

**ACID-BASE AND OPTICAL PROPERTIES OF NEUTRAL RED IN THE PRESENCE OF IONIC AND NONIONIC TENSIDES**

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Changes in the optical and acid-base characteristics of neutral red in the presence of hexadecylpyridinium bromide, hexadecyltrimethylammonium bromide,  $\alpha$ -carbethoxy-pentadecyltrimethylammonium bromide (Septonex), sodium dodecyl sulphate, Triton X-100, and BRIJ 35 in submicellar and micellar concentrations were studied spectrophotometrically. The conditional dissociation constant of neutral red  $pK_{ai}^*$  depends on the kind and concentration of tenside, kind and concentration of inert electrolyte, and concentration of the cationic dye. Changes in the  $pK_{ai}^*$  values are described in terms of formation of ionic associates of the dye with the tenside and of the inert electrolyte ions with the tenside. The validity of equations for the dependence of  $pK_{ai}^*$  on the logarithm of tenside concentration was proved experimentally over a wide region of cationic tenside concentrations. The changes in  $pK_{ai}^*$  can also be partly accounted for by changes in the nature of the solvent. A titrimetric method based on the changes in the conditional dissociation constant of neutral red is suggested for the determination of tensides in aqueous solutions using photometric end point indication.

It has been known that tensides and coloured organic reagents form ionic associates of stoichiometric composition. The stable electroneutral associates are low soluble in water and in polar organic solvents and well extractable into low polar organic solvents. The formation of ionic associates is employed for the extraction-photometric determination of tensides<sup>1</sup> or their determination by a two-phase titration with visual or photometric end point indication using dye indicators<sup>2</sup>.

Stoichiometric ionic associates are solubilized at higher total concentrations of tensides. This is accompanied by appreciable changes in the acid-base and optical properties of the coloured organic reagents. The interaction is associated with shifts of the absorption bands of the reagent or appearance of a new absorption band of the ionic associate. The conditional dissociation constants of the acid-base transitions are varied as well, the changes being dependent on the kind and concentration of tenside, kind and concentration of inert electrolyte, and total concentration of the organic analytical reagent<sup>3-21</sup>. The changes are most marked in the region of submicellar concentrations of the cationic tenside whereas in a range close to the critical micellar concentration the changes are very low or nil<sup>3-7</sup>.

Whereas interactions of acidic dyes with tensides of various kind have been studied extensively, little attention has been so far paid to interactions of basic dyes with tensides. The nature of interactions between tensides and coloured organic reagents is as yet not fully understood. The changes in the optical and acid-base characteristic have been explained in terms of formation of ionic associates or ion pairs of the reagent with molecules of the tenside or with micellar aggregates<sup>9-11</sup>. Sorption of reagent molecules or the stoichiometric ionic associates  $\{L^{\cdot} \cdot T^+\}$  on the micelle surface<sup>12-16</sup> or their embedding in the inner structure of micelles<sup>17,18</sup> has also been considered.

The quantitative description of the interaction of the reagent with tensides is based on the assumption of electrostatic interaction and on the ion exchange model<sup>19,20</sup>. The changes in the conditional dissociation constants of anionic dyes have been described<sup>21</sup> by equations derived from relations for the dissociation constant of the reagent, equilibrium constants of formation of the ionic associate of tenside  $T^+$  with the anionic reagent species  $L^{n-1}$  or the anion of the inert electrolyte  $X^-$ , and the equilibrium constants of formation of the polymeric ionic associate of the micellar aggregate  $\{T^+ \cdot X^-\}_n$ . The changes in the optical and acid-base properties of acidic dyes in the presence of nonionic tensides have also been interpreted in terms of changes in the characteristic properties of the solvent and solvation of the species present<sup>6-9</sup>.

In the present work, the validity of the models is tested on a case of a cationic dye combined with ionic and nonionic tensides in various experimental conditions, and the relation for the dependence of the change in the conditional protolytic constant of the dye in the presence of ionic tensides on the concentration of ions  $T^+$  or  $T^-$  is verified. Neutral red (NR), an azine dye whose dissociation constant lies in the neutral range ( $pK_{a,i} \approx 6.8$ ), was elected as a model dye of basic nature; this permitted the experimental conditions to be varied to a greater extent than as is feasible with the majority of other dyes.

