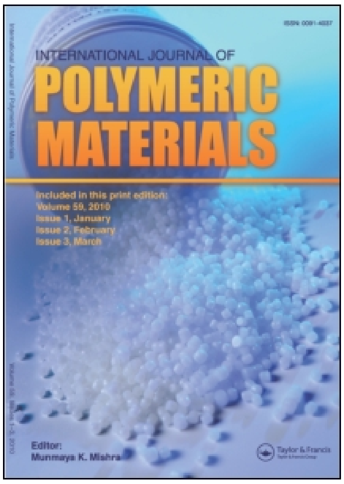

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The Influence of Ethanol on the Dye-Surfactant Complex Formation

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The formation of complexes between an anionic dye and a cationic surfactant was studied with conductometric method. The conductance of dye-surfactant mixtures in aqueous solutions and in solutions with different amount of ethanol was measured at 25°C. The results have shown that the presence of ethanol significantly decreases the formation of complexes. In the presence of 15% or 20% ethanol no interaction which would cause formation of non-conducting or less conducting species between the dye C.I. Acid Orange 7 and the surfactant *N*-dodecylpyridinium chloride was detected in the observed concentration range.

Keywords: Anionic dye; cationic surfactant; interactions; conductometry; water – ethanol mixtures

INTRODUCTION

Surfactants are used as auxiliaries in different procedures of textile finishing. Each procedure requires a careful selection of a suitable auxiliary. In the dyeing bath, the formation of complexes between the dye and the surfactant can occur. The stability of such complexes depends on the interactions between the dye and the surfactant molecule. Therefore, the understanding of those interactions enables the prediction of characteristic behaviour of the dye-surfactant mixture in the solution.

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During the last few years, several investigations were made on this area [1 – 3], showing the current importance of the problem. The present paper deals with the influence of the ethanol on the formation of the dye-surfactant complexes. The study was made in order to estimate the type of molecular forces, involved in the process of the dye-surfactant complex formation.

EXPERIMENTAL

An anionic monoazo dye C.I. Acid Orange 7 and two surfactants with different aliphatic chain length, *N*-dodecylpyridinium chloride ($n = 12$) and *N*-hexadecylpyridinium chloride ($n = 16$), were chosen to study the interactions.

A conductometric titration was adopted as a method of investigation: a solution of dye with concentration c_B° was titrated with surfactant. The measurements were made below the CMC of the surfactants at 25°C in water and in water – ethanol mixtures, containing 5, 10, 15 and 20 weight percent of the ethanol, respectively. The measurements were made using the Iskra microprocessor conductometer MA 5964 with the cell constants between 1.033 and 1.058 cm^{-1}.

RESULTS AND DISCUSSION

Figures 1 and 2 show the measured specific conductivity as a function of surfactant concentration at the titration of the solution of dye C.I. Acid Orange 7 with the surfactants *N*-dodecylpyridinium chloride and *N*-hexadecylpyridinium chloride.

If there were no interactions between the dye and the surfactant and therefore no complex formation would occur, the measured conductance would increase linearly with the concentration of the added surfactant as in the case of a simple electrolyte. From the Figures 1 and 2 it is evident that the conductance of dye-surfactant mixtures, with exception of two cases, does not increase linearly. The deviations from a hypotetical straight line can be detected, indicating a decrease in the measured conductance on account of the formation of non-conducting or less conducting species.

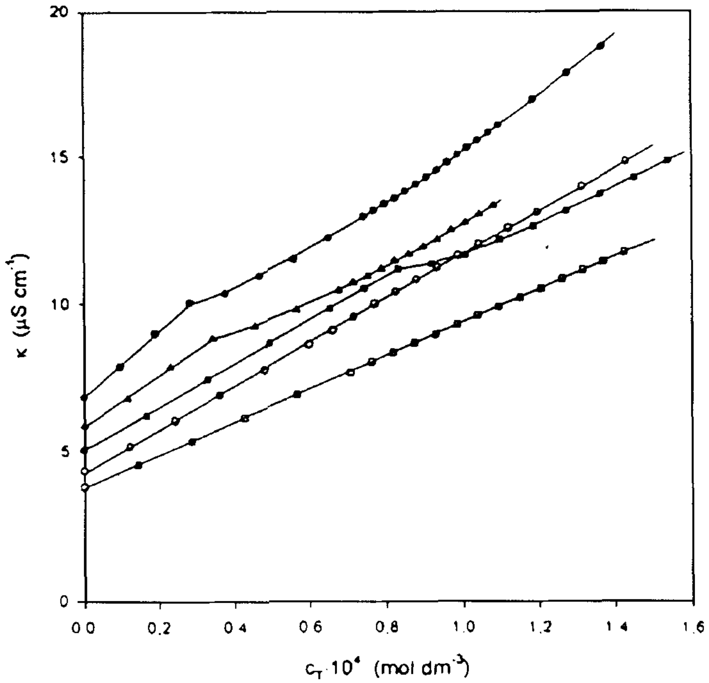

FIGURE 1 Specific conductivity as a function of surfactant concentration for the system C.I. Acid Orange 7 – *N*-dodecylpyridinium chloride at 25°C, $c_B^0 = 9.271 \cdot 10^{-5}$ M in solvents with various amounts of ethanol: ●0% ▲5% ■10% ○15% □20%.

