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Spectral Studies for Interaction Between Methyl Orange Dye and Cationic Surfactants in Acetonitrile as co-solvent with Water

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The interaction between anionic dye methyl orange and various cationic surfactants *e.g.*, *n*-alkyltrimethylammonium bromide (C_nTAB, n = 12, 14 and 16) in different volume % of acetonitrile as co-solvent with water at 25 °C is investigated by spectrophotometric method in a wide scale of concentrations. In this study, we focused on measuring the absorption bands for the above systems below and above the critical micelle concentration of the related surfactant. The maximum absorption below critical micelle concentration is found to decrease by increasing surfactants concentration in the order 0 % > 10 % > 20 % > 30 % acetonitrile. After critical micelle concentration, the absorption is increased and limit of absorption in mixed solvent is higher than in aqueous system due to increase in units of micelles which accept more dye molecules. Binding constant between dye and micelle is found to increase with chain length either in the same solvent or in different mixtures due to mutual influence of electrostatic and hydrophobic forces as the result of varying dielectric constant of the medium. Finally the standard free energy change (ΔG°) for the binding is observed to be more negative by increasing chain length of the surfactant and volume % of acetonitrile.

Keywords: Dye, Surfactants, Micelles, Mixed solvents, Binding constant, Standard free energy.

INTRODUCTION

Dyes and surfactants are two important classes of organic compounds with wide industrial uses. It is essential to understand the nature of the interaction between them and studies in this field are still important and subjects of numerous investigations [1-6]. Surfactants are used to assist in dying process by wetting and leveling or dispersing dyes of low solubility. Knowledge of dye-surfactant interaction has great value in understanding the mechanism of how the surfactants operate as leveling agents. Various techniques such as polarography and voltammetry [7], conductometry [8-11], spectrophotometry [4,12-14], membrane selective electrode [15] and potentiometry [16,17] have been employed for this purpose.

Among them spectrophotometric measurement is more extensively used in binding between dye and oppositely charged surfactant [11,18,19].

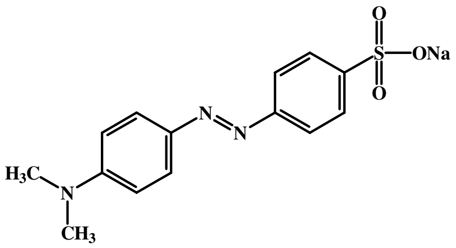
The electrostatic interaction combined with the hydrophobic interactions act concurrently to bring about the largest changes. Gokturk [20] studied the interaction of anionic acid dye with various cationic surfactants in water, has found that the binding constant values increases with surfactant length.

It was thought to carry out a systematic C_nTAB surfactants in different volume % acetonitrile as co-solvent with water to understand and characterize the role of the hydrophobic and electrostatic interactions between oppositely charged dye methyl orange and these surfactants.

Spectrophotometric method is selected for this purpose below and above the critical micelle concentration (CMC) of the available surfactants in their systems.

EXPERIMENTAL

Methyl orange (MO) was purchased from (Sigma) used directly without further purification. The chemical structure of the methyl orange is presented as follows:



Structure of methyl orange (MO)

The concentration of methyl orange is kept constant (5×10^{-5} mol L^{-1}) during the whole measurements since this concentration is sufficiently low that no dye aggregation or other cooperative effects could be detected. The absorption spectra of 5×10^{-5} mol L^{-1} methyl orange solution containing cationic surfactants in the concentration range from 1×10^{-5} mol L^{-1} to 9×10^{-1} mol L^{-1} are recorded at 25 ± 0.1 °C. The reproducibility for λ_{max} of the spectra is ± 0.1 nm. All measurements are performed in triplicate during the study.

All of the surfactants [S] alkyltrimethylammonium bromides (C_nTAB, n = 12, 14 and 16) (Fluka) are recrystallized twice from acetone and dried in vacum oven. Acetonitrile (AN) [BDH] is kept overnight in contact to molecular sieves (3 Å). Fractionating column distillate apparatus be used to obtain freshly samples of the solvent.

Freshly distilled water can be obtain by using double distillate water. The spectral studies are carried out using Shimadzu 160 A UV-visible spectrophotometer feeding with a matched pair of cuvette 1 cm path length. Ultra thermostat is joined to adjust the temperature of cuvette sample at 25 ± 0.1 °C.

