Association of neutral red with micelles and its effect on the pK_a

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Received June 22, 1992[2]

ROBIN K. DUTTA and SUBRAY N. BHAT. Can. J. Chem. **71**, 1785 (1993).

The interactions of neutral red with cationic surfactants, viz., *N*-hexadecylpyridinium chloride and alkyltrimethylammonium bromides; a nonionic surfactant, viz., Triton X100; and an anionic surfactant, viz., sodium dodecyl sulfate, were investigated spectroscopically. The equilibrium constants for the association of the indicator with the micelles were determined from the apparent association constants at constant pH at 298 K. The effects of the indicator–micelle association on the apparent pK_a of the indicator in aqueous surfactant solutions are discussed. It was shown that the apparent pK_a of the indicator in cationic surfactant solution can be predicted from knowledge of the indicator–micelle association constant.

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Faisant appel à la spectroscopie, on a examiné les interactions entre le rouge neutre et des agents tensioactifs cationiques (le chlorure de *N*-hexadécylpyridinium et les bromures d'alkyltriméthylammonium), un agent tensioactif non ionique (le Triton X100) et un agent tensioactif anionique (le dodécylsulfate de sodium). En se basant sur les constantes apparentes d'association, à pH constant, à 298 K, on a déterminé les constantes d'équilibre pour l'association de l'indicateur avec les micelles. On discute des effets de l'association indicateur–micelle sur le pK_a apparent de l'indicateur dans des solutions aqueuses d'agent tensioactif. On a démontré que l'on peut prédire le pK_a apparent de l'indicateur dans la solution d'agent tensioactif cationique à partir d'une connaissance de la constante d'association indicateur–micelle.
[Traduit par la rédaction]

Introduction

Micelles are frequently employed in combination with acid–base indicators in analytical chemistry to shift the chemical equilibrium and pK_a of the indicator to a desired degree (1). The effect of micelles on the pK_a of an indicator is due to micellar catalysis of the acid dissociation reaction (2). The shifts in the pK_a have been attributed to an electrostatic potential at the micelle surface (3), to ion exchange between the micelle surface and the bulk aqueous phase (4), and to low interfacial effective dielectric constant, interfacial salt effect, and ion-pair formation between oppositely charged indicator species and monomeric surfactant head groups (5). Nevertheless, most of the indicator equilibria in micellar medium studied so far are cases in which the indicator species are completely incorporated into the micelles. Even recently, it was considered pointless to analyse the observed p$K_{a,app}$'s of indicators in which both the conjugate acid–base forms are not fully solubilized by the micelles (5*d*). The association constants of indicators with micelles may be quite informative about the pK_a shifts of such partly solubilized indicators, as any observation can be better understood with the help of equilibrium properties (3*b*). In the present paper we report the results of a systematic study of the preferential association of 3-amino-7-dimethylamino-2-methyl phenazinium chloride (neutral red), with micelles of cationic, nonionic, and anionic surfactants at constant pH, and the effect of such associations on the observed p$K_{a,app}$ of the indicator (6). The structures of neutral red in its base (NR) and acid (NR^+H) forms are shown in Scheme 1.

Experimental

Neutral red, a Sigma product, was recrystallized twice from a water–ethanol mixture and dried before use. *N*-Hexadecylpyridinium chloride (cetylpyridinium chloride, CPC) was obtained from Hexel Corporation, U.S.A. Hexadecyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB), and Triton X100 ($(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_{10}OH$, TX100) were Sigma products. Tetradecyltrimethylammonium bromide (TTAB) was obtained from Sisco Research Laboratories, India. All cationic surfactants were recrystallized from acetone. Sodium dodecyl sulfate (SDS), obtained from Aldrich, was first washed with ether and then recrystallized from ethanol and the recrystallized samples were dried in a vacuum desiccator. TX100 was used as such. Buffer constituents were of AR grade. Triply distilled water, prepared by adding $KMnO_4$ in the first distillation, was used as solvent.

The visible absorption spectra were recorded by a Hitachi-330 spectrophotometer using a matched pair of cells of 1-cm path length fitted in a thermostated cell holder. The pH of the solutions was measured using a Systronics Digital pH meter model-335. All the experiments were carried out at 298 (±0.1) K.

