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Conductometric studies of the interaction of C.I. Reactive Orange 16 with cationic alkyltrimethylammonium bromide surfactants

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Abstract

The interactions between an anionic dye, C.I. Reactive Orange 16 (RO16) and the cationic surfactants, dodecyltrimethylammonium bromide (DTAB) and hexadecyltrimethylammonium bromide (CTAB) were studied using a conductometric method. The specific conductance of dye–surfactant mixtures was measured at five different temperatures. The equilibrium constants and other thermodynamic functions for the process of dye–surfactant ion pair formation were calculated on the basis of two theoretical models. The results showed that an increase in temperature reduces the tendency for ion pair formation as equilibrium constants decrease with increasing temperature. According to results, the surfactant which contained the longer hydrophobic chain had a stronger tendency to associate with the dye and the equilibrium constants were considerably higher than those measured for the surfactant with the shorter hydrophobic chain. These results indicate that short range, non-electrostatic interactions have a significant influence on dye–surfactant ion pair formation as well as long range electrostatic forces.

Keywords: Cationic surfactants; Anionic dye; Ion pair; Equilibrium constant; Conductometry

1. Introduction

Investigations on the interaction of surfactants with various materials have been done by different workers since 1950 [1–5]. Although many studies have already been done on the dye–surfactant interaction, the studies in this area are still important and interesting for the theory and technology of dyeing. Surfactants are used in dyeing baths as solubilizer for water-insoluble dye, as auxiliaries for improving the quality of dyeing and very often as levelling or dispersing agent [6–9]. Ionic surfactants, which are used as levelling agents, operate in two main mechanisms depending on the ionic type of the dye [10,11]. If the surfactant and the dye have the opposite charges, the attractive forces between the dye and surfactant lead to dye–surfactant ion pair (complex) formation in the solution resulting in level dyeing. In cases when the surfactant and the dye have the same charges, competition between the dye and the surfactant for sorption sites in the fibre causes level dyeing [12–15].

Reactive dyes are extensively used in dyeing processes in textile industry [16]. Dye molecules with phenyl groups can adopt a planar structure and readily tend to form intermolecular interaction that facilitates permanent aggregation under some experimental conditions. Studies of the interactions between dyes and surfactant have been made using various experimental methods to establish which interactions are decisive for the process of dye–surfactant complex formation [17–19]. In the previous studies, by spectrophotometric method, we were concerned with an anionic dye (RO16)–surfactants (anionic, cationic and nonionic surfactants) interaction in mixture of ionic and nonionic surfactants. We also discussed optimum conditions for surfactants and temperatures used in colour fastness of anionic dye [20,21]. In the present paper, we studied conductivity of mixtures of dye and surfactant over the range of concentrations at which these compounds are miscible. C.I. Reactive Orange 16 was used as anionic dye and dodecyltrimethylammonium bromide (DTAB) and hexadecyltrimethylammonium bromide (CTAB) were used as cationic surfactant.

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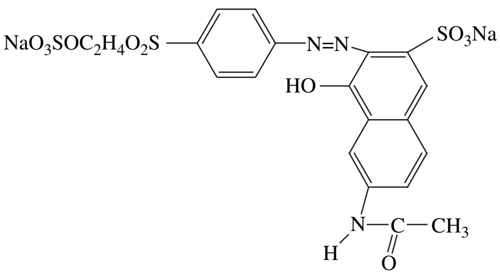
Two methods are used for calculation of equilibrium constant from which theoretical models were derived. The influence of temperature and surfactant structure on ion pair formation is observed with those methods.

2. Experimental

2.1. Materials

Anionic dye: Reactive azo dye RO16 (commercial product, gift from DyStar, İstanbul, Turkey) was used as received for the experiments.



Cationic surfactants: Dodecyltrimethylammonium bromide (DTAB) and hexadecyltrimethylammonium bromide (CTAB) was supplied by Merck and had purity of 97–98%. Before use they were twice recrystallized from 50% acetone–50% methanol mixture and dried at 50 °C in vacuum before use. The purity of DTAB and CTAB was investigated by measuring the surface tension of aqueous solution of samples. The absence of a minimum in a plot against log surfactant concentration indicated the absence of the surface-active impurities. Water used in the measurement was distilled twice from dilute alkaline permanganate solution; its conductivity was about $1.0 \times 10^{-6}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ and the air/water tension was equal to 71–72 $\mathrm{mN\,m^{-1}}$ at 298.2 K.

