

The Interaction between Hexadecyltrimethylammonium Bromide to Poly (Ethylene Glycol) with Different Molecular Weights and Some Schiff-Bases Investigated by Surfactant Ion Selective Electrode

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The interaction between ionic surfactants and different nonionic molecules and polymers are studied using ion surfactant selective electrode. From the experimental data, critical concentrations of the interaction and binding process are evaluated. The interaction between hexadecyltrimethylammonium bromide (HTAB) with polyethylene glycol (PEG) in three molecular weights (1000, 10000 and 100000) and also schiff-bases, 2-[2-carboxyphenyl nitrilomethylidene]-phenol (ortho CNP), 2-[3-carboxyphenyl nitrilomethylidene]-phenol (meta CNP) and 2-[4-carboxyphenyl nitrilomethylidene]-phenol (para CNP) with the potentiometric method were investigated using HTAB membrane selective electrode. In the case of PEG with increasing molecular weights more interaction to HTAB occurs. The electromotive force (EMF) data also showed that interaction between para CNP with HTAB is more than the other schiff-bases. It seems this case related to less space interference of COOH group for that compound. The onset of binding (T_1) of course is the same for three schiff-base molecules.

Key Words : EMF, Cationic surfactant, Polymer-mixed micelle interaction, Schiff-bases, PEG

Introduction

Polymers and surfactants are widely used in many different commercial formulations.¹ The interaction between charged and uncharged polymers and ionic surfactants have been extensively studied and discussed in many review articles.^{2,3} The behavior of specific components in these systems have been investigated by techniques which can probe, directly or indirectly. Surfactant monomers, micellar aggregates, polymer/surfactant complexes, and single polymers, as well as different macroscopic parameters characterizing the physical properties of the solution are some examples.

In fundamental studies carried out on polymer/surfactant systems, the critical concentrations referring to the total amounts of added surfactant are of prime importance. These are (i) T_1 , signaling the onset of binding; (ii) T_2 signaling the saturation of the polymer with bound surfactant (iii) T_f , signaling the formation of free micelles. It is now generally accepted that the interaction between cationic surfactants and neutral polymers are much reduced in comparison to those of anionic surfactants.¹ Indeed many synthetic polymers are known only to interact with anionic surfactants, and show little or no affinity to cationics.²⁻⁵ In some cases T_2 have not seen for cationics. In comparison with anionic surfactant/neutral polymer systems, there are very little information concerning quantitative binding characteristics of cationic surfactants. The interaction between some schiff-bases and polymers with cationic surfactant hexadecyltrimethylammonium bromide (HTAB) are investigated in this work. EMF data showed that the interaction between the schiff-bases and the surfactant are very much.

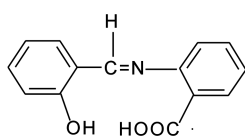
The surfactant selective electrodes offer an attractive potentiometric method for the surfactant analysis.⁵⁻¹⁰ Potentiometric sensors offer several advantages. The sensors have generally a large linear range because the signal is proportional to the logarithm of ion activity. Short response time make the devices very suitable for process control and allows a high sample throughput in, for example, flow injection analysis. Moreover, the potentiometric sensors can have very small dimensions and consequently, only small sample volumes are required. In present work we have been studied the interaction between some of the polymers and schiff-bases with HTAB using HTAB-selective electrode.

The schiff-bases used in this work are very important compounds that are formed by condensation reaction between a compound consist of carbonyl group and a primary amine.¹¹

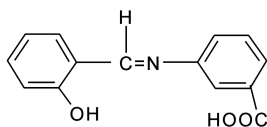
Experimental Section

Reagents. HTAB surfactant, THF, NaBr and PEG (MW =1000, 10000, 100000) were Merck products. The schiff-bases used in this work made in the laboratory of the University of Kashan.¹² The schiff-bases are ortho CNP, meta CNP and para CNP. The structure of schiff-bases are shown in Figure 1.