Results and discussion

p$K_{a,w}$ of neutral red

Neutral red, in aqueous solution, exists in two forms, viz., NR^+H and NR, which are in equilibrium with each other. NR, which has an absorption maximum at 450 nm, is yellow in color, whereas NR^+H, a red-colored product, is reported to have an absorption maximum between 535 and 545 nm (7). The position of the λ_{max} of NR^+H is dependent upon the constituents of the buffer. The variation of the λ_{max} of neutral red in different buffer media has been attributed to formation of dimers and higher aggregates of the dye where buffers are believed to influence the aggregation equilibrium differently (5*c*, 7). We have observed that in phthalate buffer of pH 4 (0.05 mol dm^{-3} potassium hydrogen phthalate) the λ_{max} is 538 nm, whereas in phosphate buffer, i.e., in the presence of 0.05 mol dm^{-3} KH_2PO_4 and 0.001 mol dm^{-3} HCl, it is 527 nm. The visible spectra of the acid–base titration of neutral red using phosphate buffer (0.05 mol dm^{-3} KH_2PO_4 with added NaOH or HCl) pass through a sharp isosbestic point at 477 nm, whereas such a sharp isosbestic point was not observed in phthalate buffer (0.05 mol dm^{-3} potassium hydrogen phthalate with added NaOH) medium.

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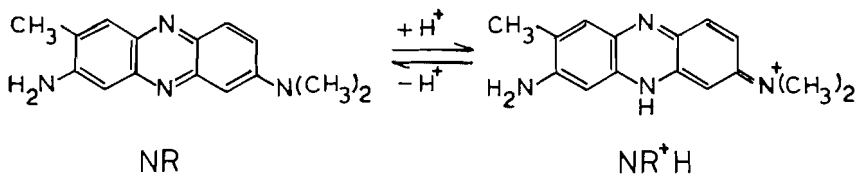
[2]Revision received June 1, 1993.



SCHEME 1

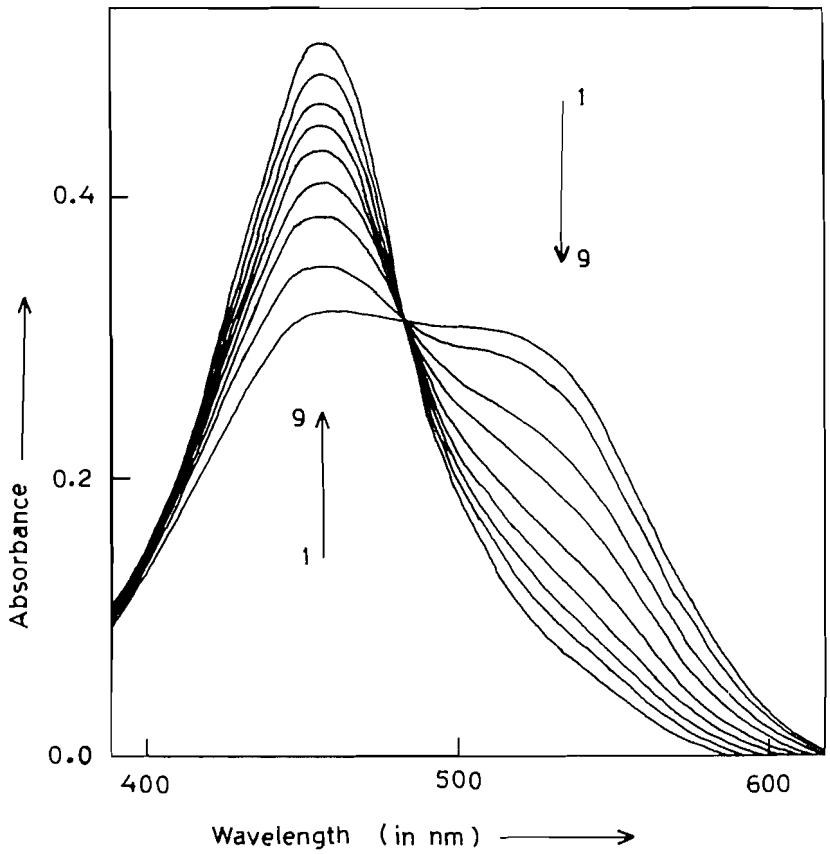


FIG. 1. Spectra of neutral red (4×10^{-5} mol dm^{-3}) at various concentrations of CPC at pH 7.25; concentrations of CPC $\times$ 10^{-4} mol dm^{-3}: 1 = 0.0, 2 = 1.2, 3 = 2.4, 4 = 3.6, 5 = 5.9, 6 = 9.5, 7 = 14.2, 8 = 24.1, and 9 = 114.9.

