

EQUILIBRIA IN MICELLAR SYSTEMS.  
PHOTOMETRIC DETERMINATION OF VANADIUM  
WITH 6-HYDROXY-5-DIBENZO(*a,j*)PHENOXAZONE-  
-8,11-DISULPHONIC ACID ACTIVATED  
BY CETYLTRIMETHYLAMMONIUM BROMIDE

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*Dedicated to Professor S. Stankovianský on the occasion of his 70th birthday.*

The reaction of cetyltrimethylammonium bromide (CTA<sup>+</sup>) with 6-hydroxy-5-dibenzo(*a,j*)pheno-  
xazone-8,11-disulphonic acid (HL)\* (*I*) was studied. At surfactant concentrations below the  
cmc, products with L : CTA<sup>+</sup> = 1 : 1 and 1 : 2 are formed, the latter being stable in solution  
in the presence of a small excess of surfactant. The changes in the dye p*K*<sub>a</sub> value can be explained  
on the basis of the common formalism of coordination reactions. Ternary complex VL<sub>2</sub>S<sub>4</sub>  
is formed in the presence of vanadate in a weakly acid medium. The equilibrium constants for  
the ternary complex were determined, its existence region found and a photometric determination  
of vanadium proposed.

Surface-active substances have recently been employed for more sensitive photometric determina-  
tions of many ions. The increase in the molar absorption coefficients is explained by the formation  
of micellar system<sup>1</sup>; sometimes the composition of the ion/dye/surfactant ternary complexes  
was found<sup>1,5</sup>. Equilibria in micellar systems are also important for the explanation of the me-  
chanism of micellar catalysis of organic reactions<sup>2-4,6</sup>. Even here the changes in the rate con-  
stant values are usually connected with formation of micellar species<sup>2,3</sup>, although the effect  
of the surfactant can sometimes be observed at concentrations lower than cmc (ref.<sup>4,6</sup>). The  
phenomenon is explained by induced formation of micelles, protomicellar species or ion-as-  
sociates<sup>4</sup>.

The present work was carried out in order to study the reaction between CTA<sup>+</sup>  
and the anionic dye (*I*) and to utilize the dye sensitized in this way for the determina-  
tion of vanadium.

\* Ionic charges have been omitted for the sake of simplicity; p*K*<sub>a</sub> corresponds only to ioniza-  
tion of the phenolic group.

## EXPERIMENTAL

## Chemicals and Instruments

A stock solution of the dye was prepared by dissolving the sodium salt in water at a concentration of  $4 \cdot 10^{-4}$  M. The dye purity was checked using elemental analysis and paper chromatography<sup>7</sup>. A cetyltrimethylammonium bromide solution was prepared in concentrations of  $10^{-3}$  M and  $4 \cdot 10^{-3}$  M. The detergent content in the stock solution was determined by titration with a  $10^{-2}$  M standard solution of sodium tetraphenylboron according to the Crosse and Uno method<sup>8,9</sup>. A standard solution of vanadium was prepared by dissolving solid  $\text{NH}_4\text{VO}_3$  in an equimolar amount of NaOH. The pH was maintained using formate, acetate and phosphate buffers and HCl solutions of various concentrations. If not stated otherwise, the ionic strength,  $I$ , was adjusted to a value of 0.1 using 1M-KCl. The absorbance was measured on Specord UV VIS (Zeiss, Jena) and Unicam SP 1800 (Cambridge, England) instruments in 1 and 5 cm cuvettes. The pH was measured on Beckman model G and PHM 62 (Radiometer, Copenhagen) instruments ( $\pm 0.02$  pH).