## EXPERIMENTAL

### Chemicals and Apparatus

Neutral red (3-amino-6-dimethylamino-2-methylphenazine hydrochloride,  $C_{15}H_{17}N_4^+Cl^-$ ) was a chromatographically pure chemical<sup>22</sup> (KEPEC Chemische Fabrik, F.R.G.). Stock solutions with  $c_L = 0.4-1 \text{ mmol l}^{-1}$  were prepared by dissolution of weighed amounts of the chemical in distilled water. Acid stock solutions of the dye (pH 4) were stable for a minimum of two weeks whereas alkaline solutions exhibited absorbance decrease in several days (daily decrease approximately 1%).

Sodium dodecyl sulphate ( $C_{12}H_{25}OSO_3Na$ , henceforth SDS) was obtained from BDH (U.K.). Stock solutions were prepared in concentrations of  $1-10 \text{ mmol l}^{-1}$  by dissolution of the solid chemical in water. Septonex ( $\alpha$ -carbethoxypentadecyltrimethylammonium bromide,

$C_{20}H_{42}O_2NBr$ , henceforth SPX) was a chemical supplied by Slovakoфарма, Hlohovec, in a purity conforming to Czechoslovak Pharmacopoeia. Hexadecylpyridinium bromide ( $C_{21}H_{38}NBr$ , henceforth CPB) and 1-hexadecyltrimethylammonium bromide ( $C_{19}H_{42}NBr$ , henceforth CTMAB) were purified chemicals obtained from Lachema, Brno. They were used in stock solutions in concentrations  $c_T = 1-10 \text{ mmol l}^{-1}$ , prepared by dissolving the chemicals in ethanol and diluting to volume with water so that the resultant ethanol fraction was 20 vol. %.

BRIJ 35 (polyoxyethylene monododecyl ether,  $M_r = 900$ ) of reagent grade purity (Merck, Darmstadt, F.R.G.) was used in stock solutions in concentrations  $q_T = 1-20 \text{ g l}^{-1}$ . TRITON X-100 (*p*-octylphenol poly(ethylene glycol) ether,  $n \approx 10$ ,  $M_r = 750$ ) of reagent grade purity (Koch-Light, U.K.) was used in stock solutions with volume fractions  $\varphi_T = 0.1-2\%$ . The stock solutions were prepared by dissolving the appropriate amounts in water.

The other compounds used were chemicals of reagent grade purity supplied by Lachema, Brno. The stock or working solutions were obtained by dissolving the chemicals or diluting to the desired concentrations (largely  $1 \text{ mol l}^{-1}$ ). Ethanol was purified by distillation and contained typically 4.5 vol. % water and 5.0 vol. % methanol.

Acidity of the solutions was measured with a PHM 84 pH-meter equipped with a G 202 B glass electrode and a K 401 saturated calomel electrode (Radiometer, Copenhagen, Denmark), or with an OP 208/1 pH-meter equipped with an OP 0808 combined electrode (Radelkis, Budapest, Hungary). The instruments were calibrated periodically using standard phosphate, phthalate, and oxalate buffers obtained from Radiometer (pH  $7.00 \pm 0.01$ ,  $4.01 \pm 0.01$ , and  $1.68 \pm 0.01$ , respectively, at  $25^\circ\text{C}$ ).

The absorption spectra were scanned and the absorbance-pH curves obtained by using a Superscan 3 double-beam spectrophotometer (Varian, Switzerland) controlled with an HP 9815A desktop computer (Hewlett-Packard, U.S.A.). The measurements were carried out at  $25^\circ\text{C}$  over the region of 320-620 nm using quartz cells 1-40 mm optical pathlength. The other dependences were measured and spectrophotometric titrations performed by using a Spekol 21 single-beam spectrophotometer (Carl Zeiss, Jena, G.D.R.) in glass cells 10 or 20 mm pathlength.

