Research Paper

Association Behavior of anionic Azo dye (AR88) with Surfactants as Seen by Electrical Conductivity Measurements

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Abstract – *A conductivity technique has been developed, being highly useful for studying the association behavior of acid azo dye (AR88) with surfactants, the conductance of aqueous solutions of (AR88) was measured in the presence of a cationic surfactant, cetyl trimethyl ammonium bromide (CTAB) , nonionic surfactant , Triton X- 100 (T X – 100) and anionic surfactant, sodium dodecyle sulphate (SDS) at different temperatures in aqueous solutions . According to the results, our study of anionic dye - ionic surfactant systems showed that interaction does not exist. The conductivity results obtained for different anionic dye with non ionic and cationic surfactant systems showed a common tendency: when the surfactant concentration of the dye-surfactant system increased, the conductivity values experienced an lower increase than expected on behalf of conductivity values of pure surfactant solution. We used this as an indication of dye - surfactant interaction. The equilibrium constants and other thermodynamic functions for the process of dye –cationic surfactant ion pair formation were calculated on the basis of a theoretical model. The results have shown that an increase in temperature lower the tendency for ion pair formation as the equilibrium constants decrease with increasing temperature.*

Keywords: Conductometry, Dye, Surfactant, Ion-pairing.

Introduction

Surfactants are present in almost every practical dyeing method as a third component of ternary system consisting of dye, electrolyte, and surfactant [1-3].The interaction between dyes and surfactants is subject of some investigations [4-9]. Although a lot of research work has already been done into dye-surfactant interactions the studies in this area are still important and interesting for the theory and technology of dyeing. Electrostatic interactions and steric factors are both important in the binding process of dye–surfactant. In aqueous media and at low concentrations, surfactant molecules exist as individual species and concentrate at the air-solution interface with their hydrophilic groups in the aqueous phase and their hydrophobic chains oriented away from the aqueous phase. As the concentration increases, surfactant molecules aggregate into clusters, known as micelles, with their hydrophobic chains directed toward the interior of the cluster and their hydrophilic groups directed toward the aqueous phase. The concentration at which micelles first become detectable is the critical micelle concentration, CMC [10]. The ion pair formation in an aqueous solution is known to be effected by organic additives. Recently, increasing attention is being devoted to the study of the
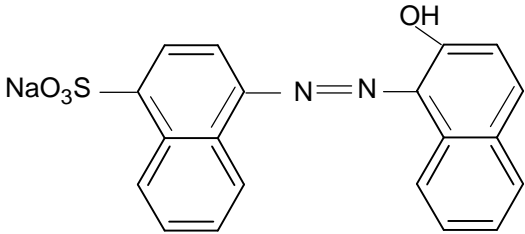
effect of neutral molecules into ion pair formation in aqueous solution. Investigation of dye interaction with surfactant aqueous solutions can give useful information about the mechanisms according to which surfactants operate as leveling agents, thermodynamics and kinetics of dyeing process and finishing of textile material [11]. Experimental methods mostly used were spectroscopy [12–17], potentiometry[18–21] and tensiometry [22,23]. Recently it was reported that the formation of dye-surfactant ion pair can be investigated by the conductometric method [7,24]. In the present work, the interactions of acid dye (AR88) with different types of surfactant (cationic, anionic and nonionic) are analyzed by electrical conductivity measurements. The extent of dye-surfactant interaction in this work has been measured by determining the conductivity of the dye solutions in the presence of different concentrations of surfactants. The equilibrium constants of ion pairing between dyes and surfactant were calculated by a method which was described in [7] and using experimental conductometric data. Analysis of the results shows how both environmental condition and temperature affect the ion pairing.

Material and Methods

A commercial sample (Ambicid Fast Red E) of monosulphonate azo acid dye C.I. Acid Red 88 (AR88) was supplied from Imperial Chemical Industries, ICI. The acid dye was purified by recrystallization several times from 50% ethanol-water mixture and then dried in vacuum at $40^{o}C$. The characterization of dye is listed in Table 1.