The surfactant solutions are prepared by weighing the required amounts of surfactant into 10 mL weighing bottles on semi micro balance, adding methyl orange to be 5×10^{-5} mol L^{-1} then complete by water or mixture volumes (0-30 V % acetonitrile) to the required concentration. The cuvette cell is filled with solution by using disposable pipettes.

RESULTS AND DISCUSSION

Determination of critical micelle concentration (CMC) for the above surfactant solutions in presence of constant anionic dye concentration at various volume % of acetonitrile (0-30 %) is very important for present studies in recording absorption spectra below and above CMC. The λ_{max} position for dye is very sensitive to medium effect where its value for methyl orange in water is located at 463 nm, while Buwalda and his coworkers [21] recorded maximum wavelength in pure ethanol located at 417 nm.

The maximum absorbance (A) for methyl orange (taken at λ_{max} = 463 nm and at 25 °C) are plotted against broad range of surfactants $C_{12}TAB$, $C_{14}TAB$ and $C_{16}TAB$ at 10 V %, acetonitrile. Fig. 1(a-c) shows this relation where the minimum absorbance is related to the CMC of that system. Other CMC values for all solutions are collected in Table-1 and the extinction coefficients of dye in absence ε_o and in present of micelle ε_m, are also recorded in the same table.

The lowering in dielectric constant ε of the medium due to addition of acetonitrile to water is strongly accompanied with change in the absorbance of dye in its environment. This behavior indicated that Beer-Lambert law obeyed in methyl orange with given surfactants in the given concentration ranges and different acetonitrile-water mixtures. The addition of V % acetonitrile to water causes variation in the relaxation of solvent dipoles attributed to change in the dielectric effect. This change, leads to change in hydrogen bonding structure of water either enhancing bonding around dye and surfactant ions, or restricted their mobilities, so the effect of medium is presumably specific [19].

Broad spectral bands of azo dye absorption in aqueous solutions has been related to wavelength (λ_{max}) at different surfactant concentrations. Absorption spectra of methyl orange upon adding different concentrations of surfactant either ($C_{12}TAB$, $C_{14}TAB$ or $C_{16}TAB$) in pure water are shown in Fig. 2(a-c). In each case, successive small addition of surfactant led to diminish the maximum absorption bands within very narrow range of shift in λ_{max}. Further addition of surfactant before CMC, the absorption is shifted into more shorter wavelength region (blue shift) at λ_{max} = 380 nm. The shift and the diminishing strength are attributed to some sort of complex formation between dye and surfactant monomer due to mutual influence of electrostatic and hydrophobic forces. The descending rate of maximum absorption for MO-C_nTAB complex, is in surfactant order $C_{16}TAB > C_{14}TAB > C_{12}TAB$ indicating that binding force between dye and surfactant is more stronger in MO-$C_{16}TAB$ system. Bracko and Span [8] stated that ion pair formation between methyl orange and cetylpyridinium chloride in water is greater than that done with dodecypyridinium chloride attributed to the effect of chain length in association.

TABLE-1
PHYSICAL PARAMETERS OF 5×10^{-5} mol L^{-1} METHYL ORANGE IN DIFFERENT CATIONIC SURFACTANTS AND IN DIFFERENT V % ACETONITRILE at 25 °C

