Effect of buffers on partition equilibrium of phenol red in benzene/water/SDS-butanol oil/water microemulsions

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The effect of buffer on the partition of phenol red, an anionic dye, between the oil–water (o/w) interface, oil droplet core and the buffered bulk water in benzene/water/SDS-butanol o/w microemulsions have been studied with phosphate and Tris buffer systems.

Keywords: o/w microemulsion, partition equilibrium, acid-base equilibrium, phenol red

Microemulsions are thermodynamically stable dispersions of droplets of diameter in the range 10–100 nm of oil in water or water in oil which are stabilised by a surfactant often along with a cosurfactant. Knowledge of partition equilibrium of acid–base indicators and dyes between the oil–water interface, droplet core and the bulk, and their dependence on pH and buffer system is important for several technological applications of microemulsions, *e.g.*, nanotechnology, drug delivery, *etc.* However, there are only a few reports in the literature on partition equilibria and acid–base behaviour of indicator dyes in microemulsion systems.[1] Recently, we have reported a method to study the equilibrium of partition of an acid–base indicator dye in o/w microemulsions and correlations of the equilibrium constants with droplet size of the microemulsions using phenol red (PR) as the dye.[2] We now report the results of a study of how the buffer system and pH of water affect the equilibrium of partition of phenol red between the oil–water interface and bulk water in o/w (benzene in water) microemulsions stabilised by sodium dodecyl sulfate (SDS) and *n*-butanol.

SDS of electrophoresis grade, obtained from Sisco Research Laboratories was used as such. PR, obtained from Merck was recrystallised and dried before use. Benzene, *n*-butanol and buffer components were of AR grade and used as such. Doubly distilled water was used in all cases. Cosurfactant–surfactant mixture, dye (both in buffered water) and oil were mixed in appropriate amounts and kept in a thermostated shaker incubator at 303 K overnight to get microemulsions. The spectra were recorded at 303 K in a Hitachi U-2001 UV–VIS spectrophotometer fitted with thermostated cell holders. Low ionic strength (*I*=0.01) buffers, adjusted following the table of Perrin,[3] were used. The pHs were measured in mixture solutions without adding oil using a Systronics μ-pH System.

PR changes colour in aqueous medium in the range of pH from 6.8 (yellow) to 8.2 (red) and has the corresponding pK_{a2w} equal to 7.74.[4] The two species involved in the equilibrium, *viz.*, DH$^-$ and D^{2-}, have absorption bands in the visible region with λ_{max} at 433 and 559 nm, respectively. With increase in the concentrations of surfactant-cosurfactant mixture in the microemulsions of different fixed volume fractions of benzene, the absorption of the band corresponding to the DH$^-$ form increased at the cost of that of the band corresponding to the D^{2-} form. The λ_{max} of the band corresponding to the DH$^-$ form is gradually shifted towards higher wavelength on increasing the concentration of surfactant–cosurfactant mixture in the o/w microemulsions and found to be 572 nm in the excess of surfactant–cosurfactant mixture.

The primary site for solubilisation of polar dye is the surfactant-rich interfacial region separating oil and water domains.[1(f)] On the other hand, for a polar dye like phenol red, which is insoluble in benzene, the fraction of the dye present

in the oil droplet core can be ignored even in the presence of the cosurfactant compared to the fraction present in the bulk water, since the volume fraction of the oil is very small compared to that of water. So, we can assume that the dye is partitioned only between the interface and the bulk water. As the D^{2-} form of the dye is unlikely to be incorporated to the negatively charged interface, we can express the equilibrium of the dye in the o/w microemulsions as:[2,4,5]

$$[PR_w] + [S_i] \overset{K_s}{\rightleftharpoons} [DH_i^-] \tag{1}$$

where, $[PR_w]= ([D_w^{2-}] + [DH_w^-])$ is the total dye concentration in the bulk water, $[S_i]$ is the concentration of surfactant forming the oil–water interface, $[DH_i^+]$ is the acid form of the dye which is bound to the interface and $[D_w^{2-}]$ and $[DH_w^-]$ are the base and the acid forms of the dye in bulk water, respectively.

