SHORT PAPER

A partition equilibrium study of benzene/water/SDS-butanol oil/water microemulsions[†]

Surashree Sarma, Biren Gohain and Robin K. Dutta*

Department of Chemical Sciences, Tezpur University, Napaam, Tezpur – 784 028, Assam, India

Partition of a sulfonephthalein dye, *viz.*, phenol red, between the pseudophases in oil/water benzene/water/SDS-butanol microemulsions has been studied by UV-VIS spectroscopy and the partition equilibrium constants have been correlated with the microstructure of microemulsions and effect of cosurfactant.

Keywords: o/w microemulsion, microemulsion microstructure, partition equilibrium

Knowledge of microstructure and behaviour of microemulsions is important for several physicochemical and technological processes. Several experimental tools and methods have been used to study the microstructure of microemulsions.[1] However the microstructure and behaviour of microemulsions are still not fully understood. The pseudophase ion exchange model, which has been quite successful in study of reactions in micellar solutions, has been applied to study partition of some phenols in microemulsions.[2] Based on the fact that any chemical observation can be described in terms of a phenomenological equilibrium constant,[3] we have shown earlier that equilibrium constants of partition of dyes between aqueous and micellar pseudo-phases can be used to predict acid-base behaviour of the indicator dyes in micellar solutions of similarly charged surfactants.[4] This partition equilibrium model has also been used for easy determination of critical micellar concentrations in buffered solutions.[5] In this paper, we report a simple visible spectroscopic study of partition equilibrium of a sulfonephthalein dye, *viz.* phenol red (PR) between the water and oil–water (o/w) interface of o/w microemulsions and correlation of these equilibrium constants with microemulsion microstructure.

The o/w microemulsion systems studied were prepared using sodium dodecyl sulfate (SDS) as surfactant, *n*-butanol as cosurfactant, and benzene as oil. SDS of electrophoretic grade (SRL) was used as such. Phenol red, (Merck) was recrystallised and dried before use. Benzene, butanol, buffer components and other chemicals were of AR grade and used as such. Doubly distilled water was used in all cases. Surfactant – cosurfactant mixture, dye (both in buffered water) and oil were mixed in appropriate amounts and kept in a thermostated shaker incubator at 303 K overnight. The spectra were recorded in a Hitachi U-2001 UV-VIS spectrophotometer. Low ionic strength (*I*=0.01) buffers, adjusted following the table of Perrin[6], were used and the pH's were measured using a Systronics μ-pH System.

PR has two pK_a's in water, *viz.*, pK_{aw2} and pK_{aw1} with values 0.90 and 7.74, respectively.[7] The species involved in the equilibria corresponding to pK_{aw1} are the mono-negative form, (DH$^-$) and the doubly-negative form, (D^{2-}) of the dye. PR binds to micelles of SDS.[4a] The dye is soluble in water and insoluble in benzene, which indicates that the dye is solubilized near the head groups, *i.e.*, in the surface region of micelles in micellar solution and does not go to the core of the micelles. Similarly, the dye is partitioned between the aqueous phase and the oil-water interfacial region in o/w microemulsions.
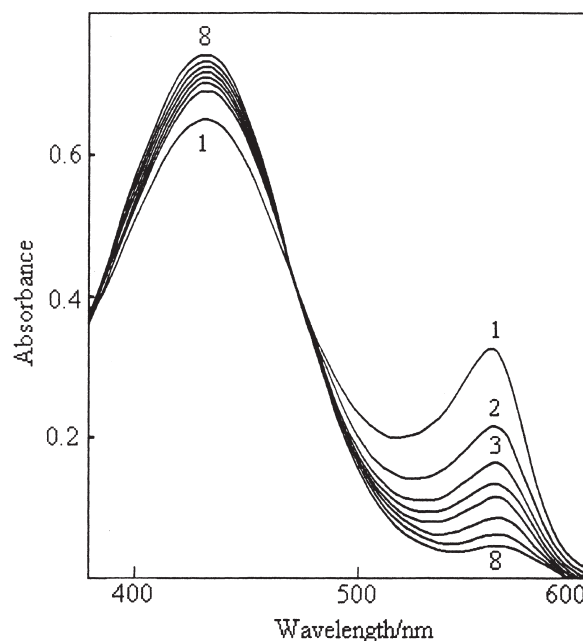
Fig. 1 The absorption spectra of PR (5x10^{-5} mol/dm^3) in microemulsions prepared by using buffered water of pH 7, benzene (ϕ = 0.01) and 1:5 weight ratio of SDS and butanol with varying amounts of SDS. [S]/(mol/dm^3) = (1) 0.0, (2)0.043, (3) 0.066, (4) 0.087, (5) 0.128, (6) 0.194, (7) 0.236 and (8) 3.02.

The DH$^-$ form of the dye associate preferentially over that of the D^{2-} form to SDS micelles.[4a] It has been observed that similar preferential association of the DH form takes place when mixture of SDS and *n*-butanol (in fixed w/w ratio) is taken in place of SDS alone. Figure 1, which shows the changes in the absorption spectra of phenol red o/w microemulsions of benzene/water/SDS-butanol, indicates similar preferential association in the case of microemulsion also. The presence of an isosbestic point in the spectra of PR in the microemulsions with varying amounts of surfactant indicates the presence of a partition equilibrium of the dye between the water and oil-water interface.

