A STUDY UPON INTERACTION OF DODECYLPYRIDINIUM CHLORIDE WITH SODIUM DEXTRAN SULFATE

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The interaction between dodecylpyridinium chloride (DoPCl) and sodium dextran sulfate (NaDxS) has been studied in the absence and presence of sodium chloride by means of potentiometry with solid-state surfactant-selective electrode, surface tension and conductometry. The obtained critical aggregation concentration (cac) values were smaller than the surfactant critical micellar concentration (cmc). The inorganic electrolyte entailed the decrease of cmc and the increase of cac. The binding isotherms revealed that DoPCl interacts cooperatively with NaDxS, and the cooperativity increases when sodium chloride is added. The results were discussed taking into consideration the electrostatic and hydrophobic forces involved in the surfactant-polymer binding.

INTRODUCTION

The interaction between surfactants and polyelectrolytes is an active field of research in colloid science, which was the subject of many reviews over the past decades.[1-5] The mixture of surfactants and polymers offers significant interest, because of their fundamental and practical importance (detergents, cosmetics, food products, pharmaceutical formulations, etc.). In aqueous solutions, surfactants are known to self-aggregate into micelles at a well-defined critical micellar concentration, cmc. The phenomenon is due to hydrophobic interactions between the surfactant tails aiming to avoid the contact with the hostile medium of water. In presence of polymer, micelle-like aggregates appear at a critical aggregation concentration, cac. Some of the papers on surfactant-polyeletrolyte mixtures have dealt with interactions between ionic surfactants and oppositely charged polymers. In these studies polymers like sodium dextran sulfate (NaDxS),[6] poly(methacrylic acid) (PMA),[7] potassium polyvinyl sulfate (PVSK),[8] sodium (carboxymethyl)cellulose (NaCMC),[9] sodium pectate,[9] sodium alginate,[9] sodium poly(styrenesulfonate) (NaPSS),[10-12] and sodium poly(acrylate) (NaPA)[4,11] were used. The interaction was driven by electrostatic forces and hydrophobic forces had only a secondary role. The binding between ionic surfactants and oppositely charged polymers takes place through a highly cooperative process of charge neutralization. This process occurs above the cac, well bellow the cmc of the respective surfactant.

Binding of ionic surfactants to oppositely charged polymers has been studied by a variety of techniques such as fluorescence,[7] surface tension,[10] electrical conductivity,[11,12] dynamic light scattering,[13] X-ray diffraction,[13] optical microscopy,[13] microelectrophoresis,[13] isothermal calorimetry[14] etc. One of the most direct method for determining the surfactant binding to a polymer is the potentiometry with surfactant-sensitive membrane electrodes.[15-22] It allows determination of the binding isotherm as a function of binding degree, β, *vs.* log free surfactant concentration. The binding between ionic surfactants and oppositely charged polymers is influenced by surfactant

hydrophobicity,[4,19,23,24] its head group,[4,25] the flexibility of polymer back-bone [7,10-12,16] and charge density.[26-29] Other factors affecting the interaction are the temperature,[18] pH,[30] and ionic strength.[6,22,28,31] Kogej and Škerjanc have studied the binding of alkylpiridinium chlorides and alkyltrimethylammonium bromides to NaPA, and NaPSS.[4] They observed that the total surfactant concentration at which started the cooperative binding of hexadecylpiridinium cations to PA⁻ anions was independent of polymer charge density, and noticed that the surfactant chain length increasing shifted the binding to lower free surfactant concentrations. Recently, Vlachy and co-workers[7] investigated the influence of polymers stereoregularity upon the interaction with surfactants. They showed that the association of hexadecylpiridinium chloride with atactic poly(methacrylic acid) is stronger than with its isotactic form. Their results were explained taking into consideration the higher hidrophobicity and charge density and the smaller flexibility of the atactic form. The binding affinity between ionic surfactants and oppositely charged polymers lowers by adding salt. Hansson and Almgren[28] found out a linear relationship between the binding affinity and the salt concentration for various systems. Temperature and pH are another parameters that affect the binding. For example, the binding entropy of dodecyltrimethylammonium bromide to sodium dextran sulfate decreased with temperature,[10] whereas the binding degree (β) of dodecylpyridinium chloride to poly(acrylic acid) or poly(methacrylic acid) depended linearly on pH.[30]

The aim of this work is to investigate the effect of electrolyte on the binding isotherms of DoPCl-NaDxS system. The isotherms were constructed using the data collected with the aid of a solid state poly(vinyl chloride) (PVC) surfactant selective electrode. To get more insight of these systems, parallel surface tension and electrical conductivity data were acquired. All together have demonstrated that the binding is a cooperative process, which increases in intensity when sodium chloride is added.