Surfactant	$K_b \times 10^{-4}$ (L/mol)	CMC (mol/L)	1/CMC (L/mol)	f_{mic}	ε_m (mol L^{-1} cm^{-1})	λ_{max} (nm)	ΔG° (KJ/mol)
0 % Acetonitrile [ε_o = 26024 mol L^{-1} cm^{-1}]							
$C_{12}TAB$	2.317	3.00×10^{-3}	3.33×10^{2}	0.998563	26038.39	463	-24.901
$C_{14}TAB$	6.930	6.00×10^{-4}	1.67×10^{3}	0.999520	26038.43	463	-27.615
$C_{16}TAB$	17.350	9.00×10^{-5}	1.11×10^{4}	0.999810	26038.41	462	-29.889
10 % Acetonitrile [ε_o = 26000 mol L^{-1} cm^{-1}]							
$C_{12}TAB$	2.32	9.00×10^{-3}	1.11×10^{2}	0.998565	26088.37	462	-24.904
$C_{14}TAB$	13.94	2.00×10^{-3}	5.00×10^{2}	0.999761	26088.35	461	-29.347
$C_{16}TAB$	23.13	6.00×10^{-4}	1.67×10^{3}	0.999856	26088.41	461	-30.602
20 % Acetonitrile [ε_o = 25504 mol L^{-1} cm^{-1}]							
$C_{12}TAB$	3.48	3.00×10^{-1}	3.33	0.999044	25518.35	460	-25.912
$C_{14}TAB$	34.85	2.00×10^{-2}	50.00	0.999904	25518.35	460	-31.617
$C_{16}TAB$	99.57	9.00×10^{-4}	1.11×10^{3}	0.999967	25518.35	460	-34.218
30 % Acetonitrile [ε_o = 26300 mol L^{-1} cm^{-1}]							
$C_{12}TAB$	6.910	3.00×10^{-1}	3.33×10^{-1}	0.99951784	26314.472	458	-27.608
$C_{14}TAB$	77.000	4.00×10^{-2}	25	0.99995671	26314.430	459	-33.581
$C_{16}TAB$	114.167	9.00×10^{-3}	1.11×10^{2}	0.99997100	26314.598	454	-34.557

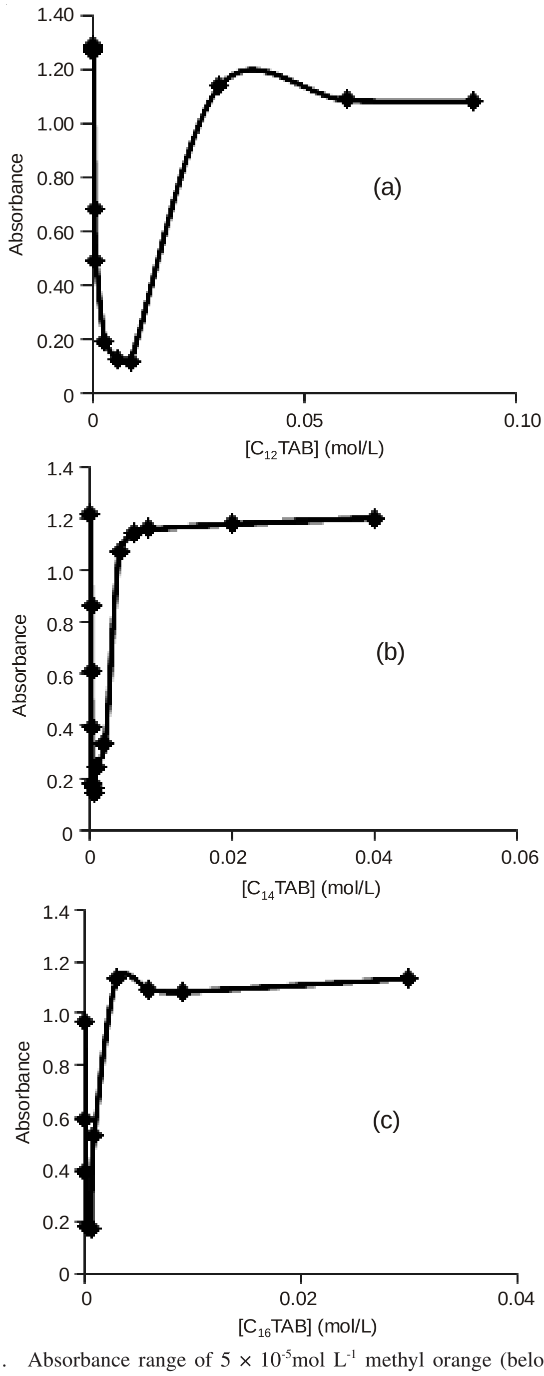


Fig. 1. Absorbance range of 5 × 10^{-5}mol L^{-1} methyl orange (below and above the CMC) with the concentration of (a) $C_{12}TAB$, (b) $C_{14}TAB$ and (c) $C_{16}TAB$ in 10 % acetonitrile at (λ_{max} = 468 nm)