### Procedures

The time stability of the stock solutions of NR in a concentration of  $40 \mu\text{mol l}^{-1}$  was monitored for a fortnight at pH 4.0, 7.0, and 9.5, adjusted with HCl and  $\text{NH}_3$ . The absorption spectra of NR at concentrations from  $0.1 \mu\text{mol l}^{-1}$  to  $1 \text{ mmol l}^{-1}$  were recorded at pH 4.00 and 10.00 over the region of 350-620 nm.

The absorption spectra of NR in dependence on the solution acidity (pH 3-12) in the presence or absence of tensides or in dependence on the concentration of tenside or inert electrolyte at a constant acidity were measured over the region of 320-620 nm at  $c_L = 40 \mu\text{mol l}^{-1}$ ,  $I = 0.01$  (HCl +  $\text{NH}_3$ ). The effect of tensides on the optical parameters was examined in 10 vol. % ethanol at  $c_T = 1$  and  $10 \text{ mmol l}^{-1}$  for cationic and anionic tensides, respectively.

For investigating the changes in the acid-base properties of NR, absorbance-pH curves ( $A = f(\text{pH})$ ) were measured at 545, 540, 533, 525, 520, 470, 460, 452, 440, and 430 nm in the presence of tensides and at 535, 530, 525, 520, 515, 470, 460, 448, 440, and 430 nm in their absence. The  $A = f(\text{pH})$  plots were constructed for  $\lambda$  525 nm, only for SPX the wavelength was 533 nm, pertaining to the absorption maximum corresponding to the ionic associate.

The effect of concentration of the inert electrolyte and of the chloride-to-nitrate or chloride-to-bromide concentration ratio at a constant total ionic strength of 0.1 ( $\text{Cl}^- + \text{NO}_3^-$ ) or 1.0 ( $\text{Cl}^- + \text{Br}^-$ ) in the presence of SPX was studied in the same experimental conditions over the region of pH 3-9 in 0.1-0.2 pH unit steps.

The effect of concentration of tenside on the  $pK_{ai}^*$  value was investigated over the regions of  $c_T = 0.001-10 \text{ mmol l}^{-1}$  (SPX and CTMAB),  $0.05-10 \text{ mmol l}^{-1}$  (CPB),  $1-10 \text{ mmol l}^{-1}$  (SDS),  $\rho_T = 1-10 \text{ g l}^{-1}$  (BRIJ 35), and  $\varphi_T = 0.001-1\%$  (TRITON X-100). The pH was adjusted with ammonia starting from pH 3-4 ( $I = 0.01$  (HCl +  $\text{NH}_3$ ), 10 vol. % ethanol) over the region of pH 3-10 in 0.1-0.3 pH unit steps.

The values of the conditional dissociation constant  $pK_{ai}^*$  were obtained by graphical or graphical-logarithmic analysis of the  $A = f(\text{pH})$  curves or from the position of the inflection point of the  $A = f(\text{pH})$  curve or by numerical calculation by using the PRCEK computer program<sup>23</sup>.

## RESULTS

### Optical Properties of Neutral Red

Two acid-base NR species exist in aqueous solutions in dependence on the acidity of solution (Fig. 1). In the basic region the yellow electroneutral species L is present; its absorption maximum lies at 448 nm where its molar absorptivity is  $\epsilon' = 0.94 \text{ m}^2 \cdot \text{mmol}^{-1}$ . With increasing acidity, this species transforms into the violet protonated species  $\text{LH}^+$ , predominating in acid solutions; it is characterized by an absorption band with maxima at 525 nm ( $\epsilon' = 1.96 \text{ m}^2 \text{ mmol}^{-1}$ ) and 377 nm. The mutual conversion of the two acid-base species is indicated by a sharp isosbestic point at 473 nm.

In concentrated sulphuric acid solutions ( $c_H > 3 \text{ mol l}^{-1}$ ), NR is present in the doubly protonated violet form  $\text{LH}_2^{2+}$  exhibiting the absorption maximum at 596 nm. At  $c_H > 7 \text{ mol l}^{-1}$ , the triply protonated blue species  $\text{LH}_3^{3+}$  appears; its absorption maximum lies at 622 nm.

The acid-base transitions between the protonated NR species give rise to isosbestic points at 405 and 553 nm or at 455, 648, and 695 nm, respectively. A survey of the optical characteristics of NR is given in Table I.