2.2. Method

2.2.1. Conductivity measurements

The conductance measurements of solutions were performed with Metrohm 712 digital conductometer using a dip type cell of cell constant $0.99\ \mathrm{cm}^{-1}$. During the measurement, the temperature was maintained at the desired value ±0.1 °C by circulating thermostat water through the jacketed glass cell used, while the sample solution was continuously stirred. Temperature control was maintained within ± 0.005 K giving rise to uncertainties in density ca. about $\pm\ 3 \times 10^{-4}\ \mathrm{g\,cm}^{-3}$. Each solvent mixture contained 20 different concentrations of CTAB precisely weighed to ± 0.1% and expressed in molal concentrations.

3. Results and discussion

The specific conductance values of dye–cationic surfactant mixture in aqueous solution were measured as a function of the surfactant concentration at the temperature range from 298.2 to 313.2 K at 5 K intervals. Specific conductivity of the dye–DTAB mixture against DTAB concentration plots is shown in Fig. 1 and specific conductivity of the dye–CTAB mixture against CTAB concentration plots is shown in Fig. 2. If there were no interaction between the dye and the surfactant in solution, the measured conductance values would be expected to be the sum of the conductivities of the individual ions in the solution. Furthermore the specific conductance would increase linearly with increasing concentration of added surfactant. As can be seen from the figures, specific conductance curve deviates from linearity at certain concentration of surfactant and at certain temperature. This indicates that a non-conducting or a less-conducting species occurred in the solution [22]. However, the deviation of measured values from linearity decreased with increasing temperature. From the figures, it can also be observed that at 313 K the measured conductance for the RO16–DTAB and RO16–CTAB mixtures increases linearly. This indicates that there are no non-conducting or less-conducting species in the solutions at this temperature. The equilibrium constants for dye–surfactant complex formation were calculated using two theoretical methods.

3.1. Method 1

This method [23] is based on a comparison between the measured conductivity of the dye–surfactant mixture and a theoretical straight line which represents the sum of the specific conductivities of the dye and the surfactant.

The dye anion will react with surfactant cation to form a non-conducting ion pair in the solution:

$$D^{-2} + 2S^{+} \leftrightarrow DS_2 \tag{1}$$

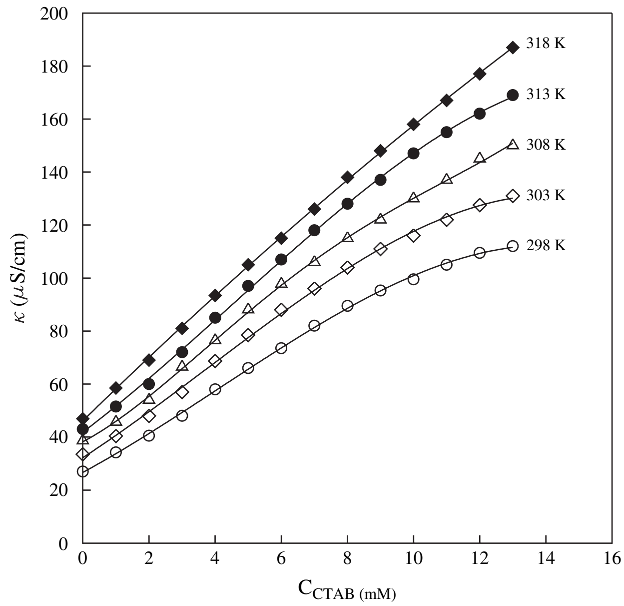


Fig. 1. Specific conductivity κ against CTAB concentration in dye–CTAB mixture in aqueous solution at five different temperatures.

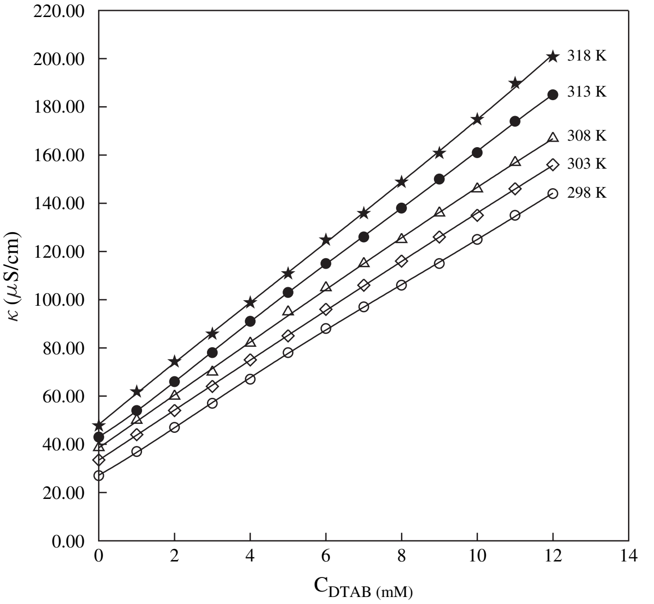


Fig. 2. Specific conductivity κ against CTAB concentration in dye–CTAB mixture in aqueous solution at five different temperatures.