Table 1: Characterization of acid dye (AR88)

C.I.	15620
Mol. formula	$C_{20}H_{13}O_4SN_2Na$
Formula weight	400.38
Appearance	Red powder
λmax.	506.58 nm
Specific conductivity of dye solution (10^{-4} Mdm^{-3} at $25^{o}C$)	15.00 µs/cm
Structure formula	

Cationic surfactant, cetyl trimethylammonium bromide (CTAB), anionic surfactant, sodium dodecyle sulphate (SDS) and nonionic surfactant,TritonX-100, were purchased from sigma. All chemicals were of analytical grade and used as received. Dye –surfactant system, in which the dye concentration was kept constant (10^{-4} mol dm^{-3}) while surfactant concentration range increased from 0.01x10^{-4} to 18x10^{-4} mol dm^{-3} for different types of surfactant were prepared by carefully mixing the necessary amounts of previously prepared stock solutions of dye and surfactants. Doubly distilled water was used for all preparations, and solutions of each surfactant of the same concentration as for the dye-surfactant systems were prepared as well as solution containing only dye (10^{-4} mol dm^{-3}). The pH of solutions was 5.65 and their temperature was thermostatically controlled at $25^{o}C$. In order to establish complete equilibrium, solutions were stored 24 hours before the measurements. Dye- cationic surfactant ion pair formation were determine also at different temperatures (15, 20, 30 and $35^{o}C$), the different concentrations of acid dye (1.33x10^{-4} – 15.43x10^{-4} mol dm^{-3}) were prepared and then measure the specific conductance at different temperatures. Furthermore the different concentrations of surfactant measured in presence of 10^{-4} moldm^{-3}acid dye(AR88) and without dye at different temperatures. Specific conductance was measured with a digital conductivity meter (Jenway 4010/REVC made in U.K.) and the conductivity cell was calibrated with KCl solution in the appropriate concentration range. The cell constant was 0.99 Cm^{-1}.

Results and Discussion

Interaction between anionic dye AR88 with anionic, nonionic surfactants

Figures 1, 2 shows the specific conductance versus surfactant concentration plots for dye-surfactant system, compared with corresponding plots for the solutions of the surfactant only. Specific conductivity (k_{DS} and k_S) is plotted against the concentration of the surfactant. We have assumed that the specific conductance of the dye-surfactant system (k_{DS}) is made up of the sum of two independent conductance values – dye conductance (k_D) and surfactant conductance (k_S). Examination of the results presented in Fig.1 indicates that the anionic surfactant (SDS) and dyes show no interaction, because for both dye-surfactant and surfactant–only systems, the increase in specific conductance follows a uniform trend in the whole concentration range examined. We expected such behavior because we could predict that interaction of the anionic dye-anionic surfactant does not exist due to repulsion of ions, since the anionic surfactant has the same ionic character as the dye. These results are in agreement with similar observations made by various workers, and with previous spectrophotometric measurements [25].

It is generally established that the interaction between anionic surfactants and anionic dyes is relatively small, and very few papers have been published on this topic. Some researchers [26] have reported on marked irregularities in the absorption spectra of sodium dodecyl sulfate (SDS) and acid dye.

The result obtained in presence of nonionic surfactant (TritonX-100) was quite different from anionic surfactant. Figure 2 show with increasing surfactant concentration in dye-surfactant system, conductance at beginning attained mostly a constant value, although in the same surfactant concentration range, conductance grew gradually in the absence of dye. Such behavior entails some sort of interaction between dye and nonionic surfactant. Collectively they make a lower contribution to the

conductance of dye-surfactant systems than had been expected on the basis of constant dye concentration and the theoretical assumption that the total conductance is found by summing the conductance of individual components.