MATERIALS AND METHODS

All the chemicals used for this study were analytical grade reagents. Sodium dextran sulfate (average molecular weight 500.000 g/mol) was purchased from Pharmacia, Uppsala, Sweden, and used whithout further purification. NaDxS is a highly charged polymer of α-D glucose. The sulfur content is approximately 17 % which corresponds to an average of 1.9 sulfate groups per glucosyl residue of the dextran molecule. NaDxS is a branched polymer which contains 1-6 glucoside linkages, making it more flexible in solution than other cellulosic polymers. The molecular structure of sodium dextran sulfate is shown in Figure 1.
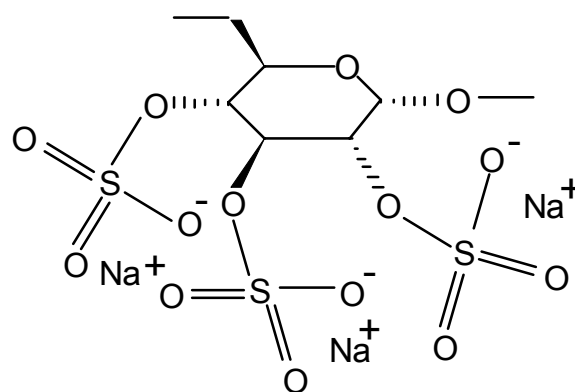

Fig. 1 – The molecular structure of sodium dextran sulfate.

Dodecylpyridinium chloride was purchased from Merck K Ga A, Darmstadt, Germany, and purified by crystallizations from acetone. The process was repeated until no minimum in the surface tension isotherm was recorded. The high molecular mass poly(vinyl chloride) and the plasticizer 2-nitrophenyl octyl ether were produced by Fluka Chemie AG, Buchs, Switzerland, and used as received.

The potential measurements were made with a digital ORION pH-meter model 420A (ATI ORION, Boston, USA). The reference electrode was of Ag/AgCl model 900200 (ATI ORION, Boston, USA). The membrane electrode selective to dodecylpyridinium ion was constructed as previously described.[32] The surface tension measurements were carried out with a home-made the Du-Nouy apparatus according the procedure described in reference 33. The electrical conductivity was measured with a conductometer model HI 9033 (Hanna Instruments, Portugal). Throughout the experiments the polymer concentration was 10.2 mM. At this concentration, the polymer was not superficial active: the surface tension values for aqueous polymer solutions, in the absence and presence of 10^{-2} M NaCl, were 71 and 71.8 mN/m, respectively. The double distilled water used to prepare the solutions had an electrical conductivity less than 1.5 μS/cm. All the measurements were done at (25 ± 0.1) °C.