If there were no interaction between the surfactant and the dye in the solution, the measured conductance would be given by Eq. (2).

$$10^3\kappa = C_D 2\lambda_{Na^+} + C_D\lambda_{D^{-2}} + 2C_S\lambda_S + 2C_S\lambda_{Br^-} \tag{2}$$

where C_D and C_S are the molar concentrations of dye and surfactant, respectively, and λ_{Na^+}, $\lambda_{D^{-2}}$, λ_S and λ_{Br^-} are the equivalent conductances of the ions Na^+, D^{-2}, S^+ and Br^-.

From the figures it can be seen that there are interactions between dye and surfactant. This interaction decreases concentration of free ions in the solution. Eq. (2) can be written as:

$$10^3\kappa = \left(C_{DS_2} + C_D\right)\lambda_{D^{-2}} + C_D 2\lambda_{Na^+} + \left(C_{DS_2} + C_S\right)2\lambda_S + 2C_S\lambda_{Br^-} \tag{3}$$

where non-conducting dye–surfactant ion pair is indicated as C_{DS_2}. With deduction of Eq. (3) from Eq. (2) we obtain:

$$10^3\Delta\kappa = C_{DS_2}\left(\lambda_{D^{-2}} + 2\lambda_{S^+}\right) \tag{4}$$

where $\Delta\kappa$ is the difference between the theoretical and measured conductances at a given surfactant concentration.

In dilute solutions, Eq. (4) is given as

$$10^3\Delta\kappa = C_{DS_2}\left(\lambda^0_{D^{-2}} + 2\lambda^0_{S^+}\right) \approx C_{DS_2}\Lambda^0_{DS_2} \tag{5}$$

where $\Lambda^0_{DS_2}$ is the equivalent conductance of the dye–surfactant ion pair at infinite dilution. $\Lambda^0_{DS_2}$ values determined experimentally for DTAB and CTAB are given in Table 1.

The equilibrium constant for reaction is given by Eq. (6)

Table 1
Equivalent conductances at infinite dilution in water for dye, CTAB, DTAB, ion pair DS_2 and S^+

T (K)	Λ^0_D	Λ^0_{CTAB}	$\Lambda^0_{DS_2(CTAB)}$	$\lambda^0_{S^+(CTAB)}$	Λ^0_{DTAB}	$\Lambda^0_{DS_2(DTAB)}$	$\Lambda^0_{S^+(DTAB)}$
298	278	168	357.60	89.90	147	315.60	68.90
303	314	190	404.28	101.75	180	384.28	91.75
308	346	210	445.50	112.38	194	413.50	96.38
313	390	224	489.48	120.13	216	4736.48	112.13
318	415	246	528.64	131.97	240	516.64	125.97

$$K = \frac{C_{DS_2}}{\left(C_{D_2} - C_{DS_2}\right)\left(2C_S - C_{DS_2}\right)} \tag{6}$$

The values for equilibrium constants (K), which are obtained using Method 1 are shown in Table 2; the numbers represent the average values of several repeats for a studied system.

3.2. Method 2

This method is based on the presumption that at the equivalent point occurred ion pair and DS_2 can be treated as partly associated electrolyte [22]. At the equivalent point, the concentration of dye, C_D, is twofold of the concentration of surfactant, C_S. In this case, the degree of ionization, α, can be defined as [24]:

$$\alpha = \frac{\Lambda}{\Lambda_\varepsilon} \tag{7}$$

where Λ is the measured equivalent conductance of dye–surfactant mixture and Λ_ε is the equivalent conductance of the hypothetic, completely ionized electrolyte at the concentration $C_i = \alpha C$. At low ion concentrations the conductivities are additive [23], Eq. (8) can be written as:

$$\Lambda_{\varepsilon DS_2} = \Lambda_{Na_2D} + 2\Lambda_{SBr} - 2\Lambda_{NaBr} \tag{8}$$