We feel that the absence of a clear isosbestic point in the spectra of neutral red, as reported by Drummond et al. (*5c*), was because these authors used more than one buffer system in the same experiment. The p$K_{a,w}$ of neutral red determined using KH_2PO_4 (0.05 mol dm^{-3}), NaOH, and HCl (for varying pH) was found to be 6.75 ($\pm$0.02), whereas the reported values vary from 6.5 to 7.4 (*5c*, 8).

Determination of K_{ass} *at constant pH*

The visible absorption spectra of neutral red in varying concentrations of CPC at pH 7.25 (0.05 mol dm^{-3} KH_2PO_4 + 0.036 mol dm^{-3} NaOH) are shown in Fig. 1. As the concentration of CPC was increased from 0 to 1.15×10^{-2} mol dm^{-3}, the absorption on the higher wavelength side (λ_{max} = 527 nm) decreased, whereas that on the lower wavelength side (λ_{max} = 460 nm) increased and a sharp isosbestic point was observed at 482 nm. The positions of the absorption maxima and the isosbestic point were not affected when the surfactant was changed from CPC to CTAB, TTAB, and DTAB. The presence of the isosbestic point indicates the existence of an equilibrium between the indicator species in aqueous and micellar pseudophases. The shift in the λ_{max} from 450 nm (in water) to 460 nm (in surfactant) is due to the association of the basic form of neutral red with the CPC micelles. The λ_{max} was found to be same in buffered micellar media of pH 7.25 (0.05 mol dm^{-3} KH_2PO_4 + 0.036 mol dm^{-3} NaOH), 7 (0.05 mol dm^{-3} KH_2PO_4 + 0.029 mol dm^{-3} NaOH), and 5.87 (0.05 mol dm^{-3} KH_2PO_4 + 0.0043 mol dm^{-3} NaOH). The effect of an increase in CPC concentration at constant pH is similar to that of an increase in pH of the aqueous indicator solution. It can be mentioned here that the pH of phosphate buffer solutions of pH 7.25, 7.00, and 5.87 (compositions as mentioned above) are unaffected on addition of cationic surfactants up to a concentration of ca. 0.02 mol dm^{-3}. This observation parallels that reported by Bunton and Minch (9).

The acid–base equilibrium of an indicator is represented by

$$[1] \quad A_w^z \overset{K_{a,w}}{\rightleftharpoons} B_w^{z-1} + H_w^+$$

where A_w^z and B_w^{z-1} are the acid and its conjugate base forms and $K_{a,w}$ is the acid dissociation constant of the indicator in

TABLE 1. Association constants of neutral red with surfactants at various pH, K_{ass}, and the equilibrium constants (independent of pH) K_s and K_e at 298 (±0.1) K

Surfactant	pH (±0.01)	The cmc of the surfactant in buffer medium (× mol dm^{-3})	K_{ass} (× mol dm^{-3})	K_s (× mol dm^{-3})	pK_e
CPC	7.25[a]	1.2×10^{-4}	3800 (±50)	5000	3.05
CPC	7.00[b]	1.7×10^{-4}	3060 (±50)	4990	3.05
CPC	5.87[c]	7.0×10^{-4}	580 (±20)	4980	3.05
CTAB	7.00[b]	7.0×10^{-5}	3630 (±50)	5920	2.98
TTAB	7.00[b]	7.0×10^{-4}	2440 (±50)	3980	3.15
DTAB	7.00[b]	7.0×10^{-3}	900 (±20)	1470	3.58
TX100	7.00[b]	5.0×10^{-4}	610 (±20)		
SDS	9.20[d]	7.4×10^{-4}	1400 (±50)		

