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Dissociation Constant Of Methyl Orange In Water Pools Of Reverse Micelles

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ABSTRACT

The dissociation constants of methyl orange were determined spectrophotometrically in the reverse micelles of CTAB, AOT and Triton X 100. No buffers were used and the acidity of methyl orange solubilised in the reverse micelles was changed by adding hydrochloric acid. The effect of water to surfactant molar ratio(W) and surfactant concentration on pKa values were investigated. All pKa values were lower than in aqueous medium even after taking into account the concentration effect. The shift in pKa at constant W and surfactant concentration follows the order CTAB>Triton×100>AOT. The variation of W has no significant effect on pKa in CTAB whereas in AOT and Triton ×100 the pKa increases on increasing W. The increase in pKa with W is more pronounced at low W values (W<4). The weak acidic nature of methyl orange(pKa=3.6) in aqueous medium is no longer observed in reverse micellar medium and the protonated form of methyl orange acts as a strong acid. In case of CTAB reverse micellar medium this can be attributed to a strong interaction between positively charged surface and negatively charged deprotonated form of dye. The shift in the pKa of the protonated methyl orange in the Triton×100 and AOT reverse micellar medium can be attributed to the more basic nature of the solubilized water, the basic nature decreasing with W.

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INTRODUCTION

The increased interest in studying the chemistry of detergent aggregates in non polar solvents(called reverse micelles) is due to their efficiency as catalysts and usefulness as models for enzymes and membranes[1-4]. Reverse micelles have polar interiors containing the hydrophilic group, whereas the hydrophobic tails lie in the non-polar solvent. These micellar 'core' are the sites of solubilization and chemical reactions.

Due to their micellar core, the reverse micelles can dissolve water in apolar solvents. This solubilized water is referred to as 'Waterpool'. Waterpools are formed by adding water to surfactant aggregates in non polar solvents. Some of the water solubilized within a reverse micelle hydrates the hydrophilic head groups of the surfactant, this water is tightly bound and is much less mobile than the bulk water. Additional water in excess of that required to hydrate the head groups is not as tightly constrained. The study of properties of reverse micelle solubilized water has received much attention, they are different from those of bulk water and depend on the water detergent molar ratio W[4].

A large number of Inorganic and organic reactions have been catalyzed[5-8] in reverse micellar media. Since the properties of water solubilized in reverse micelles are different it is possible that the physicochemical properties of the reactants may change when they are solubilized in the waterpool and this could be one of the factors responsible for reverse micellar catalysis. This realization has intensified our interest in a detailed examination of acid base equilibrium in reverse micelles.

Most of the reaction rates in reverse micellar media have been determined in buffers and it is assumed that pKa values of buffers in the water pool are equal to its value in bulk water and buffer capacity is maintained in reverse micelles[9-11]. But there is no guarantee that this assumption is true for all buffers and all reverse micellar systems.

Effective acidities in the micellar water pools can be most easily probed by studying the effect of reverse micelles on the pKa of suitable indicators[12-15]. We have made a comparative study of the dissociation constant of protonated methyl orange in the reverse micelles of cationic surfactant CTAB in 2:3 mixture of hexane/chloroform, anionic surfactant AOT in heptane and non ionic surfactant triton×100 in hexanol/cyclohexane.

MATERIALS AND METHOD

CTAB(Otto chemicals, Mumbai) and triton×100 (Ubichemicals, England) were used as received. AOT from SD Fine chemicals, Mumbai was used after purification. AR grade methyl orange was purchased from BDH. The purity of methyl orange was established by absorption spectrophotometry and by determining the dissociation constant in water. Both the spectral parameters as well as pKa values agreed well with those obtained in literature[16] (TABLE 1).

AR grade hexane, heptane, cyclohexane, hexanol and chloroform were distilled before use. All other reagents used were of analytical reagent grade. Triple distilled water was used throughout the experiment.

Determination of pKa of methyl orange in water

The pK_a of methyl orange in water was determined by the standard spectrophotometric method as given in literature[17]. The pKa of methyl orange in water was found to be 3.6.