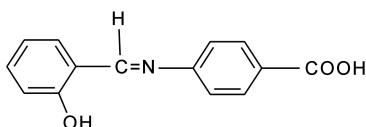
The surfactant selective membrane electrode used in the present work was constructed using a method which has been described previously.¹³⁻¹⁸ The membrane comprises a specially conditioned poly vinyl chloride (PVC) contains of 0.1% COOH from Montefibre and a commercially available polymeric plasticizer (Elvaloy 742) from Du pont. In order to make membranes selective to HTAB, the respective PVC



ortho CNP : 2-[2-Carboxyphenyl nitrilomethylidene]-phenol



meta CNP : 2-[3-Carboxyphenyl nitrilomethylidene]-phenol



para CNP : 2-[4-Carboxyphenyl nitrilomethylidene]-phenol

Figure 1. The structure of schiff-bases.

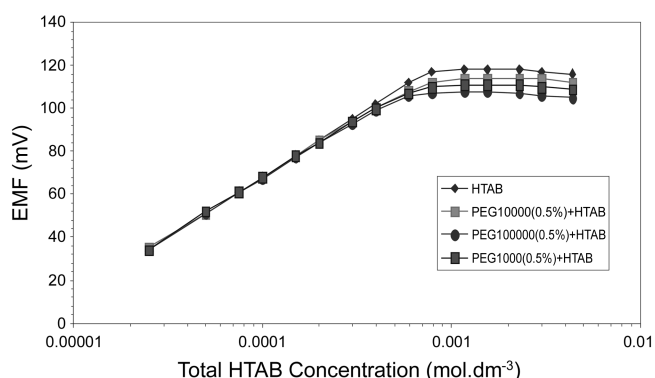
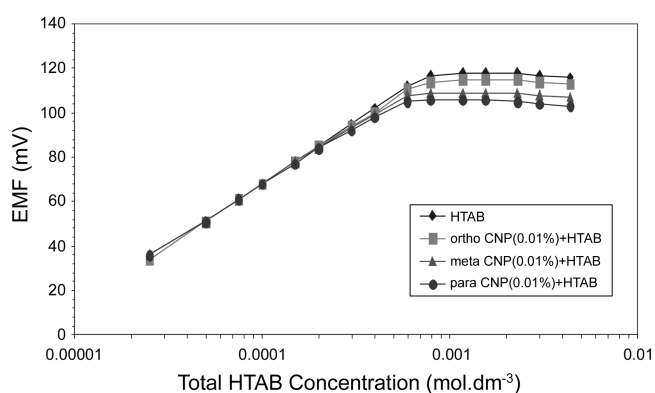
are neutralized by the oppositely charged HTAB ions before use. All solutions were prepared using doubly distilled water.

Preparation of HTAB Ion-selective Membrane. 0.5 g PVC was dissolved in 30 mL stirred double distilled THF. This solution was then added drop by drop to a solution of 1.35 g HTAB dissolved in 300 mL double distilled water in a 500 mL beaker. The solution was left to stir for 48 hours to complete the precipitation and conditioning. The results HTAB-PVC complex was then filtered, washed thoroughly using double distilled water and left to dry at room temperature. 180 mg of polymeric plastisizer, Elvaloy 742 was dissolved in 30 mL of double distilled THF and stirred until total dissolution. To this plastisizer-THF solution, 120 mg of HTAB-PVC complex was added gradually and then left to stir until was no gel left in the solution. The solution was the filtered into a flat-bottomed beaker (55 mm diameter) and left until to get a membrane of uniform thickness. The membrane was carefully cut and was placed on top of the electrode tip and connected to internal Ag/AgBr reference electrode. These conditioning and casting steps were optimized and we used optimized amount of materials.¹³⁻¹⁸

EMF Measurements. The surfactant membrane electrode selective to HTAB used to determine the concentration of monomer surfactant and counterions, respectively, by measuring their EMF relative to a commercial sodium (coming 476211) reference electrode and also bromide ion (coming solid-state ISE 30-35-00) selective electrode. The cells used for these measurements and the procedures to calculate the respective monomer concentration have been described elsewhere.¹³⁻¹⁸

Results and Discussion

For the polymer and schiff-base solutions, the deviation of

**Figure 2.** Plot of EMF versus log C_1 for Pure HTAB and HTAB/PEG 10000, 10000 and 1000 (0.5%) in 1×10^{-4} mol-dm⁻³ NaBr.**Figure 3.** Plot of EMF versus log C_1 for Pure HTAB and HTAB/ortho, meta and para CNP (0.01%) systems in 1×10^{-4} mol-dm⁻³ NaBr.