[a]Buffer composition: 0.05 mol dm^{-3} KH_2PO_4 + 0.036 mol dm^{-3} NaOH.
[b]Buffer composition: 0.05 mol dm^{-3} KH_2PO_4 + 0.029 mol dm^{-3} NaOH.
[c]Buffer composition: 0.05 mol dm^{-3} KH_2PO_4 + 0.0043 mol dm^{-3} NaOH.
[d]Buffer composition: 0.01 mol dm^{-3} $Na_2B_4O_7$.

water. It follows from the definition of $K_{a,w}$ that at constant pH

$$[2] \quad [In_w] = [B_w^{z-1}](1 + [H_w^+]/K_{a,w}) = [A_w^z](1 + K_{a,w}/[H_w^+])$$

where $[In_w]$ is the total indicator concentration. In other words, it is possible to consider the total concentration of the indicator for an equilibrium study in buffered medium since the relative concentrations of the two indicator species remain the same irrespective of the total concentration at constant pH.

The expression of the association equilibrium of the indicator with the micelles can be simplified if eq. [2] holds in the micellar pseudophase. This would be so if the buffers were able to control the pH of the micellar surfaces, about which there have been differing reports in the literature (10, 11). Quina et al. (10) are of the opinion that buffers do not control the pH of the micellar surface. Frahm and Diekmann (11) observed that, within experimental uncertainties, the micellar surface potential is independent of the surfactant concentration (up to 10 times the critical micelle concentration). Nevertheless, in the present case, the intensity of the absorption band due to the acid form of the dye decreases with increase in concentration of the cationic surfactant and the band almost disappears at higher concentrations of surfactant (e.g., at and above ca. 1.15×10^{-2} mol dm^{-3} of CPC at a pH of 7.25; Fig. 1). This indicates that only NR is partitioned between the aqueous and micellar pseudophases, whereas NR^+H is largely in water. Therefore, for the present case, the total concentration of the indicator in the micellar pseudophase can be approximated to the total concentration of NR in the micellar pseudophase, i.e., we can consider a total indicator concentration term $[In_m]$ for the indicator in the micellar pseudophase.

Thus,

$$[3] \quad In_w + S_m \overset{K_{ass}}{\rightleftharpoons} In_m$$

or

$$[4] \quad K_{ass} = [In_m]/([In_w] \cdot [S_m])$$

where K_{ass} is the association constant of indicator with micelles at constant pH and $[S_m]$ is the micellized surfactant. In principle, eqs. [3] and [4] should be applicable for any indicator–micelle association interaction at any pH. However, in the presence of other types of molecular interactions, e.g., ion-pair formation between oppositely charged indicator species and monomeric surfactant, the equations are not applicable.

The association constants, K_{ass}, of indicator with micelles at constant pH were determined using Ketelaar's equation (12):

$$[5] \quad \frac{[In]_0}{(d-d_0)} = \frac{1}{(\epsilon_{ass}-\epsilon_0)} + \frac{1}{K_{ass}(\epsilon_{ass}-\epsilon_0)[S_m]_0}$$

where $[In]_0$ is the total concentration of the indicator, d and d_0 are the optical densities of the indicator in the presence and absence of the surfactant, respectively, ϵ_{ass} and ϵ_0 are the extinction coefficients of the indicator in the micelle-associated and free states, respectively, and $[S_m]_0$ is the total concentration of micellized surfactant, i.e., $[S_m]_0$ = (total concentration of surfactant − cmc) where cmc is the critical micelle concentration of the surfactant in the buffered medium, obtained from changes in absorbance of the indicator with addition of the surfactant.

The plots of $[In]_0/(d - d_0)$ *vs.* $(1/[S_m]_0)$ are quite linear, which suggests the validity of the assumption that the change in the ratio of acid to base forms of neutral red in the micellar pseudophase with change in surfactant concentration is within the experimental uncertainty. The K_{ass} values obtained from such plots are summarized in Table 1. It can be seen from the data that, in the case of CPC, K_{ass} increases with increase in pH of the medium. This can be attributed to the fact that at higher pH the concentration of the nonionic form of the indicator is high and it has preferential affinity towards the cationic micelles (rather than the cationic form). The value of K_{ass} of the indicator with CTAB (which has the same hydrocarbon chain length as CPC but a different head group) at constant pH 7 (0.05 mol dm^{-3} KH_2PO_4 + 0.029 mol dm^{-3} NaOH) was found to be higher than that with CPC. This indicates that the association of the indicator with cationic micelles not only depends on the hydrocarbon chain length but also on the head group of the surfactant. It is quite interesting to note that, as in the case