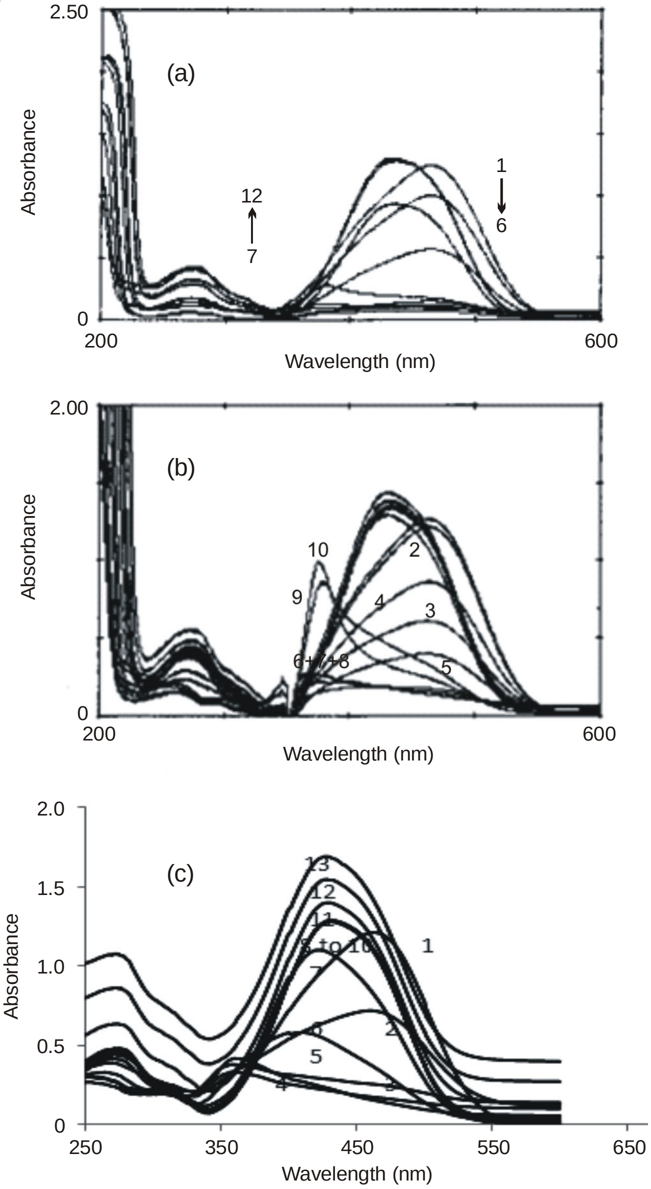


Fig. 2. Visible absorption spectra of methyl orange (5 × 10^{-5}mol L^{-1}) at various concentrations of surfactants[(a) $C_{12}TAB$, (b) $C_{14}TAB$ and (c) $C_{16}TAB$] in pure water at pH = 7.7 at 25 °C; (a) $C_{12}TAB$ before CMC [0.0 to 9 × 10^{-4}], after CMC [6 × 10^{-3} to 9 × 10^{-2}] mol L^{-1}; (b) $C_{14}TAB$ before CMC [0.0 to 8 × 10^{-5}], after [8 × 10^{-4} to 4 × 10^{-2}] mol L^{-1}; (c) $C_{16}TAB$ before CMC [0.0 to 6 × 10^{-5}], after [3 × 10^{-4} to 3 × 10^{-1}] mol L^{-1}

Typical runs to follow the absorption effect of methyl orange in presence of $C_{14}TAB$ as an example is carried out at different V % acetonitrile in range 10-30 % acetonitrile at 25 °C are shown in Fig. 3(a-c). In all models, spectral bands related to all range of surfactant concentrations below CMC are observed. At very low concentrations, maximum band of absorption slightly decreases indicating weak ion pair formation in this smaller range of surfactants. Clear displacement of band absorption is observed at highly surfactant concentrations till reach minimum value. By increasing surfactant concentration some sort of association or complex ion pair between dye and surfactant monomer be formed. This association is accompanied with lowering in absorption bands and more shift into blue region. The rate of association in pure water is more stronger than in mixtures due to higher electrostatic and hydrophobic effects in water than in mixtures.

Dutta and Bhat [17] showed the role of the solvent majority in assisting the enforcement of ion-pairing process, so the head polar group of surfactant is enforced to attach to the sulfonato group of methyl orange which explain the large blue shift in the spectrum of methyl orange upon adding small amounts of cationic amphiphile. In present solutions, the addition of small amount of acetonitrile (dipolar aprotic solvent) to flick ring structure of water breaks down the hydrogen bonding between its molecules, hence, the enforcement of water molecules around moving ions become less able to assist ion pairing leading to less absorption in their mixture.