the EMF from the ideal Nernstian behavior is fairly well defined break as are shown in Figures 2 and 3. The break point is attributed to the onset of binding and is shown by T_1 . Once binding starts, the surfactant electrode monitors the monomer surfactant concentration (m_1) as a function of total surfactant concentration (C_1). The polymer or schiff-base becomes fully saturated with bound surfactant at concentrations well in excess of the CMC. It is normally found for anionic surfactant that the EMF data with and without the polymer merge, indicating that the polymer has no longer any influence on m_1 . Unfortunately we have not been able to observe any point at which the EMF data merge after binding in the present work and also in previous electrode studies on cationic surfactants.^{14,19} We believe that part of this problem may be due to the electrode not responding ideally at higher surfactant concentrations. Certainly we have found that the high surfactant concentration response of the electrode is dependent on the origin of the modified poly vinyl chloride used for the membrane and also on high salt concentration. If we use counterion bromide electrode as a reference electrode by using the equation of $E_{\text{cell}} = E^{\circ}_{\text{cell}} + 2(RT/F) \ln(C_1 C_2)^{1/2}$ that C_2 is concentration of counterions, ($C_2 = C_1 + 1 \times 10^{-4}$), then a plot of E_{cell} against $\log(C_1 C_2)^{1/2}$ is linear below the CMC and obeys the Nernst equation. The EMF experiments also indicate that once binding starts at T_1

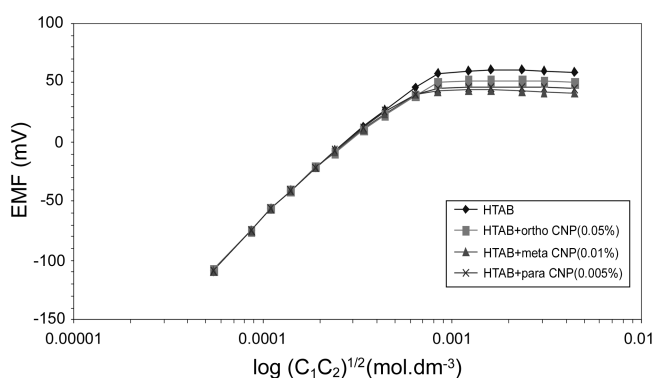


Figure 4. Plot of the EMF of the HTAB electrode (reference Br^-) as a function of $\log(C_1 C_2)^{1/2}$ concentration for the HTAB/schiff-bases systems in $1 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ NaBr.

a small amount of bromide counter ion starts binding as shown in Figure 4. This observation is often used as evidence that surfactant aggregated are formed on the polymer or schiff-base. During the initial binding stages the bound surfactant aggregates probably grow process is accompanied by an increase in the monomer surfactant concentration. This is the normal behavior expected for any binding process. The plot of monomer surfactant concentration against total surfactant concentration for HTAB/ortho, meta and para CNP are shown in Figure 5. When the monomer concentration reaches a maximum and starts decreasing with the addition of more surfactant such a behavior is indicative of the formation of free micelles in the solution. For example the maximum in the monomer concentration found from the EMF data for the pure HTAB in the absence of polymer or schiff-base corresponds to the critical micelle concentration and once this is reached the monomer concentration decreases with further added surfactant. These results are the same for schiff-base and polymer as well.

The EMF data showed that interaction between para CNP with HTAB is more than the other schiff-bases. We believe this case related to less space interference of COOH group for this compound. T_1 of course is the same for three schiff-base molecules, and this represent that difference location of COOH group has effect on decrease of CMC, but has no

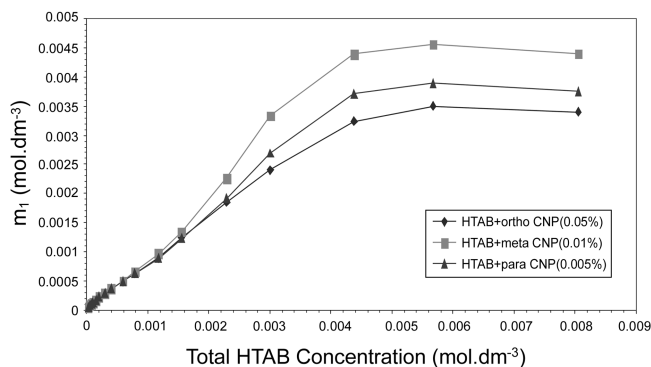


Figure 5. Plot of m_1 versus C_1 for HTAB/ortho (0.05%), meta (0.01%) and para (0.005%) CNP systems in $1 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ NaBr.