## Evaluation of the Experimental Data

The composition of the binary and ternary complexes was determined using the spectrophotometric titration<sup>10</sup>, continuous variation<sup>11</sup> and tangent ratio<sup>12</sup> methods. The stability constants were calculated numerically from the concentration curves (1) (1a) and the absorption-pH curves (2) (2a),

$$A = f(c_S)_{c_L, \text{pH}, I}, \quad (1)$$

$$A = f(c_V)_{c_L, c_S, \text{pH}, I}; \quad c_S > c_L; \quad c_V, \quad (1a)$$

$$A = f(\text{pH})_{c_L, c_S, I}, \quad (2)$$

$$A = f(\text{pH})_{c_L, c_V, c_S, I}; \quad c_S > c_L; \quad c_V, \quad (2a)$$

where  $c_L$ ,  $c_V$  and  $c_S$  are the overall analytical concentrations of the dye, vanadate and the surfactant, respectively. The dye ionization constants were measured spectrophotometrically in the usual manner. Only in the presence of the surfactant was the molar absorption coefficient of the ionized form obtained using transformation (3) (ref.<sup>13</sup>) for a pH region where no perceptible ionization of the dye occurs in pure solutions.

$$A/c_L = \varepsilon_L - [H] A/K_a c_L. \quad (3)$$

## RESULTS AND DISCUSSION

The first long-wave absorption bands of the two acid-base forms of the dye shift to longer wavelengths in the presence of surfactants. The changes in the molar absorption coefficients are insignificant (Table I). In acidic media (pH < 4.00), where only form HL is present ( $\text{p}K_a$   $7.37 \pm 0.04$  in pure solutions or  $6.09 \pm 0.02$  at a surfactant concentration of  $c_S$   $2.98 \cdot 10^{-4}$  M), the molar ratio curves indicate the formation of 1 : 1 products. The shape of the absorption curves (1) ( $c_L$   $8 \cdot 10^{-5}$  M, pH 3.15 or  $c_L$   $1.6 \cdot 10^{-5}$  M, pH 4.11) is not simple and indicates gradual formation

of micellar systems. In alkaline media ( $\text{pH} \geq 10.4$ ), absorption curves ( $I$ ) in a concentration range of  $c_S \leq 6 \cdot 10^{-5}\text{M}$ ,  $c_L 1.6 \cdot 10^{-5}\text{M}$  pass through an isosbestic point,  $\lambda_{\text{iso}} 632 \text{ nm}$ . It was found by the spectrophotometric titration method ( $c_L 1.2 \cdot 10^{-4}\text{M}$ ,  $\text{pH} 11.48$ ;  $c_L 8 \cdot 10^{-5}\text{M}$ ,  $\text{pH} 12.30$ ;  $c_L 1.6 \cdot 10^{-5}\text{M}$ ,  $\text{pH} 10.65$ ) that complex  $\text{LS}_2$  is formed (A)



Product  $\text{LS}_2$  is stable in solution in the presence of a small  $\text{CTA}^+$  excess ( $c_S \geq 3c_L$ ) and exists up to the surfactant cmc. The cmc for  $\text{CTA}^+$ , obtained by extrapolation of conductometric measurements is  $4 \cdot 10^{-4}\text{M}$  at  $I 0.5$  (ref.<sup>4</sup>).

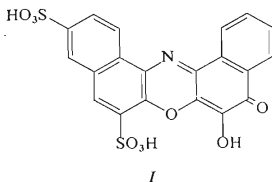
These equilibria are probably not connected with the formation of micellar species. The surfactant concentration is orders of magnitude smaller than the cmc and all the spectrophotometric titration curves obtained for various dye concentrations ( $c_L 1.6 \cdot 10^{-5} - 1.2 \cdot 10^{-4}\text{M}$ ) indicate the presence of product  $\text{LS}_2$ . On plotting the absorbance dependence on the surfactant concentration at  $\lambda_{\text{iso}}$  of equilibrium (A), a further change in the absorbance appears at concentrations close to the cmc,  $(2-4) \cdot 10^{-4}\text{M}$ . The same conclusions follow from absorption curves ( $I$ ) for eosine, which is often employed for the determination of the cmc of cationoid surfactants<sup>14</sup>.