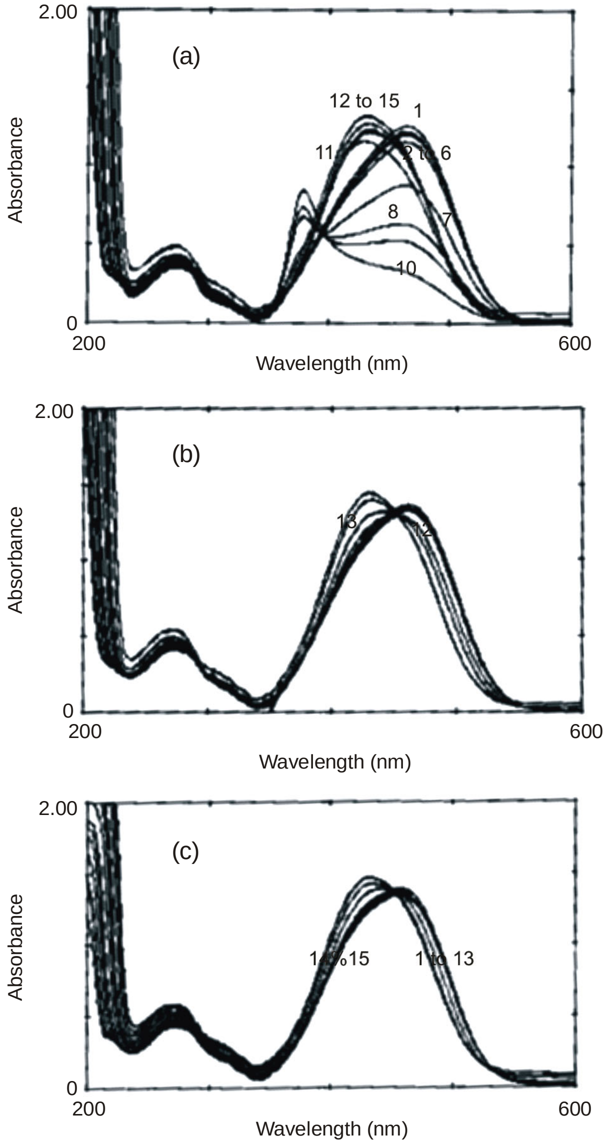


Fig. 3. Visible absorption spectra of methyl orange (5×10^{-5} mol L^{-1}) at various concentrations of $C_{14}TAB$ at 25 °C and (a) 10 % acetonitrile, (b) 20 % acetonitrile and (c) 30 % acetonitrile; The concentrations of $C_{14}TAB$ are 1 = 0.0, 2 = 2×10^{-5}, 3 = 4×10^{-5}, 4 = 6×10^{-5}, 5 = 8×10^{-5}, 6 = 2×10^{-4}, 7 = 4×10^{-4}, 8 = 6×10^{-4}, 9 = 8×10^{-4}, 10 = 2×10^{-3}, 11 = 4×10^{-3}, 12 = 6×10^{-3}, 13 = 8×10^{-3}, 14 = 2×10^{-2}, 15 = 4×10^{-2}, 16 = 6×10^{-2}, 17 = 8×10^{-2} mol L^{-1}

Above CMC, on adding more surfactant, the spectra as shown in Figs. 2 and 3 is shift into new absorption region located at λ_{max} = 430 nm. In this new position, the band maxima of absorption begin to increase by increasing surfactant due to starting incorporation of dye into micelle till attain saturated limited value. Buwalda *et al.* [21] showed the effect of adding $C_{12}TAB$ on the absorption spectrum of methyl orange as dye in aqueous solution at pH 9.4 and at 30 °C. They found that the intensity of the new bands, firstly increases upon further increasing surfactant, then decrease again until appearance of new maximum bands in shorter wavelength region at λ_{max} = 430 nm, characteristic for methyl orange incorporated to cationic micelles.