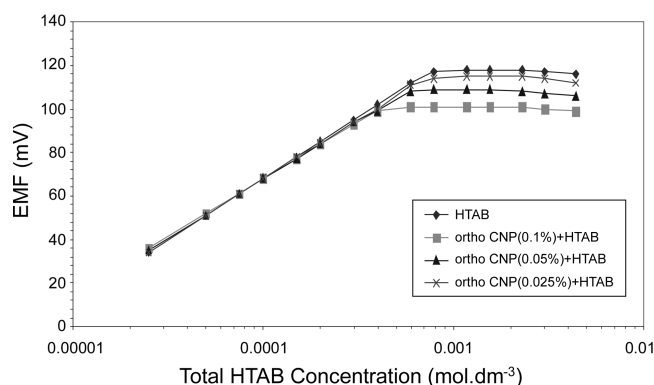


Figure 6. Plot of EMF versus $\log C_1$ for Pure HTAB and HTAB/ortho CNP (0.025, 0.05, 0.1%) systems in $1 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ NaBr.

effect on T_1 as shown in Figure 3. The interaction between HTAB with PEG (MW=100000) is also more than the other molecular weights of PEG as shown in Figure 2.

When different concentration of ortho CNP used the results shown that more interaction is for more concentration of schiff-base (Figure 6). These results are the same as polymers.

Micellization of ionic surfactants at low salt concentration is the only aggregation process that we are aware of in which the monomer concentration decreases with increasing surfactant concentration. On this basis we conclude that in the polymer or schiff-base/surfactant systems the surfactant concentration T_f corresponding to the maximum in m_1 signals to the formation of free micelles in the solution. As further surfactant is added both free micelles and polymer or schiff-base bound surfactant aggregates are formed simultaneously from T_f until T_2 is reached. For all the systems, the maximum in the EMF's data for the surfactant/polymer or schiff-base are always slightly less than the corresponding maximum for the system without the polymer or schiff-base. This statement however introduces a paradox in a sense that these polymer or schiff-base/surfactant systems free micelles start occurring in solution at a total surfactant concentration less than the critical micelle concentration of the pure surfactant. This also means that the monomer concentration in each of these systems behaves in exactly the same way.

For these systems between T_f and T_2 the decrease in m_1 is associated with a highly cooperative process and consistent with the formation of free micelles after T_f . On the other hand in the region T_1 - T_f where only binding of surfactant to the polymer or schiff-base takes place this process is also cooperative in the sense that there is distinct break at T_1 . Furthermore during this process it is likely that aggregates are formed on the polymer or schiff-base since a small degree of counter ion binding takes place in this region. These bound aggregates are not as well defined as "proper" micelles in the sense that the degree of counter ion dissociation is high which results is a high charge density on the surface of the bound aggregate. This leads to head group repulsion and a more "loosely" packed aggregate compared

Table 1. Value of T_1 , T_f , m_1 , $C_1 - m_1$ and $(C_1 - m_1)/C_p$ for HTAB/Polymer and schiff-base Systems

HTAB/Polymer or schiff-base systems	T_1 (mol·dm ⁻³)	T_f (mol·dm ⁻³)	m_1 (mol·dm ⁻³)	$C_1 - m_1$ (mol·dm ⁻³)	$(C_1 - m_1)/C_p$ (mol bound surfactant per g polymer)
PEG (1000) (0.5%)	0.0003	0.0025	0.0017	0.0008	0.0016
PEG (10000) (0.5%)	0.0002	0.0020	0.0015	0.0005	0.0010
PEG (100000) (0.5%)	0.0001	0.0015	0.0011	0.0004	0.0008
ortho CNP (0.05%)	0.0002	0.0025	0.0019	0.0006	0.0012
meta CNP (0.005%)	0.0002	0.0025	0.0018	0.0007	0.0014
para CNP (0.001%)	0.0001	0.0020	0.0015	0.0005	0.0010