At pH 4, the maxima of the absorption band of the violet  $\text{LH}^+$  species are shifted to lower wavelengths with increasing total concentration of NR, from 536 nm at

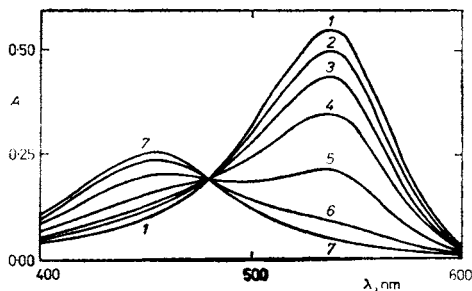


FIG. 1  
Absorption spectrum of neutral red in the presence of sodium dodecyl sulphate;  $c_L = 20 \mu\text{mol l}^{-1}$ ,  $c_T = 40 \mu\text{mol l}^{-1}$ ,  $l = 10 \text{ mm}$ ; pH: 1 1.83, 2 5.24, 3 5.93, 4 6.45, 5 7.01, 6 7.29, 7 8.46

$c_L = 0.1 \mu\text{mol l}^{-1}$  to 505 nm at  $c_L = 1 \text{ mmol l}^{-1}$ ; the conditional molar absorptivity decreases from 1.98 to  $1.72 \text{ m}^2 \text{ mmol}^{-1}$ . In the basic region (pH 10), the absorption maximum of the yellow neutral species L is shifted slightly, from 446 to 440 nm, and the molar absorptivity decreases from 0.94 to  $0.88 \text{ m}^2 \text{ mmol}^{-1}$ . These facts point to a low degree of aggregation of NR at low total concentrations and to a more pronounced aggregating ability of the protonated species as compared with the neutral form.

The character of the absorption spectra of NR remains unaltered in the presence of cationic, anionic or nonionic tensides. In the presence of SPX ( $c_T = 1 \text{ mmol l}^{-1}$ ), the absorption maxima of NR are shifted from 525 and 448 nm to 533 and 452 nm, respectively, and the molar absorptivities increase from 1.96 and  $0.94 \text{ m}^2 \text{ mmol}^{-1}$  to 2.25 and  $1.15 \text{ m}^2 \text{ mmol}^{-1}$ , respectively. The isosbestic point is shifted from 473 to 477 nm. The region of existence of the yellow NR species shifts to more acidic values. Similar changes are also observed in the presence of CPB and CTMAB in the same concentration of  $1 \text{ mmol l}^{-1}$  (see Table I).

TABLE I

Optical characteristics of neutral red in the presence and in the absence of tensides.  $c_L = 40 \mu\text{mol} \cdot \text{l}^{-1}$ ,  $\varphi = 10\% \text{ C}_2\text{H}_5\text{OH}$ ,  $I = 0.01$  (HCl + NaOH or  $\text{NH}_3$ ), pH 3–12,  $\lambda$  320–620 nm

Tenside	$c_T$ $\text{mmol l}^{-1}$	Species	pH	$\lambda_{\text{max}}$ nm	$\epsilon$ $\text{m}^2 \text{ mmol}^{-1}$	$\lambda_{\text{IP}}$ nm
—	—	L	>7	448	0.94	473
—	—	LH <sup>+</sup>	<7	525, 377	1.96, 1.04	405, 553
—	—	LH <sub>2</sub> <sup>2+</sup>	— <sup>a</sup>	596	1.38	445, 648, 695
—	—	LH <sub>3</sub> <sup>3+</sup>	— <sup>b</sup>	622	0.70	
SPX	1	L	>7	452	1.15	477
		LH <sup>+</sup>	<7	533	2.25	
CPB	1	L	>7	453	1.19	477
		LH <sup>+</sup>	<7	537	2.30	
CTMAB	1	L	>7	453	1.22	477
		LH <sup>+</sup>	<7	537	2.33	
SDS	10	L	>7	453	1.30	480
		LH <sup>+</sup>	<7	538	2.75	
BRIJ 35	— <sup>c</sup>	L	>7	451	1.17	478
		LH <sup>+</sup>	<7	535	2.30	
TRITON X-100	— <sup>d</sup>	L	>7	453	1.19	479
		LH <sup>+</sup>	<7	537	2.32	

<sup>a</sup> In  $\text{H}_2\text{SO}_4$ ,  $c > 3 \text{ mol l}^{-1}$ ; <sup>b</sup> in  $\text{H}_2\text{SO}_4$ ,  $c > 7 \text{ mol l}^{-1}$ ; <sup>c</sup>  $c_T = 2 \text{ g l}^{-1}$ ; <sup>d</sup>  $\varphi_T = 10\%$ .