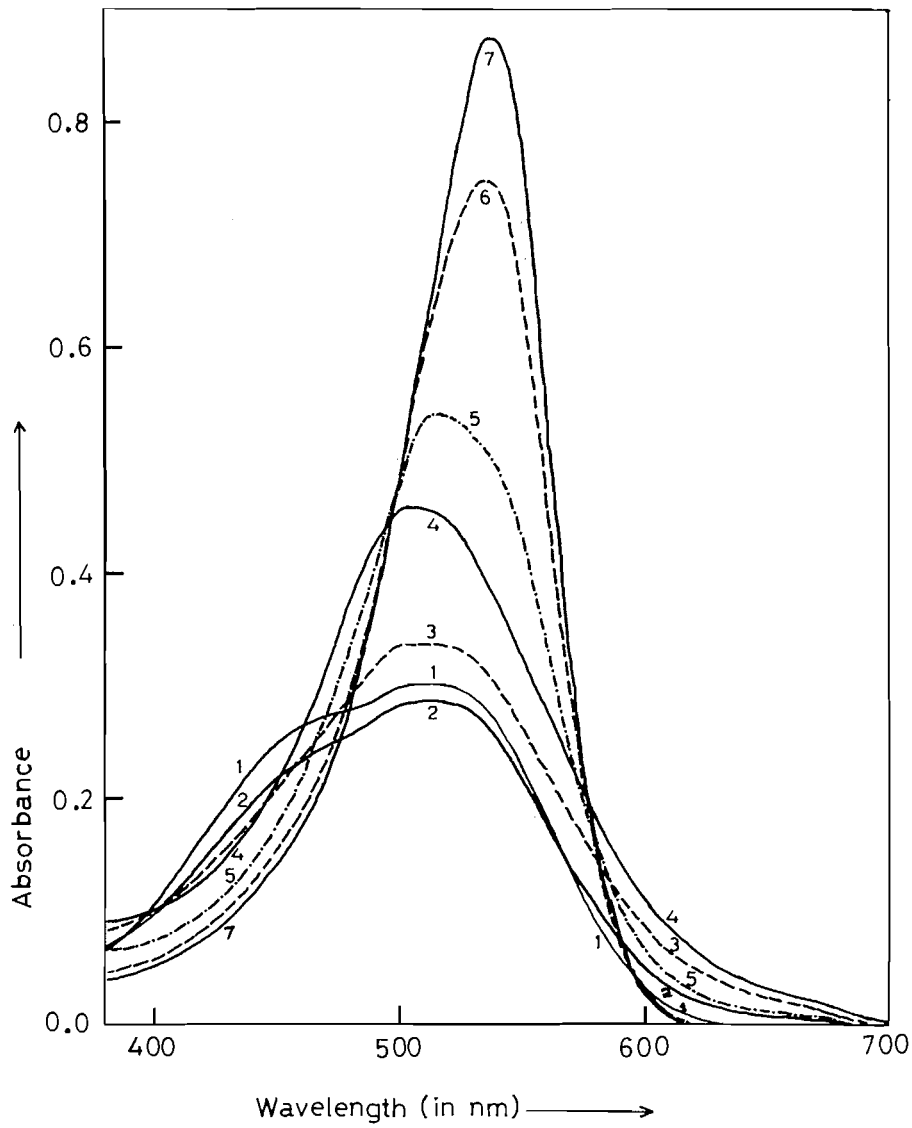


FIG. 2. Spectra of neutral red (3.2×10^{-5} mol dm^{-3}) at various concentrations of SDS at pH 7; concentrations of SDS $\times 10^4$ mol dm^{-3}: 1 = 0.0, 2 = 2.0, 3 = 2.8, 4 = 4.0, 5 = 8.0, 6 = 14.0, and 7 = 200.

of aqueous medium, the plot of the (log cmc) of CTAB, TTAB, and DTAB in buffered medium of pH 7 vs. hydrocarbon chain length is quite linear (13). This probably implies that even though the presence of the buffer components lowers the cmc, the process of micelle formation in the buffered medium is otherwise similar to that in pure water. The effect of surfactant counterions Cl^- or Br^- on K_{ass} cannot be inferred from the present study as the relatively large concentration of phosphate ion in the buffer solutions ensures that the counterion is mainly phosphate.