PEG: Poly (ethylene glycol). ortho CNP: 2-[2-Carboxyphenyl nitrilomethylidyne]-phenol. meta CNP: 2-[3-Carboxyphenyl nitrilomethylidyne]-phenol. para CNP: 2-[4-Carboxyphenyl nitrilomethylidyne]-phenol

to a “proper” micelle where the degree of counter ion dissociation is considerably lower thus allowing the head groups to pack closer together. We now turn our attention to the occurrence of free micelles in these polymer or schiff-base/surfactant systems at concentration below the CMC of the pure HTAB. The schiff-base in the maximum found for the monomer concentration and hence the concentration at which free micelles occur also follows the above trends for the different polymers and schiff-bases. This shift accompanies the relative increase in the concentration of free Br^- counter ions. We believe that the clue to the explanation for this unusual result is analogous to that proposed earlier by Holmberg *et al.* to explain the primary step in the formation of polymer/surfactant complexes.¹⁹ In the present systems the bound surfactant in the T_1 - T_f region polymer and schiff-base are a “loose” aggregate which only binds a small amount of Br^- counter ion. However the positive charge density at the surface of these bound aggregates are likely to attract Br^- counter ions in such a way that the local concentration of Br^- ions in the microenvironment of the complex is much higher than their bulk concentration. Thus any free surfactant ions in this enhanced ionic strength environment will form micelles at effectively lower surfactant concentration than the CMC and we believe that these are the precursors to the “free” micelles, which are formed in these systems.

The region T_1 - T_f is exclusively associated with the binding of surfactant to polymer or schiff-base and can be described as an equilibrium between monomer surfactant in the bulk solution and bound surfactant on the polymer or schiff-base. The value of T_1 and T_f are listed in Table 1. In the region T_1 - T_f the quantity $C_1 - m_1$ where C_1 is the total added surfactant, represent the amount of surfactant bound to the polymer or schiff-base. $(C_1 - m_1)/C_p$ (C_p is the amount of polymer gdm⁻³) versus m_1 plots for HTAB/schiff-base systems are shown in Figure 7. On the other hand between T_f and T_2 this quantity represent the amount bound surfactant in the “free” micelles and it is not possible to distinguish between these two quantities. The value of m_1 , $C_1 - m_1$, $(C_1 - m_1)/C_p$ are listed in Table 1.

In terms of molecular recognition the charged head groups and the area between these head groups on a micellar surface where the hydrocarbon chains are exposed to water provide

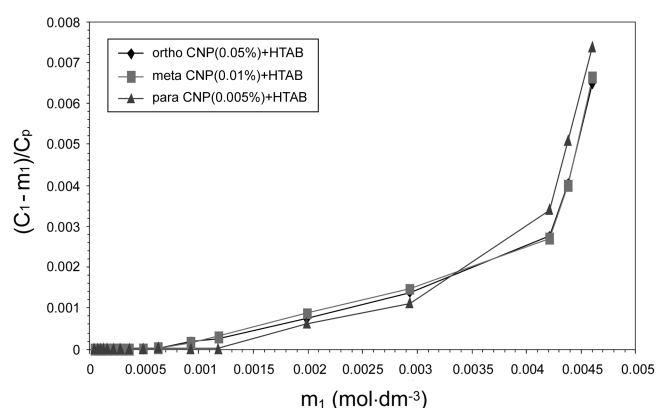


Figure 7. Plot of $(C_1 - m_1)/C_p$ versus m_1 for HTAB/ortho (0.05%), meta (0.01%) and para (0.005%) CNP systems in 1×10^{-4} mol·dm⁻³ NaBr.

two different binding sites for intermolecular attraction which allows the micelle to recognize different segment of polymers. Specifically the charged head groups offer sites for electrostatic interaction with oppositely charged species whereas the hydrocarbon in contact with water in the area between the head groups will recognize hydrophobic parts of polymer and mutual contact with water. If a typical synthetic water-soluble polymer has sufficient flexibility one can envisage a configuration-allowing ion-dipole association between the dipole of the hydrophilic group, and the ionic head group of the surfactant, and contact between the hydrophobic parts of the polymer and the hydrocarbon areas which are exposed to water at the periphery of the micelle.²⁰ The overall result of the either or both interaction is to diminish the unfavorable conditions governing the stability of the micelle, reducing its relative free energy and CMC by promoting the formation of micelles at lower surfactant concentration.

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