In the presence of SDS in a concentration of  $10 \text{ mmol l}^{-1}$ , the maxima at 525 and 448 nm are shifted to 538 and 453 nm, respectively; the molar absorptivities increase to  $2.75$  and  $1.30 \text{ m}^2 \text{ mmol}^{-1}$ , respectively, the isosbestic point lies at 480 nm. The region of prevailing existence of the species L shifts to more alkaline range.

The absorption maxima are observed at 535 and 451 nm ( $\epsilon' = 2.30$  and  $1.17 \text{ m}^2 \cdot \text{mmol}^{-1}$ ) in the presence of BRIJ 35 ( $\varrho_T = 2 \text{ g l}^{-1}$ ) and at 537 and 453 nm ( $\epsilon' = 2.32$  and  $1.19 \text{ m}^2 \text{ mmol}^{-1}$ , respectively) in the presence of TRITON X-100 ( $\varphi_T = 0.2\%$ ). The species L exists in a more acidic region.

#### Acid-Base Properties of Neutral Red

*Effect of tensides.* The absorbance-pH curves of NR are markedly shifted to more acidic region with increasing concentration of tensides over the entire concentration range. The conditional dissociation constant of the  $\text{LH}^+/\text{L}$  acid-base transition decreases in the presence of SPX from 6.4 at  $c_T = 1 \mu\text{mol l}^{-1}$  to 5.5 at  $c_T = 10 \text{ mmol l}^{-1}$ . Similar shifts also appear in the presence of CTMAB and CPB (Table II). In the region of low total tenside concentrations, the shifts of the absorbance-pH curves as well as the changes in the  $\text{p}K_{ai}^*$  values are very small.

The plot of change in the conditional dissociation constant in dependence on the logarithm of concentration of cationic tenside,  $\Delta\text{p}K_{ai}^* = f(\log c_T)$ , consists of two linear branches whose point of intersection lies at  $\log c_T \approx -3.5$ . The shape of the plots is similar for CPX, CPB, and CTMAB. With decreasing values of  $\log c_T > -4$

TABLE II  
Acid-base properties of neutral red in the presence of tensides.  $c_L = 40 \mu\text{mol l}^{-1}$ ,  $\varphi = 10\%$   $\text{C}_2\text{H}_5\text{OH}$ ,  $I = 0.01$  (HCl + NaOH)

$c_T$ $\text{mmol l}^{-1}$	$\text{p}K_{ai}^*$				$\varphi_T$ %	$\text{p}K_{ai}^*$	$\varrho_T$ $\text{g l}^{-1}$	$\text{p}K_{ai}^*$
	SDS	SPX	CPB	CTMAB	TRITON	X-100	BRIJ 35	
10	8.25	5.52	5.35	5.42	1.00	5.62	10	6.18
5	8.03	5.70	5.60	5.75	0.1	6.02	5	6.28
3	7.82	—	5.80	—	0.01	6.30	3	6.38
2	—	5.95	5.97	5.92	0.001	6.50	1	6.49
1	7.30	6.13	6.10	6.18	—	—	—	—
0.5	—	6.34	—	6.37	—	—	—	—
0.1	—	6.36	6.30	6.37	—	—	—	—
0.08	—	6.37	6.35	6.37	—	—	—	—
0.01	—	6.38	6.37	6.39	—	—	—	—
0.001	—	6.40	6.42	6.41	—	—	—	—

the conditional dissociation constant increases linearly, whereas at  $\log c_T < -4$  the  $pK_{ai}^*$  values are roughly constant (Fig. 2).