The ability of ions to migrate through solution depends on both their effective radius, i.e. hydrodynamic radius and their charge, it is realistic to expect conductivity to decrease with increasing ion size and decreasing degree of ionizing of the conducting particles. Besides the mobility of micelles, electric conductivity of the surfactant solution over CMC is governed by the degree of ionizing or ionic dissociation of the micelles [27]. Incorporating dye ions in surfactant micelles reduces the concentration of dye ions in the bulk, and produces new charged particles, a dye-surfactant adduct. Because of increased hydrodynamic radius, the mobility of dye–surfactant adducts is expected to be different compared to individual dye ions or surfactant micelles, i.e., they move through the solution more slowly than individual dye ions or surfactant micelles. Furthermore, depending on dye and surfactant structures and their concentrations, the shape and size of the micelle and the location for dye incorporation could differ gradually and some dye-surfactant adducts could be completely neutralized.

Effect of temperature on ion-pair formation between anionic dye (AR88) and cationic surfactant:

Figure 3 a and b, show plot of the specific conductance of pure solution of CTAB and AR88 against concentration and at different temperatures, respectively. These plots show how the specific conductivity of pure electrolyte solutions is varied by a range of concentrations. Base on Kohlrausch's law, we have the following relations [11]:

$$\Lambda^\circ_{SBr} = \lambda^\circ_{S^+} + \lambda^\circ_{Br^-} \qquad (1)$$

$$\Lambda^\circ_{DNa} = \lambda^\circ_{D^-} + \lambda^\circ_{Na^+} \qquad (2)$$

The Λ values were determined experimentally by measuring the specific conductivities of the surfactant and the dye and converting them to equivalent conductance by the following equation:

$$\Lambda = 10^{-3}k / C \qquad (3)$$

Then Λ° values can be determined by plot of Λ versus $\sqrt{C}$ and extrapolation of this plot to infinite dilution. The values are shown in Table 2. By applying λ_i values from literature for Br^- and Na^+, one can write:

$$\lambda^o_{S^+} + \lambda^o_{D^-} = \Lambda^o_{SBr} + \Lambda^o_{DNa} - \lambda^o_{Na^+} - \lambda^o_{Br^-} \qquad (4)$$

where $\Lambda^\circ(SBr)$ and $\Lambda^\circ(DNa)$ are the equivalent conductance of surfactant and dye at infinite dilution, respectively and $\lambda^\circ_{S^+}$, $\lambda^\circ_{D^-}$, $\lambda^\circ_{Br^-}$ and $\lambda^\circ_{Na^+}$ are the equivalent conductance of the ions S+, D-, Br- and Na+ at infinite dilution, respectively. The specific conductivity, k, of dye solutions can easily be calculated in terms of the molar ionic conductivities of ions, λ_i. Electrical conductivity before ion pair formation is written as:

$$k = \lambda_{D^-} [D^-] + \Lambda_{c+} [C^+]_f \qquad (5)$$
$$[D^-]_f = [C^+]_f = C_t$$

where $[D^-]_f$ and $[C^+]_f$ are the concentration of free dye and its counterion, respectively and λ_D^- and λ_C^+ are corresponding to equivalent ionic conductivities. The complete dissociation of ionic dye is assumed in the absence of surfactant. The slope (S_1) of molar conductivity becomes:

$$S_1 = k/ C_t = \lambda_C^+ + \lambda_D^- \qquad (6)$$

With addition of surfactant to the solution ion pair formation is occurred, and an abrupt change in concentration dependence of specific conductivity was observed. Fig. 4 shows a typical plot of the specific conductivity of the (AR88) solution as a function of the CTAB concentration at 15 °C, 20 °C, 30 °C and 35 °C.