TABLE I  
Absorption Maximum Wavelengths and the Molar Absorption Coefficients for Dye (I)

$c_S(\text{M})$	$\lambda_{\text{max}}$	$\epsilon_{\text{max}} \cdot 10^{-3}$
	form HL	
0	506	9.35
$2 \cdot 10^{-4}$	522	8.38
$4 \cdot 10^{-4}$	524	9.32
0	513 <sup>a</sup>	10.82 <sup>a</sup>
	L	
0	603	6.66
0	620 <sup>a</sup>	6.75 <sup>a</sup>
	$\text{LS}_2$	
$2 \cdot 10^{-4}$	645	5.83

<sup>a</sup> 50% (v/v) acetone.

The yellow-green fluorescence of the pure dye disappears in the presence of small  $\text{CTA}^+$  concentrations ( $c_s < 10^{-4}\text{M}$ ). The absorption maximum shifts to longer wavelengths and the spectrophotometric titration curves indicate the formation of products  $\text{LS}$  and  $\text{LS}_2$  ( $c_L 1.28 \cdot 10^{-5}\text{M}$ , pH 5.63). At surfactant concentrations close to the cmc ( $2-4 \cdot 10^{-4}\text{M}$ ), the formation of micellar systems is accompanied by a minute shift of the maximum of the first long-wave absorption band to shorter wavelengths and by reappearance of yellow-green fluorescence. In the presence of acetone the absorption maxima of the first long-wave bands of dye (*I*) are minutely shifted to longer wavelengths with a small increase in the absorption coefficients (Table I). The absorption maximum wavelengths do not change within a dye concentration range of  $3.2 \cdot 10^{-4} - 1.6 \cdot 10^{-5}\text{M}$ . The shifts discussed are not caused by a change in the degree of association, but by simultaneous ionic and hydrophobic interactions leading to the formation of defined molecular complexes.



The presence of surfactant is manifested in the vicinity of the dye  $\text{pK}_a$  by a shift in the ionization equilibrium and by a large colour change. Equilibrium (*B*) can be formulated, characterized by equilibrium constant (4).



$$\beta'_2 = [\text{LS}_2][\text{H}][\text{HL}']^{-1}[\text{S}]^{-n} \quad (4)$$

$[\text{HL}']$  is the conditional concentration of the non-ionized dye form, including the possible product of the surfactant reaction localized on some of the sulpho groups. Only the  $\text{LS}_2$  form absorbs around 700 nm and the equilibrium constant can be written as

$$\beta'_2 = A(A_0 - A)^{-1} [\text{H}][\text{S}]^{-n} \quad (5)$$

where  $A_0 = \epsilon l c_L$ , or

$$\log A/A_0 - A = \log \beta'_2 + \text{pH} + n \log [\text{S}]. \quad (5a)$$

It was found by the analysis of the concentration curves ( $c_L 8 \cdot 10^{-5}\text{M}$ , pH 5.18; 5.55; 5.59) and the pH-curves ( $c_L 8 \cdot 10^{-5}\text{M}$ ,  $c_s 2.98 \cdot 10^{-4}\text{M}$ ) that  $n = 1$  and proposed

equilibrium (B) is correct, provided that HL' is identical with the HLS form. The latter can be found in the pH region where the dye is not ionized either in pure solutions or in the presence of surfactant. The stability constants were calculated numerically from the concentration and absorption pH curves ( $c_L 8 \cdot 10^{-5}M$ , pH 5.18; 5.55; 5.59 or  $c_L 8 \cdot 10^{-5}M$ ,  $c_S 2.98 \cdot 10^{-4}M$ ) (Table II). In all cases excess surfactant was used to prevent associate formation. All measurements were carried out in 5 cm cuvettes in order not to exceed the surfactant cmc. The  $pK'_a$  for the dye in the presence of the surfactant can be calculated from absorption pH curve (2) ( $c_L 8 \cdot 10^{-5}M$ ,  $c_S 2.98 \cdot 10^{-4}M$ ). The ionization constant was calculated using the common procedure; only the absorption coefficient of form LS<sub>2</sub> was read from linear transformation (3). For  $c_S 2.98 \cdot 10^{-4}M$ ,  $pK'_a$  is  $6.09 \pm 0.02$ . The presence of the surfactant in a concentration lower than the cmc causes an increase in the dye acidity by more than one order of magnitude.