In the presence of the anionic tenside SDS, the absorbance-pH curves are shifted to the alkaline region with increasing tenside concentration over the entire region of  $c_T = 1-10 \text{ mmol l}^{-1}$ . At  $c_T = 3-10 \text{ mmol l}^{-1}$ , the  $pK_{ai}^*$  values lie within the range of 8.0-8.25. In acid solutions, where the  $LH^+$  species predominates, the absorbance decreases appreciably at  $c_T < 3 \text{ mmol l}^{-1}$  due to the formation of a precipitate of the ionic associate of NR with SDS of a composition  $\{LH^+ \cdot T^-\}$ . Because of this precipitation, the conditional dissociation constant could not be determined accurately enough. The shape of the functional dependence  $\Delta pK_{ai}^* = f(\log c_T)$  with SDS is similar as with CPB, CTMAB, and CPX (Fig. 2).

With increasing content of the nonionic tensides TRITON X-100 ( $\varphi_T = 0.001-1\%$ ) and BRIJ 35 ( $\varrho_T = 1-10 \text{ g l}^{-1}$ ), the absorbance-pH curves are shifted to more acidic region. The conditional dissociation constant of NR is within the limits of 6.5-5.6 for TRITON X-100 and 6.5-6.2 for BRIJ 35. The molar absorptivities also undergo changes due to the altered shape of the absorption spectra, particularly for the  $LH^+$  species in the acidic region. A survey of the acid-base characteristics of NR in dependence on the kind and concentration of tenside is given in Table II.

*Effect of inert electrolyte.* With the concentration of inert electrolyte (ionic strength) increasing over the region of  $c_X = 0.01-1000 \text{ mmol l}^{-1}$  for  $Cl^-$  and  $0.1-1000 \text{ mmol l}^{-1}$  for  $NO_3^-$ , the absorbance-pH curves of aqueous solutions of NR are shifted to the alkaline region and the conditional dissociation constant varies over the region of 5.9-6.8 for  $Cl^-$  and 6.1-6.5 for  $NO_3^-$ .

The shift of the absorbance-pH curves in dependence on the concentration of  $Cl^-$  or  $NO_3^-$  ( $c_X = 0.1-1000 \text{ mmol l}^{-1}$ ) is less marked in the presence of the cationic

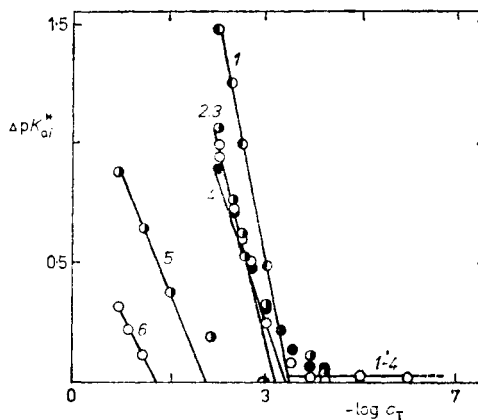


FIG. 2

Dependence of change in conditional dissociation constant  $\Delta pK_{ai}^*$  on tenside concentration or content ( $\log c_T$ ,  $\log \varrho_T$ ,  $\log \varphi_T$ );  $c_L = 40 \mu\text{mol l}^{-1}$ ,  $I = 0.10$  (HCl + NaOH),  $\varphi = 10\% \text{ C}_2\text{H}_5\text{OH}$ . Tenside: 1 SDS, 2 CPB, 3 CTMAB, 4 SPX, 5 TRITON X-100, 6 BRIJ 35

tenside SPX ( $c_T = 0.5 \text{ mmol l}^{-1}$ ). The  $pK_{ai}^*$  values lie within the ranges of 6.3–6.7 and 6.1–6.4, respectively.

Similar trends for the absorbance–pH curves and for the conditional dissociation constant of NR were also observed in the presence of  $\text{Br}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{HCOO}^-$ , and  $\text{SO}_4^{2-}$  ions over the concentration region of  $c_X = 0.1–100 \text{ mmol l}^{-1}$  (Table III).

The anions can be arranged with respect to their effect on the  $pK_{ai}^*$  values of NR in the presence of cationic tensides in order  $\text{ClO}_4^- \gg \text{Br}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{PO}_4^{3-} \approx \text{Ac}^- \gtrsim \text{Cl}^- > \text{HCOO}^-$ .