RESULTS AND DISCUSSION

The potentiometry with surfactant-sensitive membrane electrode was used to determine both calibration and polymer binding curves. By registering the electrode response (the electromotive force, emf) *vs*. total surfactant concentration, the cmc and cac values of DoPCl and DoPCl-NaDxS were obtained in absence and presence of NaCl. The electrode typical response in aqueous surfactant solutions, without and with NaCl, is presented in Figure 2. An increase in the surfactant concentration results in an increase in the activity of the free surfactant. The electrode response is a linear function of DoPCl or DoPCl +10^{-2} M NaCl concentration with a slope of 55.85 mV/decade and respectively, 56.44 mV/decade. The curve of the electrode response shows a discontinuity corresponding to the surfactant cmc. Above cmc, the activity of free surfactant ions remains relatively constant because the DoPCl forms micelles in aqueous solution. The slight potential decrease recorded at high surfactant concentrations is similar to that previously observed for liquid-membrane surfactant electrodes and attributed to the solubilization phenomenon, which is characteristic to micellized surfactant solutions.[34] By this method, the cmcs of DoPCl in the absence and presence of NaCl were of 1.8 x 10^{-2} M and respectively of 1.5 x 10^{-2} M. For the DoPCl-NaDxS system, the potentiometric method accounts for ion association between the anionic polyelectrolyte from the sample and the cationic surfactant from the titrant. In the presence of NaDxS a deviation from the linearity is found, suggesting that a part of the surfactant is bound onto the polymer, as shown in Figure 2. With further addition of DoPCl, the emf increases steeply with surfactant concentration until approaches the calibration curves and the cmc is reached.
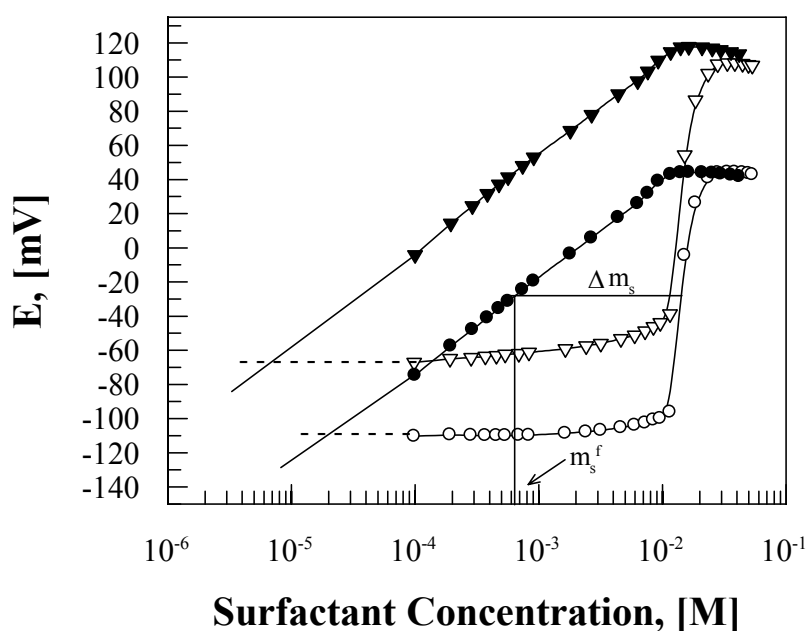

Fig. 2 – Response of the DoP$^+$ electrode to changes in DoPCl concentration in aqueous solutions. Calibration curves without (▼) and with (●)10^{-2} NaCl. Emf curves of DoPCl in presence of 10.2 mM NaDxS without (∇) and with 10^{-2} M NaCl (○).

Under the assumptions that the membrane is sensitive only to free surfactant monomer ions, but not to the bound or associated ones, and the activity coefficient of free surfactant is constant at the low levels used in this study, the degree of binding (β) can be calculated by comparing the binding curves with that of calibration using the following expression:[4]

$$\beta = \frac{\Delta m_s}{m_p} = \frac{m_s^t - m_s^f}{m_p} \qquad [1]$$

where, Δm_s represents the amount of surfactant bound to polymer, m_s^t and m_s^f are the total and free concentration, and m_p is the polymer concentration. The binding isotherms of DoPCl to NaDxS in the absence and presence of salt are presented in Figure 3. They have a typical

sigmoidal shape with a steep rise in β which is associated with the cooperative character of binding between the surfactants and oppositely charged polymers.[1,9,10] In the first binding region the system is clear. The surfactant concentration at which binding starts, refers to cac and is taken as the free surfactant concentration at the sharp increase of β.[3,35] It is $1,12 \times 10^{-5}$ M DoPCl for the system without NaCl. Addition of 10^{-2} M NaCl results in a shift of cac to a higher free surfactant concentration (*i.e.*, 2.5×10^{-5} M DoPCl). The increase in the cac with the ionic strength is generally expected owing to the decrease of electrostatic interaction.[2,31] The electrostatic attraction between the opposite charged specia is reduced by the electrolyte due to the electrical shielding. The salt increases the sharpness of the sigmoidal binding curve, indicating that the cooperative nature of binding is enhanced by salt. A saturation region is reached at higher β. At 2×10^{-5} M DoPCl (without NaCl) and 4.4×10^{-5} M DoPCl (with NaCl) the solution became hazy and