It is known that micelle have greater size in water than in water-acetonitrile-mixtures. From Figs. 2 and 3(a-c), it is found that maxima in mixed solvents system are higher than in pure water. This result is derived from knowing that micelle size in water is greater than in water-acetonitrile mixtures [22] and the number of micelles units in mixed solvents is greater than in pure water. Hence on adding dye molecules to micelle solution, it is likely that the dye with its big size attracted or incorporated into the outer region of micelle surface [23].

In pure water a great ability of methyl orange to solubilize in the core of the micelle while in mixed solvents palisade or in between head polar ions region of the micelle may still available in attaching methyl orange gave reason why dye could attain higher absorption bands in mixed solutions than in water. Hence, micelle surface in mixed solvents is considered as catalytic enhance for dye and micelle [24]. In addition, micelle shape and size have the ability to modify by increasing surfactant concentration after CMC from simple sphere into more complicated structures like monolayers, bilayers or cylindrical shapes [23]. Hence, the chance for incorporated methyl orange in micelle will be greater in water-acetonitrile mixtures than in water.

When observing Fig. 3(a-c), an isobestic point is located at about 440 min transition from below to the above CMC values. The isobestic position is more clear in 30 % $C_{14}TAB$ (Fig. 3c) due to formation of greater number of micelle units indicated that an equilibrium is attained between free dye ion and dye bound to micelle [17].

It is noted that great shifts in the absorption bands for dye may not necessarily attributed to strong interaction between dye and micelle units, but largely affected by another factors such as the dielectric constant of the microenvironment of the dye, hydrogen bonding of the chromospheres with the solvent [25].

Determination of binding constant: The spectrophotometric data are employed to calculate the binding constant (K_b) of dye-surfactant interaction. The equilibrium for the interaction between dye (D) and micellized surfactant [S_m] can be written as [26]

$$D + S_m \rightleftharpoons DS_m \tag{1}$$

or,

$$K_b = \frac{[DS_m]}{[D][S_m]} \tag{2}$$

where [DS_m] stated for the dye concentration bound to surfactant and [S_m] is equal to ([S]-CMC) [27]. The equilibrium constant for the interaction between dye and methyl orange at 0-30 % v/v % acetonitrile, have been determined by using the modified eqn. 3 which is valid only for surfactant above CMC [26,28].

$$\frac{D_t}{\Delta A} = \frac{1}{(\varepsilon_m - \varepsilon_o)} + \frac{1}{K_b(\varepsilon_m - \varepsilon_o)S_m} \tag{3}$$

where ε_o, ε_m are the molar extinction coefficients of dye and that fully bound to micelles respectively. D_t is the total concentration of the dye, $\Delta A = A - A_o$ is the difference between the absorbance of methyl orange in presence and in absence of surfactant. Fig. 4(a-d) for 0, 10, 20 and 30 % acetonitrile, respectively, shows typical runs for plotting $D_t/\Delta A$ against $1/S_m$ where straight lines are obtained, K_b and ε_m can be derived from the slope and the intercept respectively. Table-1 shows K_b and ε_m values for all the solutions. It can be readily seen

