

Interaction between two anionic dyes and cationic surfactant



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The interaction of the triphenylmethane dye xlenol orange with cationic surfactants cetyltrimethylammonium bromide and cetylpyridinium chloride was studied by absorption spectrophotometry and principal component analysis of infrared spectra by A. Gojmerac Ivšić et al. [24]. Upon the addition of surfactants the yellow color of the acidic xlenol orange solution changed to purple-red. Changes in the absorption spectra of the mixture indicate strong interactions between dye and surfactants. These interactions were also monitored using ATR spectroscopy and the most prominent changes were observed in the vibration of the carbonyl group. The comparison of principal component loadings obtained from spectral data matrices for xlenol orange and mixtures of xlenol orange with surfactants revealed differences in infrared spectra caused only by the interaction of the surfactants with the dye.

The interactions of Acid Green 25 (AG), an anionic dye, with two cationic surfactants tetradecyltrimethylammonium bromide (TTAB), and hexadecyltrimethyl ammonium bromide (CTAB) in aqueous solutions far below the CMC are studied at different temperatures using the conductometric method by H. Dezhampah et. al. [25]. Various thermodynamic functions and equilibrium constants for the process of dye-surfactant ion pair formation were calculated using the conductometric data. These results indicate that the longer hydrophobic chain surfactants had a greater tendency and higher equilibrium constant as compared to shorter hydrophobic chain surfactants and short range, non-electrostatic interactions along with long range electrostatic forces have a significant influence on dye - surfactant ion pair formation.

Interaction of a food dye, tartrazine, with some cationic conventional and gemini surfactants, tetradecyltrimethylammonium bromide (TTAB), N, N'-ditetradecyl-N, N, N', N'-tetramethyl-N, N'-butanediyl-diammonium dibromide (14, 4, 14), and N, N'-didodecyl-N, N, N', N'-tetramethyl-N, N'-butanediyl-diammonium dibromide (12, 4, 12), were first investigated comprehensively by A. Asadzadeh Shahir et al. [26], employing conductometry, tensiometry, and UV-visible spectroscopy. Tartrazine was found to behave in the same manner as aromatic counterions. The formation of ion pairs reflected as a considerable increase of the surfactant efficiency in tensiometry plots and their stoichiometry were determined by Job's method of continuous variations. For the tartrazine/TTAB system, nonionic DS³, ionic DS²⁻, and/or DS² ion pairs, their small premicelles, and tartrazine rich micelles were constituted as well as dye-containing TTAB-rich micelles. Insoluble J-aggregates of DS⁻ ion pairs and cylindrical surfactant-rich micelles were also formed in tartrazine/gemini surfactant systems and recognized by transmission electron microscopy. The zeta potential and the size of the aggregates were determined using dynamic light scattering and confirmed the suggested models for the processes happening in each system. Cyclic voltammetry was applied successfully to track all of these species using tartrazine's own reduction peak current for the first time.

Reza Hosseinzadeh et al. [27] investigated the solubilization and interaction of azo-dye light yellow (X6G) at/with cationic surfactants cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC) spectrophotometrically. The effect of cationic micelles on solubilization of anionic azo dye in aqueous micellar solutions of cationic surfactants was

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studied at pH 7 and 25 °C. The binding of dye to micelles implied a bathochromic shift in dye absorption spectra that indicates dye-surfactant interaction. The results showed that the solubility of dye increased with increasing surfactant concentration, as a consequence of the association between the dye and the micelles. The binding constants, K_b , were obtained from experimental absorption spectra. By using pseudo-phase model, the partition coefficients between the bulk water and surfactant micelles, K_x , were calculated. Gibbs energies of binding and distribution of dye between the bulk water and surfactant micelles were estimated. The results show favorable solubilization of dye in CTAB micelles.

The aggregation induced by Alizarin Yellow R (AYR) in the cationic surfactant, cetyltrimethylammonium bromide (CTAB), was investigated by measuring their UV-visible absorption spectra by M. F. Nazar et al. [28]. Conductance measurements as a function of surfactant concentration below and above the critical micelle concentration (CMC) were studied. CTAB aggregation takes place at the concentration far below its normal CMC in the presence of AYR. Both hydrophobic and electrostatic interactions affect the aggregation process in aqueous solution. Different parameters obtained from spectroscopic measurements and conductance data indicate an enhanced solubility of AYR dye in the micellar region. Intramolecular hydrogen bonding within the dye molecule effectively reduces intermolecular attraction, thereby increasing solubility in non-polar solvents (micelles). Medium effects on the position of the long wavelength absorption band of the azo dye characterize it as a pH chromic reporter molecule. A partitioning study of the solubilized system provides useful insight into the process of solubilization

that is applicable to the general problem of membrane solubilization properties and in drug delivery to quantify the degree of drug-micelle interaction. The partition coefficient value obtained is important in micellar electro-kinetic capillary chromatography and high pressure liquid chromatography (HPLC) for drug quality control. Thus, interaction with micellar aggregates induces significant pKa shifts of Alizarin Yellow R that can be rationalized in terms of the partitioning of species and electrostatic contribution. Likewise, knowledge of the effects of organic additives on the CMC of surfactants is used both for theoretical and practical purposes because some additives are likely to be present as impurities or byproducts in the manufacturing of surfactants and their presence may cause significant differences in supposedly similar commercial surfactants.