The spectra of neutral red (at constant pH 7) in varying amounts of TX100 are almost similar to those of neutral red in CPC and this indicates that the TX100 micelles associate with NR in preference to NR^+H. At higher concentrations of TX100, a weak shoulder at ca. 538 nm appears, which can be ascribed to a comparatively weaker but appreciable interaction of NR^+H with the micelles. The presence of an NR^+H–micelle association does not invalidate eqs. [3] and [4] as K_{ass} includes the associations of both species (i.e., NR and NR^+H) with micelles. The low K_{ass} of the indicator with TX100 (Table 1) suggests that the interaction is weak.

The spectra of neutral red in varying amounts of SDS at pH 7 are shown in Fig. 2. The lack of a single isosbestic point indicates the presence of more than one type of equilibrium between the indicator and the surfactant. At very low concentrations of SDS (i.e., below the cmc, the cmc in this buffer found, from surface tension measurements, to be ca. 7.4×10^{-4} mol dm^{-3}) the indicator absorbs in the high-wavelength region, ca. 580–680 nm. This absorbance has been attributed to the doubly protonated neutral red that is obtained in strong acidic medium of pH <1 in aqueous medium (7). Recently we showed that phenazinium dyes, which are generally protonated in highly acidic medium (below pH 1), can undergo protonation in submicellar anionic surfactant solutions even in neutral media, where the protonation is enforced by the strong hydrophobicity of the dye–surfactant ion pair (14). So, the absorption band above 580 nm can be attributed to doubly protonated neutral red in the dye–surfactant ion pair, viz., $NR^{2+}H_2 \cdot SDS^-$. At higher concentration of SDS (above the cmc) the λ_{max} was found to be 538 nm. The absorbance at this wavelength can be attributed to micelle-associated NR^+H. The determination of K_{ass}

of the indicator with SDS micelle at this pH was not possible due to the presence of more than one type of interaction. The spectral changes of the indicator with addition of SDS at pH 4.5 (acetate buffer) were almost similar to those at pH 7. However, at pH 9.2 (borate buffer), the spectral data (Fig. 3) show that there is no interaction (e.g., formation of $NR^{2+}H_2 \cdot SDS$) in the submicellar concentration range, whereas at higher concentration of surfactant (above the cmc) there is a clear isosbestic point at 466 nm, indicating the presence of an equilibrium. As the concentration of SDS is increased, the absorbance of the band on the higher wavelength side (λ_{max} = 538 nm) increases. Unlike the results obtained in CPC and TX100, the increase in intensities at higher wavelengths is much more comparable to the decrease in intensities of the 450-nm band (which shifts to 461 nm with increase in concentration of SDS). With the addition of more and more SDS, the anionic micelles associate with NR^+H in preference to NR. Therefore, the new band at λ_{max} = 538 nm can be ascribed to NR^+H_m. Absorption in the region of ca. 580–680 nm is absent above the cmc, possibly due to association of indicator with micelles, whereupon the protonated ion pairs are dissociated (Figs. 2 and 3). The shift of the 450-nm band of NR to 461 nm indicates that the conjugate base form, NR, is also associated (even though to a lesser extent than NR^+H) with the anionic micelles of SDS.

It has been seen that neutral red associates with cationic micelles only in the deprotonated form, NR. The association of the protonated form, NR^+H, is negligible compared to that of NR because of electrostatic repulsion between similar charges on the indicator and the micelle. Such behaviour is expected when the indicator is less hydrophobic (or more water soluble). Thus, substituting $[In_m]$ by $[B_m^{z-1}]$ in eq. [4] gives

$$[6] \quad K_{ass} = [B_m^{z-1}]/([In_w][S_m])$$

Now, we can examine the overall equilibrium constant, K_e, of neutral red in the cationic micellar medium (15):

$$[7] \quad NR^+H_w + S_m \overset{K_e}{\rightleftharpoons} NR_m + H_w^+$$

This equilibrium is the product of the partial equilibria [8] and [9]:

$$[8] \quad NR^+H_w \overset{K_{a,w}}{\rightleftharpoons} NR_w + H_w^+$$

and

$$[9] \quad NR_w + S_m \overset{K_s}{\rightleftharpoons} NR_m$$

where K_s is the pH-independent association constant of NR_w with similarly charged micelles (16) and is related to K_{ass} and K_e by

$$[10] \quad K_s = K_{ass}(1 + [H_w^+]/K_{a,w})$$

and

$$[11] \quad K_e = K_s \cdot K_{a,w}$$

A direct determination of K_s for the base form of neutral red is difficult as the indicator is unstable in strong basic medium, the condition required for the same. The equilibrium constants K_s and K_e calculated for neutral red with cationic micellar systems at various pH are included in Table 1. It can be seen from the table that K_s and K_e are independent of pH and are true thermodynamic quantities.

$pK_{a,app}$ of neutral red

The apparent dissociation constant, $K_{a,app}$ of an indicator in micellar solution is defined (9) as

$$[12] \quad K_{a,app} = \frac{[\text{total indicator in conjugate base form}]\,[H_w^+]}{[\text{total indicator in acid form}]}$$

For neutral red in cationic micellar medium:

$$[13] \quad K_{a,app} = ([NR_m] + [NR_w])\,[H_w^+]/[NR^+H_w]$$

or,

$$[14] \quad K_{a,app} = K_{a,w} + K_{ass} \cdot [S_m]\,([H_w^+] + K_{a,w})$$

or,

$$[15] \quad K_{a,app} = K_{a,w}(1 + K_s \cdot [S_m])$$

Thus, once the value of K_{ass} at (a suitable) fixed pH or the value of K_s is known, $K_{a,app}$ of the indicator at any concentration of the surfactant can be predicted. The $pK_{a,app}$ thus predicted for neutral red at various concentrations of CPC are shown in Fig. 4 along with the experimentally determined values. Here it can be mentioned that an error in the experimental $pK_{a,app}$ values is expected to be involved due to the variation in ionic strength of the medium, as the experimental values were determined using buffer (3*a*, 17). However, the variation in ionic strength of the medium (due to addition of NaOH) was within 0.04. It has been reported that when the ionic strength of the medium was varied from 0.1 to 0.5, the pK_a of neutral red altered by ca. 0.07 (18). Therefore the variation in the ionic strength or the interfacial salt effect is not likely to have any significant effect on the acid–base equilibria of neutral red in micellar medium (5*c*). The predicted $pK_{a,app}$, obtained from K_{ass} of different pH, were within the experimental error limit of ±0.1. The $pK_{a,app}$'s (predicted as well as observed) decrease with increase in concentration of CPC and finally level off. Our observations parallel those of Rychlovsky and Nemcova (19) who had observed such a trend in similar systems. The decrease in $pK_{a,app}$ with increase in concentration of CPC is expected from the fact that the higher the micelle concentration, the greater is the incorporation of NR into the micelles (in preference to that of NR^+H), which causes an increase in the relative concentration of the conjugate base form of the indicator at the expense of the acid form. It can be noted here that the predicted and observed pK_a values for the indicator in TTAB also agreed well with each other.

The acid–base equilibria of neutral red in aqueous nonionic and anionic surfactants were studied by Drummond et al. (5*c*). As both the base and conjugate acid forms of the indicator associate with nonionic micelles, such acid–base equilibria cannot be explained simply in terms of indicator–micelle association. In nonionic surfactants, considering partition of both forms of the indicator between the micellar pseudophase and aqueous phase, one can predict the $pK_{a,app}$. But for such predictions, the dissociation constant of the indicator in the micellar pseudophase is required. As in the case of nonionic micelles, both forms of the indicator associate with anionic micelles. Drummond et al. (5*c*) were of the opinion that ion-pair formation between NR^+H and the anionic headgroup of SDS, a "specific molecular interac-