In the case of the surfactant *N*-hexadecylpyridinium chloride, the deviations appear already with very small additions of the surfactant solution. With the *N*-dodecylpyridinium chloride, however, the situation is different. In this case, at low surfactant concentrations, the conductance increases linearly and the deviations from the straight line appear only after a certain limiting concentration of the surfactant.

As can be seen from the Figures 1 and 2, the deviations from the straight line increase with decreasing amount of ethanol in the solvent for both surfactants. These results indicate the highest tendency for the complex formation in water and its decrease with increasing ethanol concentration. In the presence of 15% and 20% of ethanol, the dye C.I. Acid Orange 7 and the surfactant *N*-dodecylpyridinium chloride do not form non-conducting or less conducting complexes

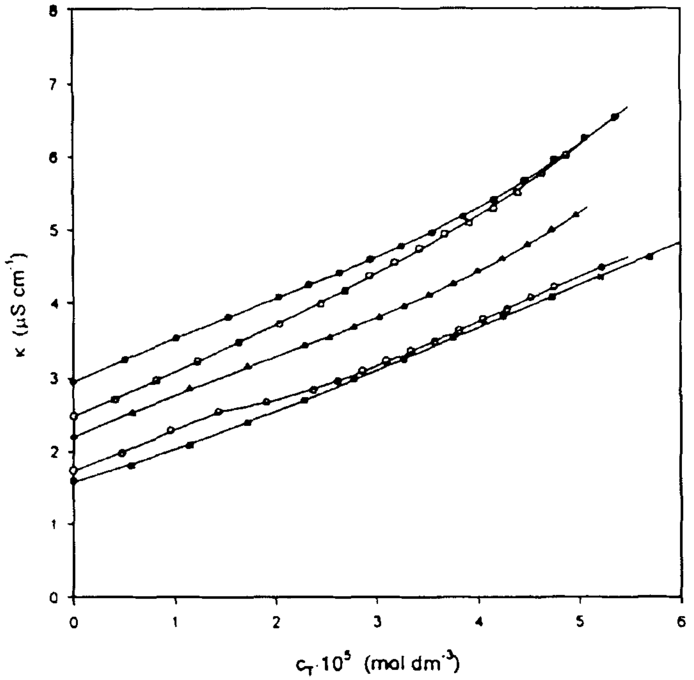

FIGURE 2 Specific conductivity as a function of surfactant concentration for the system C.I. Acid Orange 7–*N*-hexadecylpyridinium chloride at 25°C, $c_B^o = 3.825 \cdot 10^{-5}$ M in solvents with various amounts of ethanol: ●0% ▲5% ■10% ○15% □20%.

and the conductance of those mixtures increases linearly, as can be seen from Figure 1.

The dielectric constant of the solvent reduces with increasing amount of ethanol, therefore an increased complex formation in solvents with higher amount of ethanol would be expected because of the increased electrical attractive forces. However, the results have shown the opposite: the deviations from straight line decrease with increasing amount of ethanol in the solvent and therefore it can be concluded that the addition of ethanol reduces the tendency for complex formation.

These findings indicate a significant contribution of nonelectric short range interactions in the process of dye-surfactant complex formation. The importance of these interactions is also confirmed by the fact that the surfactant *N*-hexadecylpyridinium chloride is capable of forming complexes with dye in the solvent containing 20% of ethanol. Comparing to the *N*-dodecylpyridinium chloride, *N*-hexadecylpyridinium chloride has a longer aliphatic chain and therefore an increased possibility to establish hydrophobic and other short range interactions with the dye molecule. It is very likely that the increased possibility for the short range interactions due to a longer hydrophobic chain is also the main cause for the fact that *N*-hexadecylpyridinium chloride is capable of forming complexes already at very low surfactant concentrations. The conductance of the C.I. Acid Orange 7 – *N*-dodecylpyridinium chloride mixtures at such low concentrations, however, increases linearly and the complexes are not formed until a certain limiting amount of the surfactant is present in the solution.

CONCLUSIONS

- The addition of ethanol significantly decreases a tendency for the dye-surfactant complex formation.
- The surfactant with a longer aliphatic chain can form complexes with the dye also in the presence of 20% of ethanol, which is not the case with the surfactant including a shorter aliphatic chain.
- According to the results, the nonelectric short range interactions are very important for the dye-surfactant complex formation.

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