For verifying the decisive effect of the kind of the inert electrolyte anion, the conditional dissociation constants of NR were determined at a variable composition of binary mixtures of  $\text{Cl}^-$  with  $\text{NO}_3^-$  or  $\text{Br}^-$  and at a constant total concentration of the inert electrolyte,  $c_X = 0.1$  or  $1.0 \text{ mol l}^{-1}$ , respectively. In the case of the  $\text{Cl}^- : \text{NO}_3^-$  mixture,  $pK_{ai}^*$  varied over the region of 6.55–6.35 in dependence on the chloride-to-nitrate ratio; the limiting values pertain to  $0.1 \text{ mol l}^{-1} \text{ Cl}^-$  and  $\text{NO}_3^-$ , respectively. With the  $\text{Cl}^- : \text{Br}^-$  mixture the effect was less marked because of the higher total concentration of the inert electrolyte used.

*Effect of total concentration of NR.* This effect over the region of  $c_L = 5$  to  $320 \mu\text{mol l}^{-1}$  was investigated in the presence of SPX ( $c_T = 0.5 \text{ mmol l}^{-1}$ );  $\varphi = 10\% \text{ C}_2\text{H}_5\text{OH}$ ,  $I = 0.15$  ( $\text{HCl} + \text{NaOH}$ ), optical pathlength 1–40 mm. For the sake of clarity, the absorbance–pH curves are plotted in normalized absorbance units. The curves are shifted to the more acidic region and the  $pK_{ai}^*$  value at  $c_L = 3, 20, 40, 100,$  and  $320 \mu\text{mol l}^{-1}$  are 6.18, 6.15, 6.08, 6.01, and 5.88, respectively.

TABLE III

Effect of inert electrolyte concentration on the conditional dissociation constant of neutral red.  $c_L = 40 \mu\text{mol l}^{-1}$ ,  $c_{\text{SPX}} = 0.5 \text{ mmol l}^{-1}$ ,  $\varphi = 10\% \text{ C}_2\text{H}_5\text{OH}$

$c_X$ $\text{mol l}^{-1}$	$pK_{ai}^*$							
	$\text{Cl}^-^a$	$\text{NO}_3^-^a$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{Br}^-$	$\text{SO}_4^{2-}$	$\text{PO}_4^{3-}$	$\text{Ac}^-$
1 000	6.85	—	6.72	—	—	—	—	—
100	6.38	6.45	—	6.35	6.20	6.53	6.50	6.42
10	6.18	6.35	—	6.30	6.10	6.25	6.20	6.20
1	6.03	—	—	—	—	—	—	—
0.1	5.88	6.12	6.28	6.10	6.00	6.05	6.10	6.00
0.01	5.88	—	—	—	—	—	—	—

<sup>a</sup> In the absence of tenside.



*Titrimetric Determination of Tensides*

Based on the investigation of the effect of ionic tensides on the optical and acid-base properties of NR, a rapid titrimetric method was worked out for the determination of ionic tensides with photometric end point indication using NR. The method makes use of the change in the character of the absorption spectrum at a constant pH in dependence on the concentration of a cationic or anionic tenside due to the changing value of the conditional dissociation constant  $pK_{ai}^*$ . In dependence on the degree of titration, the absorbance is measured at 540 nm for anionic tensides determination or at 460 nm for cationic tensides determination; pH is held constant at  $8.3 \pm 0.1$  or  $8.0 \pm 0.1$ , respectively. Tensides can be determined in concentrations of  $0.1$  to  $100 \text{ mmol l}^{-1}$  using titration cells of 20 mm optical pathlength and 30 ml volume; the accuracy is better than 5% rel. and occasionally even than 1% rel. (ref.<sup>24</sup>).

## DISCUSSION

The changes in the conditional dissociation constant  $pK_{ai}^*$  of NR in dependence on the concentration of anionic tensides of SDS type are related with the formation of stable NR-tenside ionic associates. Their existence is proved unambiguously in aqueous solutions with low total concentrations of tenside ( $c_T < 3 \text{ mmol l}^{-1}$ ) by the appearance of a precipitate or a colloidal haze. The ionic associates are easily extracted from acid solutions into chloroform or other low polar organic solvents. The stoichiometric composition  $\{LH^+ \cdot T^-\}$  was confirmed by the continuous variations and molar ratios methods after extraction into the organic phase<sup>25</sup>.