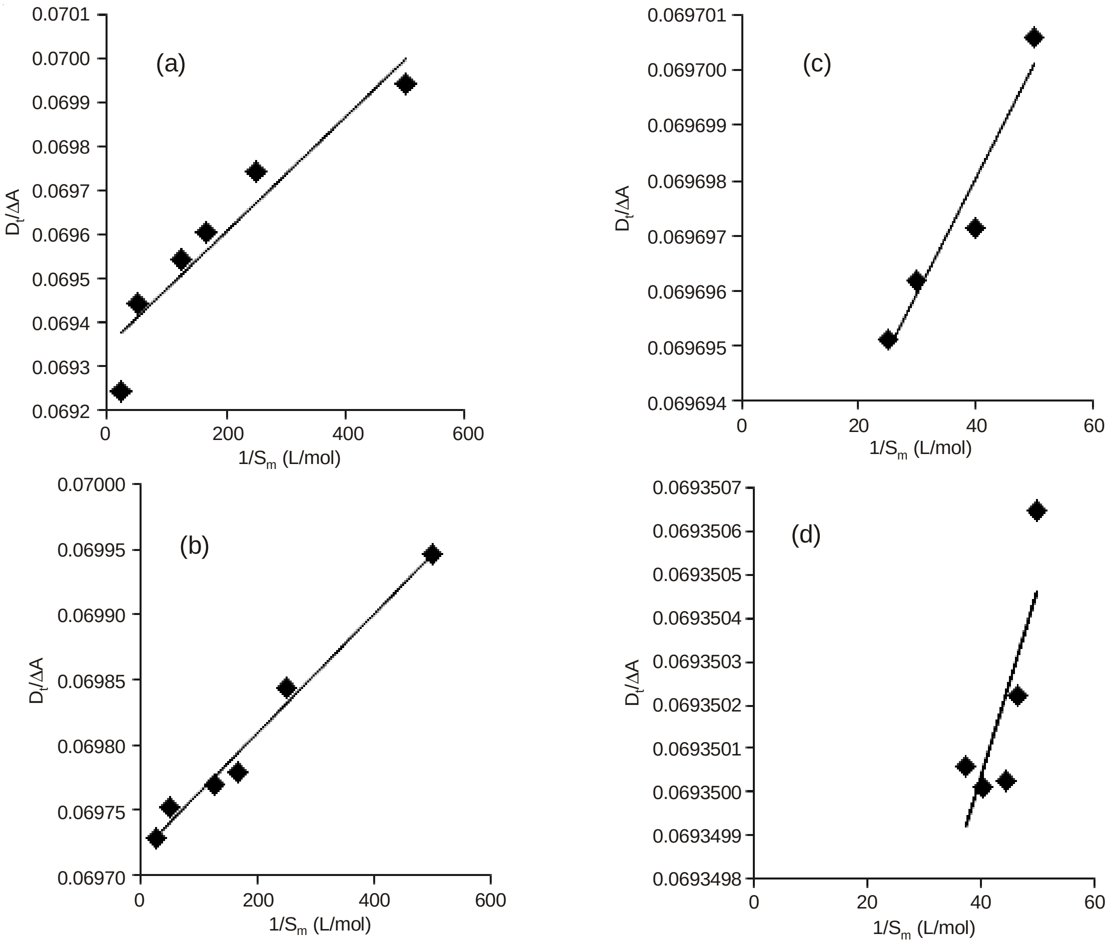


Fig. 4. Plot of ($D_t/\Delta A$) against $1/S_m$ for $C_{14}TAB$ at (a) 0 % acetonitrile, (b) 10 % acetonitrile, (c) 20 % acetonitrile and (d) 30 % acetonitrile

that K_b values for different surfactants at given solvent are increased by increasing chain length of the surfactant in the order $C_{12}TAB < C_{14}TAB < C_{16}TAB$. This trend explained that the incorporation capacity of the dye into micelle will be more stronger by increasing micelle size in the same solvent where the greater chain length of surfactant the greater its micelle size effect. Also K_b values for the surfactant type are observed to be greater in mixed solvents than in pure water Table-1. The decrease in polarity enhance the binding between dye and charged sphere of micelle due to the reduction of electro repulsive force between them. The incorporation process depends partially on the micelle shape, size and on the selective solvation of dye and micelles in given two different solvents water and acetonitrile [24,29].

The efficiency of cationic micelle on holding methyl orange, can be seen from the fraction of micellized methyl orange (f_{mic}) value shown in eqn. (4) [30]:

$$f_{mic} = \frac{K_b M}{1 + K_b M} \tag{4}$$

Table-1 listed f_{mic} data for all the above solutions taken at constant micelle concentration (0.03 mol L^{-1}). The accuracy of these data will be in concordance with limiting of > 0.998 where their values are slightly inversely proportional to chain length of the surfactant in each % acetonitrile. Fig. 5(a-d) shows the variation of f_{mic} with different concentrations of $C_{14}TAB$ at different V % acetonitrile. The relation curves gave strong confidence that the dye will be attached to micelle more strongly by increasing V % acetonitrile.

The standard free energy change $\Delta G^\circ_{d\text{-}m}$ related to binding between dye and surfactant can be derived from K_b value as given by eqn. 5 [31]:

$$\Delta G^\circ_{d\text{-}m} = -RT \ln K_b \tag{5}$$

where $\Delta G^\circ_{d\text{-}m}$ value is the function for the tendency of binding dye (methyl orange) into micelle. Table-1 shows that in the same solvent, $\Delta G^\circ_{d\text{-}m}$ is found to be more negative by increasing chain length of surfactant indicating that hydrophobic moiety of different surfactants is predominantly controlling the incorporation process. Also $\Delta G^\circ_{d\text{-}m}$ data for all systems found to be more negative on adding V % acetonitrile. The results are in concordance with the following eqn. 6:

$$\Delta G_{el} = -\frac{[Z_1 Z_2] NA}{\varepsilon a} e^2 \tag{6}$$

where ε is the dielectric constant of the medium and "a" is the closest approach distance between two opposite charges.

