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Visible Spectra of Methyl Red in Benzene–Water Microemulsions

Tapash K. Barman, Babul C. Paul, and Kochi Ismail*
Department of Chemistry, North-Eastern Hill University, Bijni Complex, Laitumkhrah, Shillong 793003, India

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Synopsis. Visible absorption spectra of Methyl Red in buffered benzene–water microemulsions (MEs) stabilized by sodium dodecyl sulfate and 1-butanol were recorded at 25 °C and at various pH values. Three compositions of the ME were used with $R=24$, 32, and 48 where R is the water (aqueous buffer)-to-surfactant molar ratio. $\mathrm{p}K_\mathrm{a}$ of Methyl Red is found to be 6.12, 6.38, and 6.6 in MEs of $R=24$, 32, and 48, respectively. The effective dielectric constant of the ME is estimated to be about 45 ± 3.

The acid-base equilibria of several organic weak acids and bases were studied in aqueous solutions, aqueous micellar solutions, and also in organic solvent–water mixtures.[1—6] However, relatively few such studies are made in water microemulsions (MEs). MEs have attracted in recent years more attention not only because of their useful applications in industry but also due to the fact that they serve as suitable model systems for biological membranes. Recently, Oldfield et al.[7] reported the acid-base behavior of 4-nitrophenol and disodium salt of 4-nitrophenol-2-sulfonic acid in water-in-oil (heptane) MEs stabilized by Aerosol-OT (AOT). In another recent study Moulik et al.[8] reported the acid-base behavior of Neutral Red in water–AOT–oil (heptane/isooctane/decane/toluene/benzene/cyclohexane) MEs and also in water–AOT–butanol–decane and water–AOT–hexanol–decane MEs. We report here the results of a study made on the acid-base behavior of Methyl Red in buffered benzene–water MEs stabilized by SDS and 1-butanol. This ME was chosen with a view to understanding how an ionic surfactant in a ME medium affects the $\mathrm{p}K_\mathrm{a}$ of Methyl Red.

Experimental

Sodium acetate (SD fine chemicals (India), Analytical reagent grade) and glacial acetic acid (Merck) were used for preparing buffer solutions. Buffer solutions of pH=5.2, 5.6, 6.0, 6.4, and 6.6 were prepared by mixing appropriate amounts of 0.2 M sodium acetate solution ($1\ \mathrm{M}=1\ \mathrm{mol\,dm^{-3}}$), 0.2 M acetic acid solution, and double distilled water according to the standard buffer table.[9] Buffer of pH=2.7 was obtained by diluting glacial acetic acid and of pH=12.3 was obtained by preparing 0.2 M sodium hydroxide (Merck) solution.

Methyl Red (SD fine chemicals (India)) was purified by slow crystallization from distilled toluene solution. A $3.5\times10^{-3}\ \mathrm{mol\,kg^{-1}}$ solution of Methyl Red was prepared first in 1-butanol (Merck, synthesis grade) which was further diluted to $1.8\times10^{-4}\ \mathrm{mol\,kg^{-1}}$ by adding 1-butanol so that the absorbance of Methyl Red indicator was in the range of 0.2 to 0.8 in the final solution. This dilute solution was used as the stock solution.

MEs containing Methyl Red were prepared by mixing weighed amounts of benzene (Merck, Guaranteed reagent grade), sodium dodecyl sulfate (SDS) (SISCO (India), extra pure grade), aqueous buffer solution, 1-butanol, and Methyl Red solution in 1-butanol in the following respective ratio: 0.263 : 0.105 : 0.316 : 0.158 : 0.158 ($R=48$), 0.250 : 0.150 : 0.300 : 0.150 : 0.150 ($R=32$), and 0.238 : 0.190 : 0.286 : 0.143 : 0.143 ($R=24$). All chemicals except Methyl Red were used as they received. To check the purity of the SDS sample used, we determined its critical micelle concentration at 25 °C conductometrically which was found to be $0.0082\ \mathrm{mol\,kg^{-1}}$ and this value is in good agreement with the reported value.[10] In the case of every ME, the pH of the buffer was varied between 2.7 and 12.3 (total of seven different pHs). To evaluate the ratio of the concentration of the base form, $\mathrm{MR^-}$ to that of the acid form, HMR of Methyl Red, the visible absorption spectra of Methyl Red at different pHs were recorded. These spectroscopic measurements were made using the Hitachi 330 spectrophotometer. The cell holder was thermostated at 25.00 ± 0.02°C. Viscosity of the MEs was measured at 25 °C using a Cannon–Ubbelhode viscometer.

Results and Discussion

The ME chosen here for study may be considered to behave like an oil-in-water ME on the basis of its reported[11] phase diagram. It is a thermodynamically stable and optically transparent ME. The measured viscosity of the ME at 25 °C is found to be 3.5275, 3.0576, and 2.6152 cP ($1\ \mathrm{cP}=10^{-3}\ \mathrm{Pa\,s}$) for $R=24$, 32, and 48, respectively. Since the viscosity values are not too high, this ME appear to have no extended aggregates.