The concentration C_i can be determined by a series of successive approximations the first of these is obtained as:

$$C'_i = \frac{c\Lambda}{\Lambda^0_{DS_2}}$$

Table 2
Equilibrium constants K and standard free enthalpy changes ΔG^0 for surfactant–dye ion pair calculated using Method 1

T (K)	K (dm^3 mol^{-1}) CTAB–dye	ΔG^0 (kJ mol^{1-}) CTAB–dye	K (dm^3 mol^{-1}) DTAB–dye	ΔG^0 (kJ mol^{1-}) DTAB–dye
298	2.47×10^6	−36.5	1.79×10^6	−35.7
303	1.56×10^6	−36.6	1.07×10^6	−35.0
308	1.20×10^6	−36.4	0.69×10^6	−34.4
313	1.07×10^6	−36.1	0.50×10^6	−34.1
318	0	–	0	–

$$\Lambda'_{\varepsilon} = \Lambda_{\mathrm{Na_2D}} + 2\Lambda_{\mathrm{SBr}} - 2\Lambda_{\mathrm{NaBr}}$$

$$C''_i = \frac{c\Lambda}{\Lambda'_{\varepsilon}}$$

The procedure is complete when C_i and Λ_{ε} are constant within the experimental error. The equilibrium constant is then given by Eq. (9):

$$K = \frac{1-\alpha}{4\alpha^3 C^2} \tag{9}$$

The calculated equilibrium constants obtained with Method 2 are shown in Table 3. Furthermore, Tables 2 and 3 contain the values of ΔG^0 which were calculated using the usual thermodynamic equation (10).

$$\Delta G^0 = -\mathrm{R}T \ln K \tag{10}$$

When calculated equilibrium constants are compared according to both methods, there is only slight difference between those values, hence it can be said that the results are in good agreement.

It can be seen from Tables 2 and 3 that equilibrium constant of the systems decreases with increasing temperature. Also, calculated standard free enthalpy changes (ΔG^0) slightly increase with increasing temperature for both surfactants. Therefore, the tendency to form dye−surfactant ion pair is decreased at higher temperatures. At certain temperature, this tendency disappears. As can be seen from Figs. 1 and 2, at 318 K the values of conductance increased linearly with increasing concentration for both surfactant systems, therefore $K = 0$.

When the equilibrium constants for both surfactant systems are compared, the equilibrium constant for the dye−CTAB systems is higher than those for dye−DTAB systems. This situation is in accordance with Traube's rule [25]. Both surfactant and dye molecules have a strong polar group. In aqueous solutions these molecules dissociate into ions and there are electrostatic attractive interactions between opposite charged ions (long range interaction). Furthermore, there is hydrophobic interaction between non-polar part of the surfactant and other short range attractive forces. The CTAB molecules have a longer aliphatic chain due to DTAB molecules and therefore, CTAB has greater interaction with dye in solution.

Table 3
Equilibrium constants K and standard free enthalpy changes ΔG^0 for surfactant−dye ion pair calculated using Method 2

T (K)	K ($\mathrm{dm^3\,mol^{-1}}$) CTAB−dye	ΔG^0 ($\mathrm{kJ\,mol^{1-}}$) CTAB−dye	K ($\mathrm{dm^3\,mol^{-1}}$) DTAB−dye	ΔG^0 ($\mathrm{kJ\,mol^{1-}}$) DTAB−dye
298	2.85×10^6	−36.8	1.81×10^6	−35.7
303	1.54×10^6	−35.9	1.04×10^6	−34.9
308	1.23×10^6	−35.9	0.66×10^6	−34.3
313	1.08×10^6	−36.2	0.51×10^6	−34.2
318	0	−	0	−

4. Conclusions

Reactive Orange 16 (RO16) forms a non-conducting ion pair with dodecyltrimethylammonium bromide (DTAB) and hexadecyltrimethylammonium bromide (CTAB) at certain temperatures. In this paper we introduced two methods for calculating the equilibrium constant of interactions between dye and surfactants. With both methods the equilibrium constant can be determined from the conductance measurements. The determination of K is very simple with these methods and the values of K can give us basic data about the strength of the interaction between the dyes and surfactants. The formation of dye−surfactant ion pair is a consequence of mutual influences of long range electrostatic force and short range hydrophobic interactions. The increase of the hydrophobicity of surfactant increases the tendency to associate. Since the equilibrium constant was higher in the case of the surfactant with the longer aliphatic chain, this indicates that hydrophobic effects are important for dye−surfactant ion pair formations. Furthermore, the tendency to form dye−surfactant ion pair is decreased at higher temperatures and at certain temperature ion pair formation does not appear.

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