The above equation is indicated that by adding acetonitrile, the negativity of the free energy transfer be more negative, methyl orange enhance to interact more spontaneously to surfactant at lower polar solution. This process make "a" value be smaller in mixture than in water where the variation in structure of mixed solvents enhance forming more micelle units

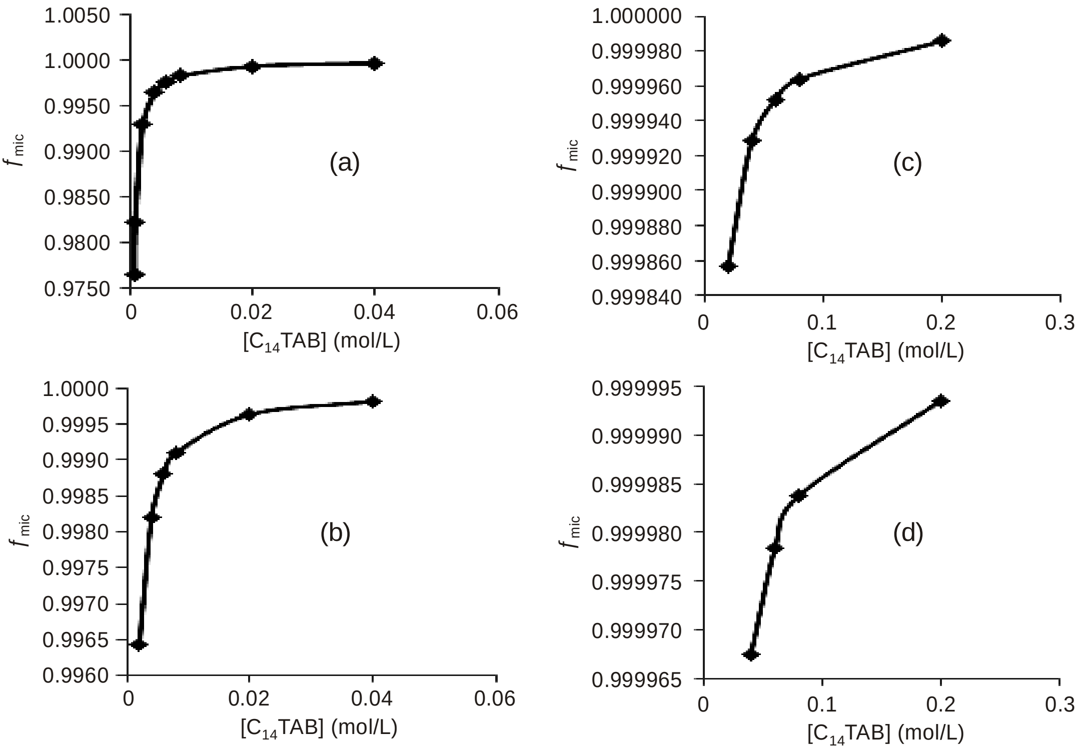


Fig. 5. Plot of the fraction of micellized dye against concentration of C_{14}TAB at (a) 0 % acetonitrile, (b) 10 % acetonitrile, (c) 20 % acetonitrile and (d) 30 % acetonitrile

with smaller sizes, facilitate the incorporation process above CMC. Also, in this field, long range as well as short range interactions at different solutions are responsible for the arrangement of dye and micelle to incorporate.

Conclusion

Spectrophotometric studies of methyl orange as dye in presence of different cationic surfactants C_nTAB (n = 12, 14 and 16) at different V % acetonitrile depends strongly on the polarity of the medium. By increasing V % of the organic solvent, the CMC increases as well as K_b where the solvent play an important role in solubilizing the dye into micelle. $\Delta G°_{d-m}$ is the standard free energy of binding between dye and micelle is found to increase with more negative value by increasing V % acetonitrile attributed to more spontaneously of binding process.

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