The change in the electrical conductance of aqueous ionic dye solution with addition of surfactant solution is due to the ion pair formation between surfactant ion and opposite charge dye ion. In the presence of surfactant ion, for a 1:1 ion pair formation one should be able to define the equilibrium for this reaction:

$$S^+ + D^- \leftrightarrow S-D, \ K = [S\text{-}D] / [S^+]_f[D^-]_f \qquad (7)$$
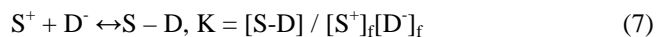
where $[S^+]_f$ and [S–D] are the concentration of free surfactant and ion pair, respectively. The mass conservation law equations for above equilibrium could be written for the total surfactant and dye concentrations as:

$$[S+]_t = [S+]_f + [S–D] \qquad (8)$$
$$[D^-]_t = [D^-]_f + [S–D] \qquad (9)$$

where $[S^+]_t$ and $[D^-]_t$ are total surfactant and dye ion concentrations, respectively. In this case, the observed specific conductance could be expressed as:

$$k_{obs} = k_S + k_D \qquad (10)$$

where k_{obs}, k_S and k_D are observed, surfactant and dye specific conductance, respectively. If ion pair is considered as a nonconducting species, and if there was no interaction between the surfactant and dye, we can explain Equation (10) based on equivalent ionic conductivity as follows:

$$10^3 k_{obs} = \lambda_S^+[S^+]_t + \lambda_C^-[C^-]_t + \lambda_D^-[D^-]_t + \lambda_C^+[C^+]_t \qquad (11)$$

where $[C^-]t$ and λ_C^- are the total concentration and ionic molar conductivity of surfactant counter ion, respectively. The ion pair formation caused a decrease in the concentration of free ions, hence:

$$10^3 k_{obs} = \lambda_S^+([S^+]_t - [S–D]) + \lambda_C^-[C^-]_t + \lambda_D^-([D^-]_t - [S–D]) + \lambda_C^+[C^+]_t \qquad (12)$$

After deduction of Eq. (11) from Eq. (12) we have:

$$10^3 \Delta k = [S–D](\lambda_D^- + \lambda_S^+) \qquad (13)$$

where Δk is the difference between the theoretical and measured specific conductances at a given surfactant concentration. Now, Kohlrausch's law for infinite dilute

solution of an electrolyte can be used for the above system, hence Eq. (13) can be written as:

$$10^3 \Delta k \approx [S–D](\lambda^o_D{}^- + \lambda^o_S{}^+) = [S–D]\Lambda^o_{(S-D)} \quad (14)$$

where $\Lambda^o_{(S–D)}$ is the equivalent conductance of the surfactant– dye ion pair at infinite dilution. The $\Lambda°(S–D)$ values were determined experimentally by measuring the specific conductivities of the surfactants and the dyes. Obtained data are tabulated in Table 2. By using Equation (14), we can estimate ion pair concentration at each concentration of dye and surfactant.

Thermodynamic parameters can be extract by calculating of equilibrium constant for ion pair formation. Eq. (7) can be written in the form:

$$K = \frac{[S–D]}{([S]_t - [S–D])([D]_t - [S–D])} \quad (15)$$

where $[S]_t$ and $[D]_t$ are the total concentration of surfactant and dye in the solution, respectively. Values of K were determined by application of Eq. (15), and used to determine the values of

the Gibbs free energy of ion pair formation, $\Delta G°$:

$$\Delta G° = - RT \ln K \quad (16)$$

The enthalpy of ion pair formation was obtained from the temperature dependence of the equilibrium constant (K) using the van't Hoff relation:

$$d(\ln K) / d(1/T) = - \Delta H° / R \quad (17)$$

and finally the $\Delta S°$ values could be obtained from the following equation:

$$\Delta G° = \Delta H° - T \Delta S° \quad (18)$$

Calculated thermodynamic parameters are listed in Table 3. The negative values of $\Delta H°$ could be attributed to the attraction between the cationic head of surfactant and anionic dye species.