Determination of pKa of methyl orange in reverse micelle

The stock solution of CTAB was prepared by

TABLE 1: Properties of methyl orange

System	λmax(nm)		log ε	
	Protonated form	Unprotonated form	Protonated form	Unprotonated form
Water	510	465	4.89	4.59
CTAB/Hexane/Chloroform	520	430	4.42	4.38
AOT/Heptane	517	430	4.67	4.27
Triton × 100/Cyclohexane	520	430	4.72	4.63

dissolving accurately weighed CTAB in 2:3 v/v hexane, chloroform mixture. AOT solution was similarly prepared in n-heptane. Stock solution of triton×100 was prepared by mixing triton×100 and hexanol in the ratio 4:1v/v and then dissolving this blend in required amount of cyclohexane to obtain a stock solution of fixed concentration of triton×100. Aqueous solution of methyl orange was added to the stock solution of surfactant reverse micelle with help of a micro pipette. The concentration of methyl orange was kept constant at 1.9×10^{-4} mole dm^{-3}.

The distribution coefficient of methyl orange between water and organic solvents were determined by shaking equal volumes of solvent and aqueous solution of indicator for several hours. After complete phase separation at 25^0C, the residual indicator in aqueous layer was determined spectrophotometrically. It was found that the methyl orange partitions 99.9% in favor of water rather than organic solvents.

Acidities of methyl orange solubilized in reverse micelles was varied by injection of small volume(0.025-0.3ml) of aqueous hydrochloric acid(0.01-3.0mol dm^{-3}) to 5ml of solution(surfactant/organic solvent/water/methyl orange system). In all the cases, subsequent to mixing, optically isotropic solutions were obtained. The absorption spectra of these solutions were measured shortly after mixing on a Milton Roy(Spectronic 1201) spectrophotometer with thermostatic arrangement and the absorption spectra remained unaltered for a period of one week.

RESULTS AND DISCUSSION

The addition of increasing concentration of hydrochloric acid altered the absorbance of methyl orange solubilized in reverse micelles in a manner similar to that observed for their titration in water. The Beer Lambert's law was tested for all reverse micellar systems and absorbance versus concentration curves were linear passing through the origin in the concentration range of methyl orange employed.

Dissociation constant of methyl orange can be represented as:

$$HIn \overset{H_2O}{\leftrightarrow} H_3O^+ + In- \quad (1)$$

The classical dissociation constant is given by:

$$K_a = [H_3O^+]\,[In-]/\,[HIn] \quad (2)$$

$$-\log [H_3O^+] = -\log K_a + \log [In-] / [HIn] \quad (3)$$

If D_1 and D_2 are the absorbance of a solution of a particular hydronium ion concentration at two wavelengths 1 and 2 then:

$$D_1 = D_{1(HIn)}\,[HIn] + D_{1(In-)}\,[In-] \quad (4)$$

$$D_2 = D_{2(HIn)}\,[HIn] + D_{2(In-)}\,[In-] \quad (5)$$

Where $D_{1(HIn)}$ and $D_{1(In-)}$ are the absorbances of molecular and ionic form of the indicator at wavelength 1 and $D_{2(HIn)}$ and $D_{2(In-)}$ are those at wavelength 2. Solving the simultaneous equations 4 and 5, the ratio [In-]/[HIn] can be calculated. A plot of -log $[H_3O^+]$ against log [In-]/[HIn] is linear as shown in figure 1 with intercept equal to pKa.

The hydronium ion concentration $[H_3O^+]$ in the waterpool can be calculated from its stoichiometric value by using appropriate correction factor(f). Since all the added acid is expected to be localized in waterpool, the stoichiometric $[H_3O^+]$ should be multiplied[8] by f =55.5/Molarity of micelle solubilized water.

For example in presence of 0.55 M water, the concentration of hydronium ion in the waterpool will be hundred fold greater than in the conventional aqueous system, thus $[H_3O^+]$ should be multiplied by 100 or pH reduced by 2 units. Thus in our system the concentration effect can be simply estimated as

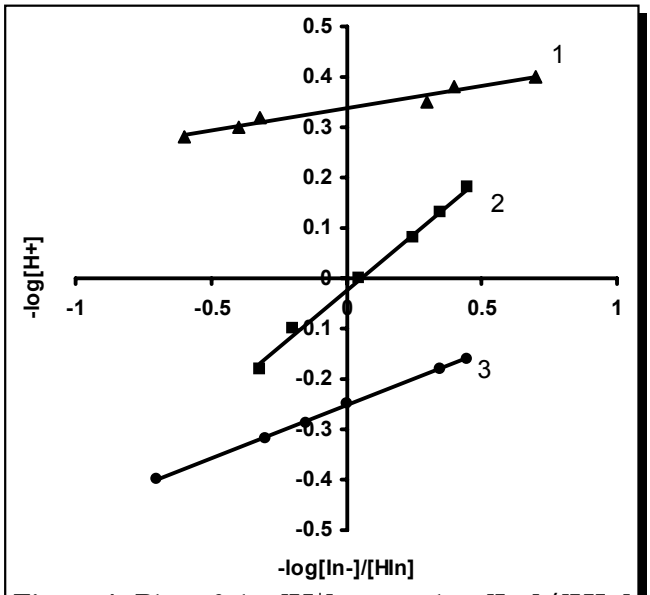

Figure 1: Plot of -log[H^+] versus log [In-]/[HIn] [Surfactant] =0.2 mol dm^{-3}; W =2.5 (1) AOT; (2) T ×100; (3) CTAB