with surfactant addition the insoluble complex with one-to-one composition was formed. An interesting feature of these binding isotherms is the β value well above the unity at free surfactant concentration over 10^{-2} M DoPCl. This means more binding than that required for charge neutralization. At this surfactant level the solutions become clear again indicating the dissolution of the complex. The phenomenon is due to supplementary incorporation of the surfactant into the existing surfactant-polymer aggregates. The region when $\beta > 1$ is assessed to the interaction between DoPCl and the one-to-one surfactant-polymer complex. Similar results were reported by Isogai et al.[35] for the interaction of dodecylpyridinium chloride with the cross-linked copolymer of N-isopropylacrylamide and 2-(acrylamido)-2-methyl propane sulfonic acid. In these cases the major force for the continued uptake of surfactant by the polymer is the hydrophobic interaction, which is also available in our case.
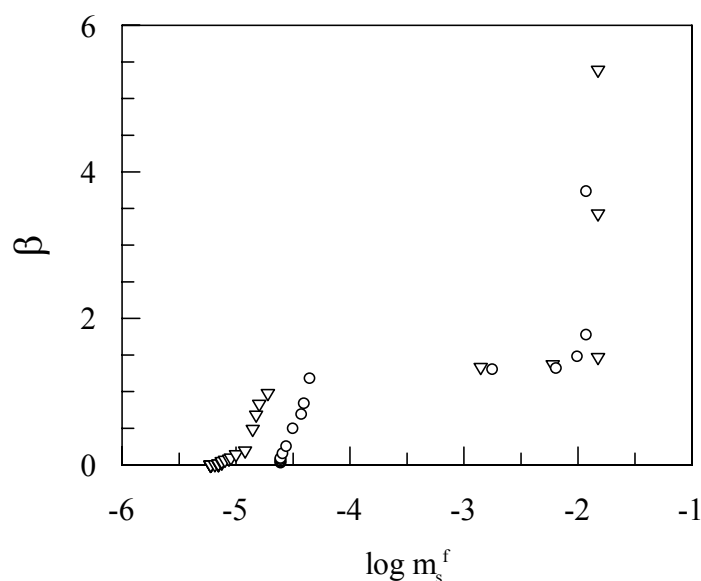

Fig. 3 – Binding isotherms of DoPCl by NaDxS in the absence (∇) and presence ($\circ$) of 10^{-2}M NaCl. NaDxS concentration is 10.2 mM.

Figure 4 shows the surface tension isotherm of dodecylpyridinium chloride. The descending part of the isotherm intercepts the horizontal part, and the intersection point is taken as cmc. This value reasonably agrees with literature data.[36] Figure 4 also illustrates the data obtained on DoPCl with NaDxS system, in the absence and presence of NaCl. At small surfactant concentrations the system is transparent. The surface tension values

decrease until a minimum at 1×10^{-4} M, a concentration that corresponds to the cac.

Beyond cac a plateau region appears. In this region clouding occurs and gradually increasing precipitate in equilibrium with a clear phase is observed. The maximum amount of precipitate in the system corresponds to a sudden increase of the surface tension value, which denotes diminution of the surface-active specia at the interface. The surface tension jumping occurs for surfactant

concentrations around 1.5×10^{-2} M. Thereafter, the surface tension value approaches that of the free surfactant micelles, indicating their appearance in the system. The effect of sodium chloride upon the DoPCl-NaDxS interaction is also illustrated in Figure 4 (see the curve with open circles). One may observe that the point where the descending part of the surface tension curve levels off is shifted to a higher surfactant concentration value

(*i.e.,* 10^{-3} M DoPCl). The added electrolyte screens the electrostatic forces of attraction between polymer and surfactant and increases the cac. Beside, the jumping of the surface tension around 10^{-2} M DoPCl is much lesser when the salt is added. The surface tension method gives higher values of cac than those obtained by potentiometry, because the former is a much more sensitive method (see Table 1).
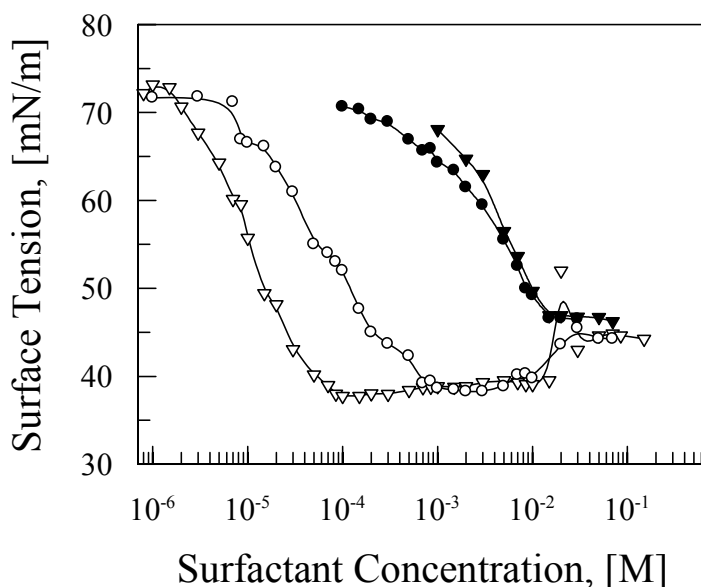

Fig. 4 – Surface tension isotherms of DoPCl without (▼) and with (•) 10^{-2} NaCl, and of DoPCl + 10.2 mM NaDxS mixtures without (∇) and with 10^{-2} M NaCl (○).