Based on the relations for the dissociation constant  $pK_{ai}$  of the acid-base transition of NR,



and the equilibrium constant  $\beta_{LT}^*$  of formation of the ionic associate between NR and the tenside  $\{LH^+ \cdot T^-\}$ , the relation between the conditional dissociation constant  $pK_{ai}^*$  and  $\beta_{LT}^*$  can be written as

$$pK_{ai}^* = pK_{ai} - \log(1 + \beta_{LT}^* c_T), \quad (I)$$

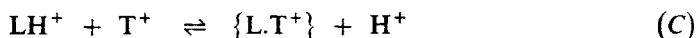
which is analogous to the relation for the dependence of the conditional dissociation constant of acid dyes (bromocresol green, Chromazurol S, etc.) in the presence of cationic tensides<sup>21</sup>.

Because of the lower solubilizing ability of SDS as compared to cationic tensides, verification of this relation is limited to the region of higher concentrations ( $c_T > 3 \text{ mmol l}^{-1}$ ).

The changes in the conditional dissociation constant of NR in the presence of cationic and nonionic tensides are in relation to the competitive equilibrium of formation of the ionic associate of the tenside with the neutral acid-base species



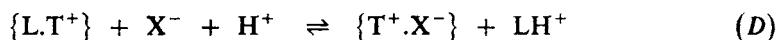
which brings about a considerable increase in the degree of deprotonation of the  $LH^+$  species (hinders the protonation), thereby increasing the acidity of NR more than a  $pK$  unit, in dependence on the kind and concentration of tenside. The equilibrium



shifts to the right with increasing tenside concentration. The dependence of the conditional dissociation constant  $pK_{ai}^*$  on the concentration of tenside can be described by a relation analogous to Eq. (1).

The characteristics of NR are also affected appreciably by the total concentration of free ions in the solution (ionic strength), determined not only by the concentration of the inert electrolyte but also by the concentration and degree of dissociation of the ionic tenside present. For inert electrolytes involving ions with large radii such as  $ClO_4^-$  or  $Br^-$ , formation of stable ionic associates of the tenside with the corresponding counter-ions,  $\{T^+.X^-\}$  or  $\{M^+.T^-\}$ , plays a significant role as well. The stability of these ionic associates and their extractability into low-polar organic solvents decrease in order  $ClO_4^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $PO_4^{3-}$ ,  $Ac^-$ ,  $Cl^-$ ,  $HCOO^-$ , in relation to the hydrophobic nature of the ions and their size. The effect of the inert electrolyte on the conditional dissociation constant of NR in the presence of tensides also decreases in this order.

The changes in  $pK_{ai}^*$  can be explained in terms of the competitive equilibrium between the formation of ionic associates of the tenside with the dye and of the tenside with the counter-ions of the inert electrolyte, described by the equation



in favour of the ionic associate  $\{T^+.X^-\}$ .

Based on the relations for the dissociation constant of the  $LH^+/L$  acid-base transition of the dye and for the equilibrium constants of formation of the ionic associates of the tenside with the dye  $\beta_{LT}^*$  and with the counter-ions  $\beta_{TX}^*$ , the dependence of the conditional dissociation constant  $pK_{ai}^*$  on the kind and concentration of the inert electrolyte can be described by the relation

$$pK_{ai}^* = pK_{ai} - \log [1 + \beta_{LT}^*c_T / (1 + \beta_{TX}^*c_T)]. \quad (2)$$

It follows from this relation that to a first approximation, the conditional dissociation constant  $pK_{ai}^*$  depends inversely proportionally on the equilibrium constant of formation of the ionic associate  $\{T^+ \cdot X^-\}$  and on the total concentration of inert electrolyte. It is clear that tensides in the chloride form are more convenient for practical application than tensides in the bromide form or in the form of sodium salts, and that aqueous solutions with minimal concentrations of inert salts ( $I \leq 0.1$ ) should be generally used.

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