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TABLE 2: Dissociation constant of methyl orange in CTAB/Hexane/Chloroform

[CTAB] (mol dm^{-3})	W	pKa	Ka
0.1	5.0	-0.15	1.41
0.1	7.2	-0.13	1.36
0.1	12.8	-0.11	1.29
0.1	16.1	-0.08	1.19
0.3	2.5	-0.18	1.51
0.3	3.9	-0.16	1.44
0.3	6.5	-0.11	1.29
0.3	16.1	-0.09	1.23
0.056	12.8	-0.11	1.29
0.074	12.8	-0.10	1.26
0.278	12.8	-0.09	1.23

all hydronium ions are located in the polar core of the surfactant aggregates. Any effect over and above this need to be ascribed to difference in the dissociation of protonated methyl orange in the surfactant solubilized water and conventional aqueous medium.

The pKa values of methyl orange, assuming all the acid is localized in the solubilized waterpool in the three reverse micellar systems as function of concentration of surfactant and W, (W =[H_2O]/[Surfactant]) are presented in TABLES 2-5. The standard error in determination of pKa was 5-6%.

TABLE 2 includes the pKa values of methyl orange, in reverse micelles of CTAB in chloroform/hexane as obtained by spectrophotometric titration. All the pK_a values are lower than those in water.

The pK_a values decrease from 3.6 in aqueous medium to -0.18 in the CTAB reverse micellar system at W value of 2.5 and [CTAB] =0.3mol dm^{-3}. With increase in W from 2.5 to 16.1, the pKa value of the dye changes from -0.18 to -0.09 or the Ka changes from 1.51 to 1.23. Similarly in the presence of 0.1mol dm^{-3} CTAB, on changing W from 5.0 to 16.1 pKa changes from -0.15 to -0.08. It appears therefore, that change in W does not appreciably alter the pKa values. This can also be noted from figure 2 which shows the variation of Ka with W.

The weak acidic nature of the protonated form of methyl orange(K_a =2.5×10^{-4} in aqueous medium) is no longer observed in this reverse micellar system and the protonated form acts as a fairly strong acid. This can only be attributed to a strong interaction between the positively charged interface and negatively charged deprotonated form(In$^-$) of the dye, In$^-$ being strongly bound at the interface. This is also reflected in the constancy of the value of pKa to change in the CTAB concentration at constant W (TABLE 2). It is known that change in CTAB concentration at constant W, proportionately changes the micellar concentration without changing the dimensions; the constancy in pKa can only be explained by assuming near saturation condition, the deprotonated form(In-) of the dye almost completely clinging to positively charged interface. This explains the abrupt decrease in pKa(or increase in Ka) values when medium is changed from aqueous to reverse micellar system. (Without appreciable change when W is changed from 2.5 to 16.1).This view is supported by the strong interaction between the positively charged CTAB regular micelles and deprotonated form of methyl orange reported earlier[18] . A binding constant of 5.9×10^5 has been reported for binding of methyl orange to positively charged micellar surface of CTAB.