The partition constant K_s were determined by using Eqn (2) described earlier:[2,5b]

$$(d_o-d)/d = K_s [S_i] = - K_s(cac) + K_s[S] \tag{2}$$

where d_o, and d are the absorbances of the dye, in the absence and in the presence of surfactant or surfactant-cosurfactant mixture. [S] and (cac) are the total concentration and the critical aggregation concentration of the surfactant (analogous to critical micelle concentration), respectively. The K_ss were determined at varying oil fractions at different fixed pH at a fixed surfactant–cosurfactant ratio of 1:5. The plots of $(d_o-d)/d$ *vs* [S] were quite linear as expected. The results are shown in Fig. 1.

It is interesting to note that the association constant increased quite linearly with increase in the oil fraction for all pH values. The values of R^2 for the linear fittings of K_s *vs* volume fraction of benzene were 0.9901, 0.9968, 0.9913 and 0.9157 for pH 7.04, 7.43, 7.75 and 8.32 respectively. The correlation in each case is remarkable. The increase in the K_s with the increase in the oil fraction, at two different pH values, were almost parallel in both buffer systems. The increase in the K_s with increase in the oil fraction can be attributed to decreased droplet curvature, which makes more room for incorporation of the dye in the acid form into the hydrocarbon region of the interface.[6]

The lower increase in K_s with increase in the oil fraction in the case of the Tris buffer system than in the phosphate buffer system can be attributed to higher hydrophobicity of tris (hydroxymethyl)aminomethane.[7] In the Tris buffer systems, tris (hydroxymethyl)aminomethane competes with phenol red for occupying the space made available in the interface due to decrease in the droplet–bulk interface curvature with increase in the oil fraction. On the other hand, in the phosphate buffer systems, the phosphate ion does not compete with phenol red for the vacant space due to its hydrophilicity. Hence, with increase in oil fraction, the association of phenol red increases more in phosphate buffer than in Tris buffer.

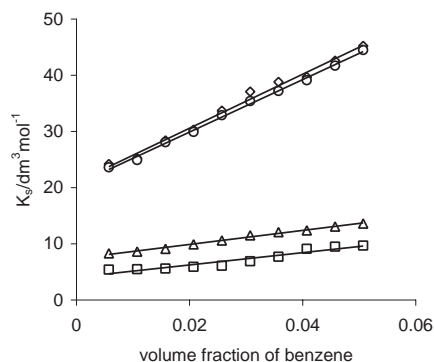* Correspondence. E-mail: robind@tezu.ernet.in

Fig. 1   Plots of K_s *vs* volume fraction of benzene for phenol red – SDS microemulsion systems at different pH values at fixed surfactant–cosurfactant w/w ratio of 1:5. ◊, SDS: Butan-1-ol at pH=7.04; ○, SDS: Butan-1-ol at pH=7.43; △, SDS: Butan-1-ol at pH=7.75; □, SDS: Butan-1-ol at pH= 8.32.

It can be seen from the figure that the partition constant decreased markedly with increase in the pH from 7.75 to 8.32 in case of the Tris buffer system, whereas it decreased relatively little with the increase in pH from 7.04 to 7.43 the case of the phosphate buffer system. The decrease in K_s with increase in pH goes in parallel with the observations in case of micellar systems.[5] With increase in pH, the concentration of the D^{2-} form of the dye increases at the cost of the DH^- form. Since the former has a lower tendency for association with the anionic oil-water interface, the K_s decreases.

The marked decrease in K_s with increase in the pH in the Tris buffer system compared to that in the phosphate buffer system can also be attributed to competition between phenol red and tris(hydroxymethyl)aminomethane for incorporation to the hydrophobic palisade layer of the oil–water interface. With increase in the pH the incorporation of phenol red to the interface decreases to a greater extent due to electrostatic repulsion, compared to the incorporation of the organic buffer component.

Conclusions

From the present study we can conclude that the equilibrium constant for partition of phenol red between the oil–water interface and bulk water increases with increase in the oil fraction due to incorporation of the dye in the hydrocarbon region of the interface with decreasing droplet curvature. In the Tris buffer system, the organic buffer component competes with the dye for incorporation in the interface.

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