The association constant or partition constant of the dye to micelles and water can be defined by[4a]

$$K_{ass} = [D_m] / [D_w] [S_m] \tag{1}$$

where, $[D_m]$, $[D_w]$, $[S]$ and $[S_m]$ = ([S] – cmc) are concentrations of dye in micelles, dye in water, the total surfactant in the mixture and the surfactant in the micellised form, respectively. The K_{ass} and c.m.c. have been determined for PR-SDS and PR-(SDS-butanol) systems at fixed pH by using the Eqn(2) described earlier:[5]

$$(d_o-d)/d = K_{ass}[S_m] = -K_{ass}(cmc) + K_{ass}[S] \qquad (2)$$

where, d_o, d and d_m are the absorbances of the dye, in the absence, in the presence, and in the excess of surfactant or surfactant-cosurfactant mixture. The plots of $(d_o-d)/d$ *vs* [S] were found to be linear as expected. The values of K_{ass}, the cmc of the surfactant so obtained at pH 7.00 for SDS alone were 17.9 dm^3 mol^{-1} ($r = 0.9937$) and 2×10^{-2} mol dm^{-3}, respectively. The values of K_{ass} for SDS-cosurfactant mixtures were found to be 11.4, 12.6 and 22.2 (r values greater than 0.99) dm^3 mol^{-1} for weight ratios of surfactant to cosurfactant of 1:1, 1:2 and 1:5, respectively. The difference in K_{ass} values in the absence and in the presence of butanol indicates modification of the dye – micelle surface interaction by the cosurfactant.[8]

Since, the concentration of the surfactant in micellar form, $[S_m]$ is proportional to the total surface area of the micelles, a_m, Eqn (2) gives:

$$(d_o-d)/d = K_m \cdot a_m \qquad (3)$$

where, K_m is another proportionality constant. The a_m of micelles were calculated by using the equations: [9]

$$a_m = 4\pi(l+\Delta)^2(\text{number of micelle}) \qquad (4)$$
and $\qquad$ Number of micelle = $([S]-cmc)L/n \qquad (5)$

where, l is the length of hydrocarbon chain, Δ is the increment for the polar group, L is the Avogadro's constant and n is micellar aggregation number. The aggregation number increases with increase in surfactant concentration[10] and ionic strength[10] and decreases on addition of *n*-butanol.[11] The aggregation number of SDS at concentration of the surfactant 2.5×10^{-2} mol dm^{-3} at 303 K has been reported to be 52.72 and 54.25 in absence of added salt.[12] Keeping these facts in mind, in the absence of experimentally determined value, we have arbitrarily chosen a value of 54.25 for the aggregation number of SDS in the present experimental conditions and assumed it to be independent of concentration of SDS in its small experimental concentration range.[13] A linear regression of $(d_o-d)/d$ *vs*. a_m gave a value of 9×10^{-5} ($r = 0.9982$) for K_m.

The partition of the dye takes place between water and micelle surface in micellar solutions and water and droplet surface or oil–water interface of microemulsion as the dye is insoluble in oil. Considering the same value of K_m for micellar solutions and microemulsions for fixed surfactant-cosurfactant ratio, one can calculate the total oil-water interfacial area in the microemulsions, a_{me} by replacing a_m in Eqn (3) with a_{me}.

Assuming the microemulsion droplets to be mono-dispersed spheres, the radius of microemulsion droplets, R were calculated by using the Eqn (7):[1a]

$$R = 3V/a_{me} \qquad (7)$$

where, V is the volume of the oil. The results for the microemulsions at pH 7 are shown in Fig.2. For a fixed ϕ, the radius decreased with increase in amount of surfactant. On the other hand, the radius increased with volume fraction of oil at a particular concentration of the surfactant. The value of R has been found to be in a normally expected range except at high concentration of surfactant for low volume fraction of oil, where R has been predicted to be rather small. The presence of more micelles at lower ϕ might have resulted in underestimated R. It can also be seen from the figure that R is the same within experimental error limit for different surfactant cosurfactant ratios at the same surfactant concentration for $\phi = 0.010$. With increase in ϕ, the value of R
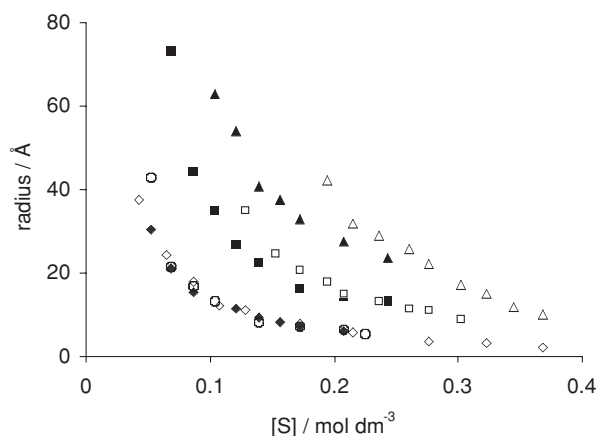

Fig. 2 Variation of radius with [S] for different surfactant–cosurfactant weight ratio and ϕ at 303K in the microemulsions: SDS : butanol = 1 : 1 , $\phi = 0.010$ (O); SDS : butanol = 1 : 2, $\phi = 0.010$ (♦), 0.020 (■) and 0.035 (▲); SDS : butanol = 1 : 5.1, $\phi = 0.010$ (◊), 0.020 (□) and 0.035 (△).

increased with increase in amount of the cosurfactant. This effect of cosurfactant, however, disappears with increase in the concentration of the surfactant. This observation may be attributed to greater incorporation of the cosurfactant into oil at higher volume fraction of oil and lower concentration of the surfactant. [14]

Microemulsions were not formed below the minimum values of [S] for the respective ϕs as shown in Fig.2. The microemulsions at higher [S] could not be studied because the differences in absorbances were too small.

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