Eosin B and eosin Y have been used to estimate micro- and submicrogram quantities of proteins respectively. A. A. Waheed et al. [29] describe the mechanism of eosin binding to proteins. At pH lower than 3.0 the absorbance of unbound dye is greatly reduced. After the dye binds to protein, the absorption maximum of the dye changes from 514 to 530 ± 5 nm. The absorbance and bathochromic shift in absorption maximum of the protein-dye complex are proportional to the concentration of protein. The pH of the assay solution does not change due to protein. Arginine, histidine, and lysine (at both acidic and neutral pH) and tryptophan (at acidic pH) residues of a protein bind electrostatically to carboxylic and phenolic groups of the dye to produce a stable water-soluble protein-dye complex. The binding constants of eosin B with poly-L-arginine, poly-L-histidine, poly-L-lysine, and poly-L-tryptophan at pH 1.96 are 0.37, 0.32, 0.33 and 0.33 nmol/nmol of

amino acid, respectively. The binding constants of eosin B and eosin Y with bovine serum albumin (BSA) at pH 1.96 are essentially the same, i. e., 0.82 nmol/nmol of reactive amino acid of BSA. The binding constant varies with solution pH so that a wide range of protein concentrations can be estimated. The reason for the higher absorbance of protein-eosin Y complex compared to that of protein-eosin B complex is discussed.

Javadian et al. [30] studied the interaction of Congo Red (CR) with a series of Alkyl trimethyl ammonium bromide (C_n TAB), N-hexadecyl pyridinium bromide (CPB) and N-hexadecyl pyridinium chloride (CPC) using conductometry and UV-Vis spectroscopy technique. Job's method of continuous variations demonstrated that only DS^- complexes are formed in the studied mixtures. The formation of DS^- complexes results in decreasing the system's order so it is an enthalpy-driven reaction under the influence of both hydrophobic and electrostatic interactions. The amount of ion pairs forming through the process is highly dependent on physical conditions and structure of the dyes and the surfactants such as chain length, head group and counterion. By increasing the length in the hydrophobic chain or the charge density of headgroup of a cationic surfactant, the strength of dye-surfactant interaction increases. In addition, the results show that the counter ion has no significant effect on dye-surfactant interaction. The tendency to form DS^- complexes decreases with increasing temperature in the range of 298.0-313.0 K.

K. Fujio et al. [31] examined the effect of added salt on micelle size, shape, and structure the solubilization of Orange OT in aqueous NaBr solutions of

decylpyridinium bromide (DePB), dodecylpyridinium bromide (DPB), tetradecylpyridinium bromide (TPB), and hexadecylpyridinium bromide (CPB). The solubilization powers of DePB and DPB micelles increase with increasing NaBr concentration up to 2.86 and 3.07 mol dm⁻³, respectively, but above these concentrations remain unaltered. This suggests that spherical micelles of DePB and DPB can have a maximum and constant size at NaBr concentrations higher than these threshold concentrations. On the other hand, the solubilization powers of TPB and CPB micelles increase in the whole range of NaBr concentration studied. The dependencies of the solubilization powers of their micelles on the counterion concentration change at 0.10 and 0.03 mol dm⁻³ NaBr, respectively, as suggests that TPB and CPB micelles undergo the sphere-rod transition at those concentrations. Orange OT is a more suitable probe for detecting the presence of the maximum- and constant-size spherical micelle than Sudan Red B.

The interactions between two anionic dyes and a cationic surfactant were studied by conductometric technique by A. A. Rafati et al. [32]. The conductance of aqueous solutions of methyl orange (MO) and methyl red (MR) was measured in the presence of a cationic surfactant, cetylpyridinium bromide (CPB) at different temperatures in water-ethanol, water-propanol and water-butanol mixed solvents, containing different concentration of alcohols. The equilibrium constants and other thermodynamic functions for the process of dye-surfactant ion pair formation were calculated on the basis of a theoretical model. The results showed that the presence of alcohol, as well as increasing the length of the alcohol chain, decreases the tendency for ion pair formation. The results have shown that an increase in temperature

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lowers the tendency for ion pair formation as the equilibrium constants decrease with increasing temperature. According to the results, long range as well as short range interactions are responsible for the formation of the ion pair. The importance of long range electrical forces is basically to bring the dye anion and the surfactant cation close enough to enable the action of short range interactions whose contribution represents the major part of the standard free energy change for the formation of the anionic dye-cationic surfactant ion pair. By using the association constant (K_1) for the first step of the association [$D^- + S^+ \rightarrow (DS)^\circ$], the standard free energy change, standard enthalpy change, and standard entropy change of the association were calculated at low surfactant concentrations.