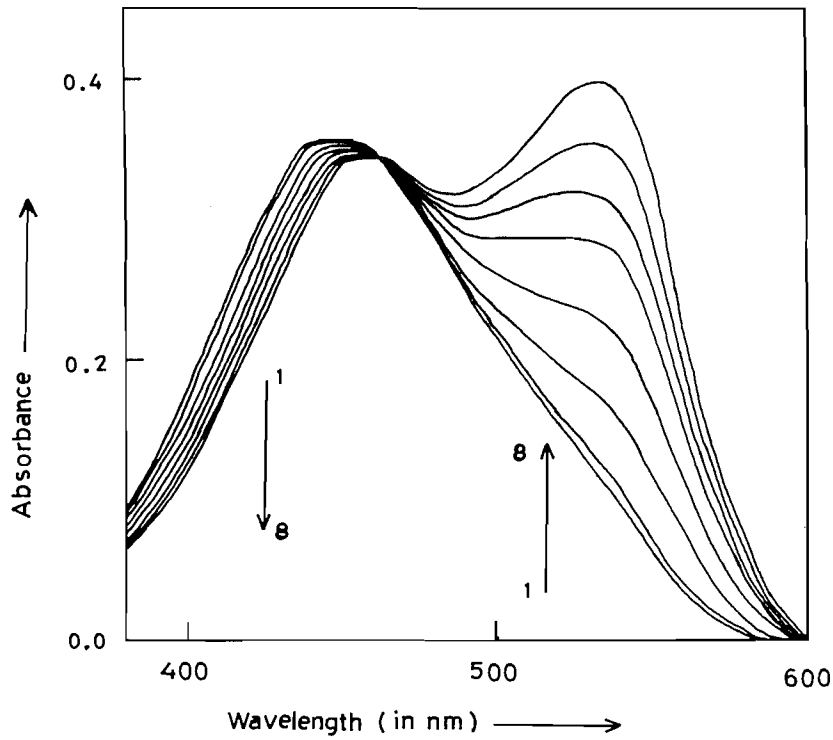


FIG. 3. Spectra of neutral red (4×10^{-5} mol dm^{-3}) at various concentrations of SDS at pH 9.2; concentrations of SDS $\times 10^4$ mol dm^{-3}: 1 = 0.0, 2 = 7.5, 3 = 10.0, 4 = 12.6, 5 = 17.6, 6 = 25.1, 7 = 50.2, and 8 = 251.0.

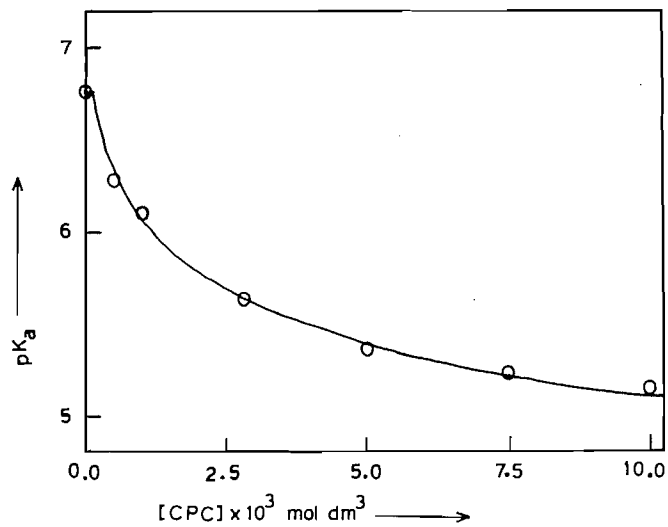


FIG. 4. Plot of predicted and observed $pK_{a,app}$ of neutral red in aqueous micellar medium of CPC *vs.* concentration of CPC; solid curve: predicted; O: observed.

tion," is one of the factors that affects the $pK_{a,app}$ of neutral red in SDS. Our observation indicates that the so-called specific molecular interaction is not simply an ion pair between NR^+H and SDS head groups but in fact $NR^{2+}H_2 \cdot SDS^-$, where the strong hydrophobicity of the hydrocarbon tail of the monomeric surfactant induces the second protonation.

Conclusion

The apparent association constants of neutral red with micelles at constant pH can be determined by the present method. The equilibrium constant for the association of the indicator with the cationic micelles can be determined from the apparent association constant. The apparent pK_a of the indicator in cationic micellar solutions can be predicted from the equilibrium constants.

Acknowledgement

One of the authors (R.K.D.) thanks North-Eastern Hill University and the University Grants Commission for the award of a senior research fellowship.

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