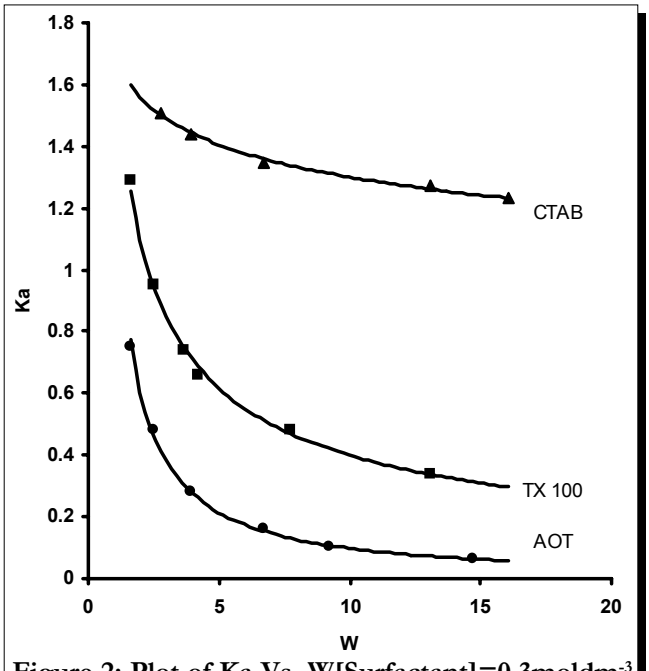

Figure 2: Plot of Ka Vs. W[Surfactant]=0.3moldm^{-3}

We consider that there is similar strong binding of the deprotonated form of the dye at the reverse micellar interface. This view is supported by the results obtained in the reverse micellar as well as regular micellar medium. The shift in the λ_{max} of the deprotonated form of methyl orange has been re-

ported[18] to be from 465 to 428 nm in CTAB regular micelles which is in very good agreement with one found in the CTAB reverse micellar system(465 to 430 nm). The molar extinction coefficient values of methyl orange in regular and normal micelles of CTAB are also very close to each other. ($\log \varepsilon$ =4.37 in aqueous micelles and 4.38 in reverse micelles).

TABLE 3 and 4 include the dissociation constant of methyl orange in reverse micelles of AOT and triton×100 respectively. The pKa values are lower than in aqueous medium. In TABLE 5 the pKa values of the three surfactants are compared at constant surfactant concentration of 0.2 mol dm^{-3} and W =2.5. The results in TABLE 5 show that the decrease in pKa after separating the concentration effect is maximum in CTAB and least in AOT reverse micelles. The shift is intermediate in the case of nonionic triton×100 reverse micelles.

In case of triton×100 reverse micellar system, the shift in pKa is far less pronounced compared to one in CTAB reverse micellar medium.

Presumably, In- is stabilized(bound) less strongly at triton×100 surface. It is well known that the binding of the substrate at neutral micellar surface is weaker than at charged micellar surface. This may be responsible for lower shift in pKa.

TABLE 3: Dissociation constant of methyl orange in AOT/Heptane

[AOT] (mol dm^{-3})	W	pKa	Ka
0.3	1.6	0.17	0.75
0.3	2.5	0.33	0.481
0.3	3.9	0.55	0.282
0.3	6.7	0.80	0.158
0.3	9.2	0.98	0.105
0.3	14.7	1.20	0.063
0.1	6.7	0.88	0.132
0.2	6.7	0.85	0.141

TABLE 4: Dissociation constant of methyl orange in Triton×100/Hexanol/Cyclohexane system

[Triton × 100] (mol dm^{-3})	W	pKa	Ka
0.3	1.6	-0.11	1.29
0.3	2.5	+0.02	0.95
0.3	3.6	+0.13	0.74
0.3	4.2	+0.18	0.66
0.3	7.7	+0.32	0.48
0.3	13.1	+0.47	0.34
0.2	2.5	-0.02	1.04
0.4	2.5	-0.01	1.02

TABLE 5: Dissociation constant of methyl orange in reverse micelles of different surfactants[surfactant] =0.2 mol dm^{-3}; W =2.5

Surfactant	pKa	Ka
AOT	+0.33	0.47
Triton × 100	-0.02	1.04
CTAB	-0.25	1.78

In case of AOT and triton×100 reverse micellar medium the increase in pKa or decrease in Ka with W is much more pronounced as compared to CTAB reverse micellar medium(Figure 2) In AOT reverse micellar system pKa increases from 0.17 to 1.20 when W is varied from 1.6 to 14.7 at constant AOT concentration. In triton×100 reverse micelle, the pKa of methyl orange increases from -0.11 to +0.47 when W is varied from 1.6 to 13.1. the shift in the pKa of the protonated methyl orange in the triton×100 and AOT medium can be attributed to more basic nature of the solubilized water[19,20], the basic nature declining with increase in W.

It is interesting to note from figure 2 that decrease in Ka(or increase in pKa) with W is more pronounced at low values of W and at W>4 ,the change is less pronounced. Probably the free water in excess of hydration of the head groups on surface of the surfactant molecule is increasingly formed at W>4.

The smaller shift in pKa in the AOT reverse micellar medium as compared to triton×100 medium may be attributed to the presence of large concentration of sodium ions in the AOT reverse micelles making the medium less nucleophilic and consequently reducing the basic nature of the medium.

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