Conclusion

Our study of anionic dye–anionic surfactant systems showed that interaction does not exist. The conductivity results obtained for different anionic dye–nonionic surfactant systems showed a common tendency. The increase of surfactant concentration leads to an increase in the degree of interaction. The conductometric technique allows us to estimate value for ion pair formation constants between anionic dye and cationic surfactants in aqueous solutions. The main drawback to conductometric investigations of dye–surfactant ion pair formation is that for a numerical description, namely the calculation of equilibrium constants, a suitable theoretical model is required and this can include certain simplifications. The equilibrium constants and thermodynamic parameters have been calculated for ion pair formation between anionic dye AR88 with a cationic surfactant, the values of

thermodynamic parameters indicate that ion pair formation is an enthalpy driven process for interaction between cationic surfactant and ionic dyes. In addition, at higher temperatures, a higher concentration of the surfactant CTAB was required to initiate the process of ion pair formation. 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.

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Table 2: Equivalent conductances at infinite dilution in water for individual species and correspondence ion pairs [units: $\Lambda°(\Omega^{-1} cm^2 mol^{-1})$]

Temperature degree (t ^{o}C)	$\Lambda°_{(CTAB)}$	$\Lambda°_{NaBr}$	$\Lambda°_{AR88}$	$\Lambda°_{(AR88 - CTAB)}$
15	90.11	102.90	75.96	60.50
20	101.23	118.00	90.11	75.00
30	110.00	128.20	100.14	85.69
35	139.63	145.40	120.63	97.01

Table 3: Thermodynamic parameters for AR88 - CTAB ion pair formation in water

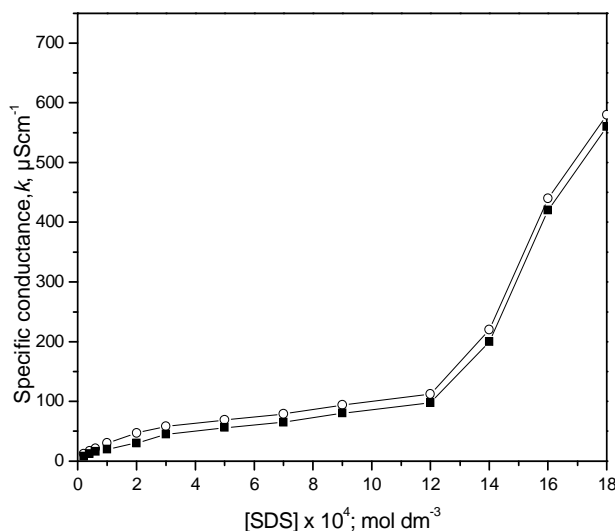| Temperature degree (t ^{o}C)	K (mol^{-1} dm^3)	$\Delta G°$ kJ mol^{-1}	$\Delta H°$ kJ mol^{-1}	$\Delta S°$ J mol^{-1}
15	3.96 x10^5	-30.85		-2.26
20	3.25 x10^5	-30.90	-31.50	-2.05
30	2.32 x10^5	-31.11		-1.29
35	1.89 x10^5	-31.10		-1.30