Table 1

The cmc and cac values of the studied systems obtained by various methods. [NaDxS] = 10.2 mM and [NaCl] = 10^{-2} M.

Method	DoPCl	DoPCl + NaCl	DoPCl + NaDxS	DoPCl + NaDxS + NaCl
	cmc, M	cmc, M	cac, M	cac, M
Potentiometry	1.8×10^{-2}	1.5×10^{-2}	1.1×10^{-5}*	2.5×10^{-5}*
Surface Tension	1.5×10^{-2}	1.0×10^{-2}	1.0×10^{-4}	1.0×10^{-3}
Electrical Conductivity	1.5×10^{-2}	-	1.0×10^{-4}	-

*The cac values are taken as the free surfactant concentration.

Electrical conductivity measurements were also employed to study the aggregation of DoPCl in the presence of NaDxS. The results for polymer-free and mixed system are presented in Figure 5. In the former case, the electrical conductivity curve presents a discontinuity at 1.5×10^{-2} M DoPCl. The concentration indicates the surfactant cmc and the value agrees within experimental errors with that derived from potentiometric and surface tension measurements. In the case of mixed system the electrical conductivity variation presents two breakpoints, at low (see inset) and high surfactant concentration, which respectively agrees within

experimental errors with cac and cmc obtained by surface tension and potentiometry. One may observe that for DoPCl-NaDxS system the interaction begins at surfactant concentration smaller with two orders of magnitude than the corresponding cmc, a result that confirms the emf and surface tension data, and usually happens in polyelectrolyte opposite charged surfactant systems.[34] The second breakpoint indicates the polymer saturation with surfactant, and the appearance of free micelles is suggested by surface tension measurements.
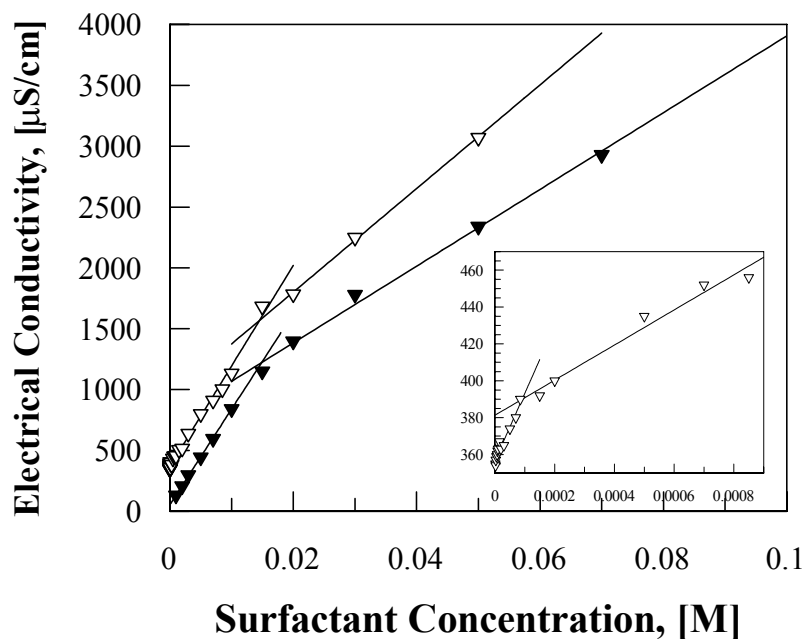
Fig. 5 – Electrical conductivity of DoPCl without (▼) and with (▽) 10.2 mM NaDxS. The inset shows the mixture electrical conductivity values at very low surfactant concentrations.

CONCLUSIONS

The DoPCl-NaDxS system was investigated in the absence and presence of sodium chloride by potentiometry with surfactant-selective electrode, surface tension and conductometry. The results revealed that the cmc values obtained by the above mentioned methods agreed within experimental errors. The potentiometry gave smaller cac values than those obtained by surface tension and conductometry. It was attributed to the fact that potentiometry responds to free surfactant activity in solution. On the other hand, the cmc's were always higher than the cac values, which is in agreement with the literature data on the different polymer-surfactant systems. The inorganic electrolyte decreased the cmc and increased the cac. The shape of binding isotherms showed that surfactant binding is a highly cooperative process, which is further increased when NaCl is added.

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