values from ITC were 4.8 and 4.5 times higher in the systems formed with PVOH and PVCOOH, respectively. This result corroborates our hypothesis revealed by the turbidity experiments with PVCOOH systems. C2 values determined by conductimetry was not associated with the saturation of the polymer, but only a concentration in which the monomers of the surfactant formed aggregated structures on the polymer chain with similar charge density to those of the free micelles in the same solvent. Then, the ionization degree of these aggregates is similar to that of the free micelles formed in the bulk. This result shows that conductimetry was not adequate to determine the concentration where the interaction process between the surfactant and the polymer ceased.

The $\Delta\Delta G_{agg}$ values for the PVOH systems were negative, indicating that the $C_{16}Py^+$ aggregates formed on the polymer chain are more stable than those formed in the bulk (micelles). However, as the salt concentration increased to up to 4.00 mmol L^{-1}, these values become less negative, indicating that the higher relative stability of the aggregates formed with the PVOH regarding the surfactant micelles in the bulk was decreased. Conductimetric results showed a more intense effect of the salt on the reduction of the dissociation degree of the micelles in the bulk (α_{mic}) when compared with that of the surfactant aggregates binding to PVOH (α_{agg}) (Table 1). Then, the decrease in the magnitude of $\Delta\Delta G_{agg}$ promoted by NaCl was probably associated with the more efficient electrostatic shielding of the head groups of $C_{16}Py^+$ in the free micelle, associated with changes in the processes of desolvation of the polymer as the surfactant interacted with the macromolecular chain.

In fact, as observed in Table 2, ΔH_{agg} values were negative for all salt concentrations, becoming more negative in the presence of NaCl, which shows that the $C_{16}Py^+$/PVOH

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aggregates were enthalpically stabilized. This was probably associated with the salt effect on the disappearance of the first endothermic peak in the $\Delta H_{ap\text{-}int}$ versus $C_{C16PyCl}$ curves at higher NaCl concentrations. As a consequence, the contribution of the entropic gain associated with the desolvation process of the macromolecular chain was decreased, contributing to the decrease of the $\Delta\Delta G_{agg}$ module. It is interesting to note that at NaCl 10.0 mmol L^{-1} the $\Delta\Delta G_{agg}$ module increased, indicating a higher stabilization of the aggregates formed on the polymer chain.

For the PVCOOH systems, in the absence of NaCl, the ΔH_{agg} value was very close to that obtained for PVOH, showing that in the global interaction process, the salt was not the main responsible interaction for determining the ΔH_{agg}, although the electrostatic attraction between the $C_{16}Py^+$ and the $-COO^-$ groups enthalpically favored the formation of the aggregates. This result suggests that most of the interaction sites on the macromolecular chains were the same for both polymers and that the $-COO^-$ groups participated mainly for small concentrations of $C_{16}Py^+$.

4. CONCLUSIONS

Conductimetric and turbidimetric measurements, combined with ITC analyses, provided an energetic understanding of the interaction between the amphiphilic antimicrobial agent, hexadecylpyridinium chloride ($C_{16}PyCl$), and biodegradable polymers, poly(vinyl alcohol) (PVOH) or poly(vinyl alcohol) modified with carboxyl groups (PVCOOH) in pure water and NaCl aqueous solutions.

In pure water, at low surfactant concentration (cac), monomers of $C_{16}PyCl$ started to interact with PVOH and as the surfactant concentration increased, monomers of $C_{16}PyCl$ began to form small aggregates anchored on the polymer. In these molecular processes, two endothermic events were observed associated with partial desolvation and rehydration of the PVOH polymer chains.

The change of the molecular structure of the polymer strongly affected the interaction with the surfactant. $C_{16}PyCl$ interacted more favorably with PVCOOH, in which some carboxylic groups were deprotonated, favoring simultaneously hydrophobic and electrostatic interactions and leading to the formation of macroscopic aggregates ($C_{16}PyCl$-PVCOOH). The ionization degree of the $C_{16}PyCl$ micelles in the bulk was similar to that of the surfactant monomer aggregates anchored on the polymer chain (near the saturation concentration), suggesting a small effect of the polymer on the charge density of the aggregates.

The increase of the ionic strength favored the formation of surfactant−polymer complexes when compared with surfactant monomers in the bulk. The kosmotropic behavior of NaCl led to an enthalpic favorability for the formation of the aggregates. For higher concentrations of NaCl, the −COOH interaction sites on the macromolecular chains of PVCOOH played a less important role for the aggregation process, with macroscopic aggregates being suppressed for the system of 100 mmol L^{-1} concentration of the salt.

Compilation of results and explanations reported in this work are fundamental for future industrial implementations of colloid science involving antimicrobial amphiphilic compounds and new biodegradable polymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.2c05054.

PVOH and PVCOOH molecular structures; ΔpH versus pH_i for estimation of PVCOOH PZC; conductivity (K) versus $C_{C16PyCl}$ obtained for PVOH and PVCOOH in pure water and different water + NaCl mixtures; ITC curves for titration of systems in the absence or presence of polymers in pure water with $C_{16}PyCl$, at different NaCl concentrations; N_{agg} versus [NaCl] obtained in 0.200% (w/v) PVOH (or PVCOOH) + NaCl + water mixtures; cmc and ΔH^o_{mic} values as a function of the NaCl concentration; parameters of the linear fit applied to the conductivity curves; and thermodynamic properties of micellization (PDF).

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Á.J.P.-A.: conceptualization, methodology, validation, investigation, visualization, formal analysis, writing—original draft, and writing—review and editing. M.L.B.: methodology, validation, and investigation. L.H.M.d.S.: supervision and funding acquisition. G.M.D.F.: conceptualization, methodology, validation, investigation, visualization, formal analysis, writing—original draft, writing—review and editing, supervision, project administration, and funding acquisition.

Notes

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