Figure 1: Comparison of specific conductivity versus surfactant concentration of the aqueous solutions of SDS: ○without dye, ■ with10^{-4} mol dm^{-3} acid dye 88
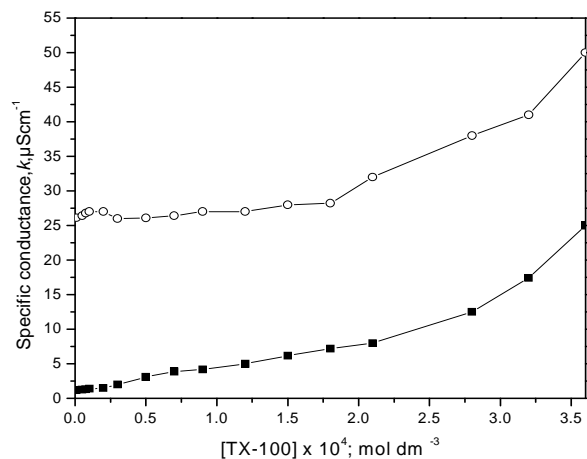
Figure 2: Comparison of specific conductivity versus surfactant concentration of the aqueous solutions of Triton X-100:○ without dye, ■with10^{-4}moldm^{-3}acid dye 88
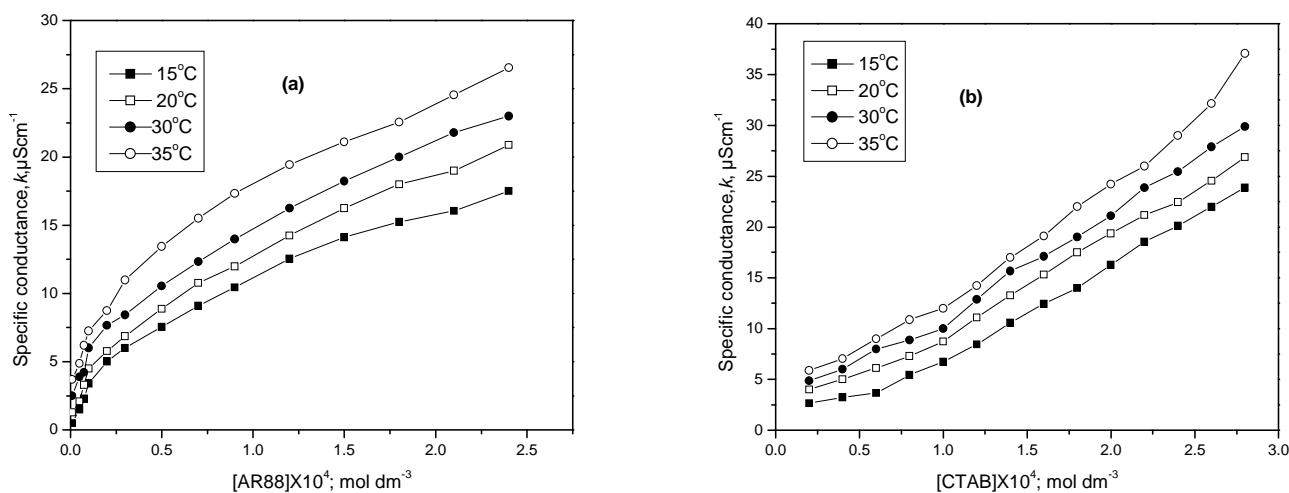

Figure 3: Plot of the specific conductance of pure solution of (a) acid dye AR88 and (b) cationic surfactant CTAB, versus concentration at different temperatures
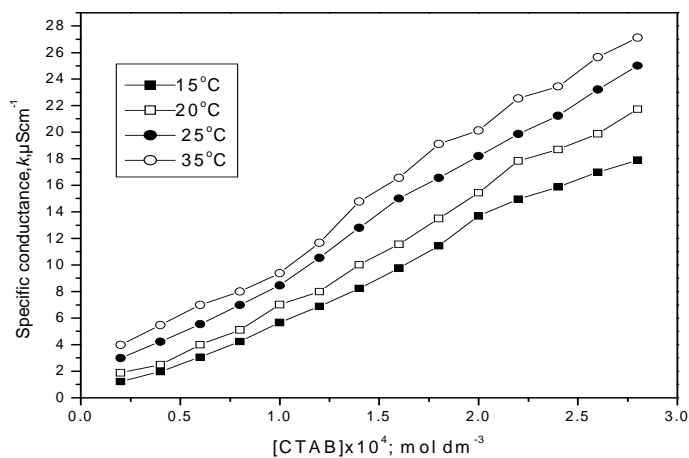

Figure 4: Plot of the specific conductance of AR88 versus [CTAB] in water at different temperatures .The concentration of AR88 is equal to 10^{-4} mol dm^{-3}