The visible absorption spectra of Methyl Red as a function of pH of the aqueous buffer in the benzene–water ME is shown in Fig. 1 for $R=32$. The λ_max for HMR is found to be 502 nm and that for $\mathrm{MR^-}$ is 413 nm (Table 1). Similar spectra of Methyl Red are obtained at $R=48$ and 24. No change in λ_max was observed as a function of R. The extinction coefficients of both HMR and $\mathrm{MR^-}$ are found to decrease with decrease in the value of R. The λ_max for HMR in the ME is 20 nm less than that reported[4] in aqueous and aqueous micellar SDS media. The λ_max for $\mathrm{MR^-}$ in the ME is, on the other hand, almost same as that reported[4] in aqueous micellar SDS medium but less by 10 nm than that in aqueous medium. It is interesting to note that a similar shift of λ_max values of HMR and $\mathrm{MR^-}$ is also reported[4] in 1,4-dioxane–water mixtures containing 60 weight per cent of dioxane. Such a shifting of λ_max was reported[7] for 4-nitrophenolate and 4-nitrophenol in heptane–water ME stabilized by AOT. The shift of

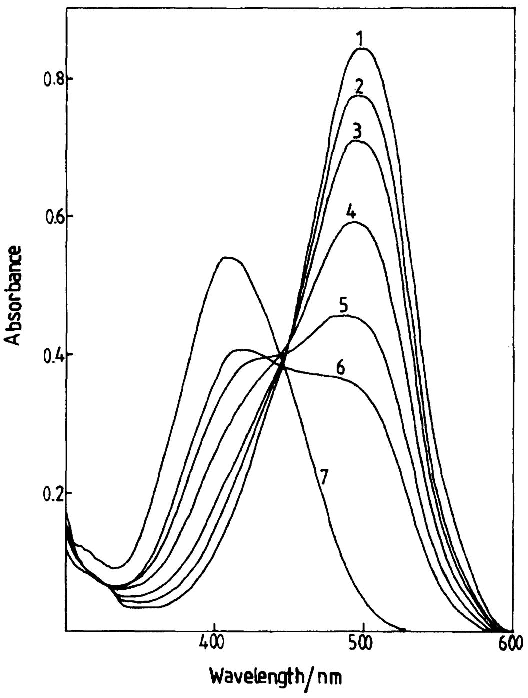

Fig. 1. Absorption spectra of Methyl Red at 25 °C in benzene–water ME of R=2.00. pH values of the buffer are 2.7(1), 5.2(2), 5.6(3), 6.0(4), 6.4(5), 6.6(6), and 12.3(7).

Table 1. Absorbance[a)] Values of Methyl Red as a Function of pH in Different Benzene–Water MEs Stabilized by SDS and 1-Butanol at 25 °C

pH of the buffer	ME I (R=48)	ME II (R=32)	ME III (R=24)
2.7	0.900 (A_a)	0.856 (A_a)	0.825 (A_a)
5.2	0.838	0.789	0.742
5.6	0.796	0.721	0.650
6.0	0.681	0.605	0.502
6.4	0.586	0.463	0.337
6.6	0.457	0.361	0.223
12.3	0.051 (A_b)	0.058 (A_b)	0.052 (A_b)

a) A at 502 nm.

λ_{max} indicates the partitioning of HMR or MR^- or both these species between aqueous and interfacial domains.

pK_a of Methyl Red in the ME was estimated using the expression:

$$pK_{a,app} = pH^w - \log[(A_a - A_x)/(A_x - A_b)], \qquad (1)$$

where A_a is the absorbance at minimum pH, A_b is the absorbance at maximum pH and A_x is the absorbance at any intermediate pH. The subscript 'app' indicates that in the calculation of pK_a the pH of the aqueous buffer solution (pH^w) used to prepare the ME has been used rather than the pH of ME (pH^m). The least-squares fitted values of p$K_{a,app}$ are 6.6, 6.38, and 6.12 in MEs of R=48, 32, and 24, respectively. Therefore, p$K_{a,app}$ tends to increase with increase in the value of R. In fact, empirically it is found that p$K_{a,app}$ varies almost linearly with $1/R$ and p$K_{a,app}$ at $1/R$=0 is estimated to be 7.11. If HMR and MR^- species are residing in the aqueous domain of the ME, then one expects a value 5.0[4)] for p$K_{a,app}$ at $1/R$=0. The higher estimated value of p$K_{a,app}$ at $1/R$=0 as well as the similarity of the visible absorption spectra of Methyl Red in the present ME to that in 60 weight per cent 1, 4-dioxane–water mixture envisage that the HMR and MR^- species are residing in the ME at domains of lower effective dielectric constant (ε_{eff}) than 78.6 (ε of H_2O). From the correlation suggested by Drummond et al.[4)] between pK_a shift and ε_{eff} of the medium, the ε_{eff} of the MEs under study is estimated to be about 45±3.

A noteworthy feature of the spectra of Methyl Red in the ME (Fig. 1) is the shifting of isosbestic wavelength at higher pH (> 6.0). This indicates that the acid-base equilibrium of Methyl Red in the ME involves more than two species unlike what we considered above. In fact, two isosbestic points at different regions of pH corresponding to two acid-base equilibria (due to protonation of azo and carboxylic groups of Methyl Red) involving three species, viz., MR^-, HMR, and H_2MR^+ were reported[4)] for Methyl Red in water, aqueous micellar solutions and 1, 4-dioxane–water mixtures. However, in these media only one isosbestic point has been observed for Methyl Red in the pH range used for the present study (excluding the two extreme pH values) and it refers to acid-base equilibrium between MR^- and HMR species.[4)] Shifting of the isosbestic wavelength noticed in the present work therefore envisages a drift in the pH range of acid-base equilibria of Methyl Red in the ME. This may be attributed to the fact that the estimation of the actual pH of MEs has not been possible. Moreover, the species involved in the acid-base equilibria of Methyl Red might be residing at the different regions (which are equivalent to different solvent systems) of the ME and this can also cause the shifting of isosbestic wavelength in ME. Absence of distinct isosbestic points in the spectra of indicator dyes in MEs of constant pH but varying R values has also been reported by Fletcher[12)] and Moulik et al.[8)]

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