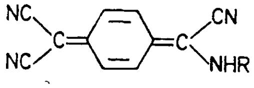
Interactions of Alkylammonium Propionate Surfactants with 7,7,8,8-Tetracyanoquinodimethane

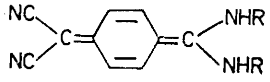
By Maria J. da Silva, Monica I. El Seoud, Frederico Perracini, and Omar A. El Seoud*
(*Instituto de Quimica, Universidade de Sao Paulo, C.P. 20.780, Sao Paulo, Brazil*)

Summary Alkylammonium propionates react with 7,7,8,8-tetracyanoquinodimethane (TCNQ) in organic solvents to produce the TCNQ anion radical and monoaminotricyanoquinodimethane in a ratio that depends on the initial surfactant–TCNQ ratio; this may affect critical micelle concentration determinations using TCNQ.

The dye 7,7,8,8-tetracyanoquinodimethane (TCNQ) has been used to determine the critical micelle concentrations (CMC's) of surfactants in water and in organic solvents,[1,2] from plots of the absorbance of the micelle-solubilized TCNQ radical ion against the surfactant concentration. Recently this method was used to determine the CMC of dodecylammonium carboxylates in organic solvents.[3] However, TCNQ reacts with butylamine to produce either the monosubstituted (I) or disubstituted (II) TCNQ derivative,[4] and so in general it is important to find out whether the dye radical ion is the only product of the interaction between alkylammonium carboxylates and TCNQ. Hexyl-, octyl-, and dodecyl-amines react with TCNQ in a similar way to butylamine. Compounds of the type (I) are dark purple solids and those of type (II) are metallic yellow crystals.† Addition of an alkylamine to TCNQ in nitrogen-saturated dichloromethane resulted in the disappearance of the neutral dye peak (395 nm) and the appearance of peaks at 420, 685, 749, 768, and 842 nm attributed to the TCNQ radical anion.[2,5] The intensity of the peaks then



(I)



(II)

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† Satisfactory microanalyses were obtained for all new compounds.

decreases and a spectrum similar to that of type (I) compounds is produced (for R = Bu^t, peaks at 531, 568, and 613 nm). Similar changes took place when butylammonium propionate (BAP), hexylammonium propionate, or dodecylammonium propionate were added to TCNQ solutions, showing that radical ions and monosubstituted compounds (I) are also produced from the reaction of alkylammonium carboxylates and TCNQ. The product distribution depends on the initial surfactant–TCNQ ratio, the proportion of the radical ion decreasing as this ratio increases. A 15:1 BAP–TCNQ mixture produces 4% of the radical ion and 71% of the compound of type (I) after 5 h;‡ after 24 h the isolated yields were 1·5 and 67%, and after 48 h 0 and 78%, respectively.

The above results show that the use of TCNQ for determining the CMC of alkylammonium carboxylates may lead to inaccurate results because of the occurrence of a chemical reaction between the dye and the surfactant. Moreover, the CMC will change owing to solubilization of the reaction products. The reported CMC's for dodecylammonium octanoate both in carbon tetrachloride and in cyclohexane[3] are much lower than their expected values based on other solubility methods.§[6]

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‡ In the published procedure, TCNQ and the surfactant were shaken for 5 h before the CMC determination (see ref. 3).

§ For a series of alkylammonium carboxylates, in both solvents, the CMC's increase as the chain length of the acid radical increases (refs. 3 and 8). The CMC for dodecylammonium octanoate should be > 0·04M in CCl_4 and > 0·01M in cyclohexane (ref. 6).

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