Vanadate alone does not undergo a more important reaction with the dye studied and only a minute change in the colouration can be observed in equimolar mixtures. In the presence of CTA<sup>+</sup>, blue-green solutions of the ternary complex are formed in approximately equimolar mixtures of the dye and vanadate at pH 2.5–6.5. The colouration develops almost instantaneously and does not change for more than 24 hours. Vanadate oxidizes the dye irreversibly in acidic media (pH 2). The dye is more resistant toward this effect in the presence of CTA<sup>+</sup> and the oxidation is not observed in the studied pH interval. The vanadate reaction can analogously be made more pronounced with other dyes (pyrocatechol violet, alizarine sulphonate, etc.).

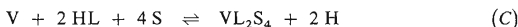
The absorption curves of solutions with constant concentrations of the dye and the surfactant and with a variable concentration of vanadate, obtained at pH 3.96, 4.08, 4.65 and 5.30, pass through an isosbestic point  $\lambda_{iso}$  556 nm. The absorption curves

TABLE II  
Equilibrium Constants of the CTA<sup>+</sup>/Dye Binary Complex

$-\log \beta'_2(B)$	$I$	Equation	$pK'_a$	$I$
2.34	0.1	(2) <sup>a</sup>	$6.09 \pm 0.02^e$	0.1
2.36	0.1	(1) <sup>b</sup>	—	—
2.35	0.1	(1) <sup>c</sup>	—	—
2.10	0.036	(1) <sup>d</sup>	—	—

<sup>a</sup>  $c_L 8 \cdot 10^{-5}M$ ,  $c_S 2.98 \cdot 10^{-4}M$ , average of 13 values converted to the logarithmic scale. <sup>b</sup>  $c_L 8 \cdot 10^{-5}M$ , pH 5.18, average of 5 values converted to the logarithmic scale. <sup>c</sup>  $c_L 8 \cdot 10^{-5}M$ , pH 5.55, average of 5 values converted to the logarithmic scale. <sup>d</sup>  $c_L 8 \cdot 10^{-5}M$ , pH 5.60, average of 6 values converted to the logarithmic scale. <sup>e</sup>  $c_L 8 \cdot 10^{-5}M$ ,  $c_S 2.98 \cdot 10^{-4}M$ .

of equimolar solutions of vanadate and the dye containing excess surfactant pass through the same isosbestic point in a pH range of 2–3.5. The composition of the V/dye/ surfactant ternary complex was determined by spectrophotometric titration ( $c_L$   $2.56 \cdot 10^{-5}M$ ,  $c_S$   $4 \cdot 10^{-4}M$ , pH 4.08, 4.63, 5.21; or  $c_L$   $8 \cdot 10^{-5}M$ ,  $c_S$   $4 \cdot 10^{-4}M$ , pH 5.30) ( $c_L$   $8 \cdot 10^{-5}M$ ,  $c_V$   $2 \cdot 10^{-4}M$ , pH 5.35; or  $c_L$   $1.2 \cdot 10^{-4}M$ ,  $c_V$   $2.5 \cdot 10^{-4}M$ , pH 6.45), by the Job method ( $c_0$   $8 \cdot 10^{-5}M$ , pH 4.08) and by the tangent ratio method, varying the vanadate concentration at excess dye and varying surfactants concentration with excess dye and vanadate. It was found that at complex ratios of V : L 1 : 2, L : S 1 : 2 and V : S 1 : 4 ( $VL_2S_4$ ) is formed (C).



$$*\beta_{2,4} = [H]^2[VL_2S_4][V]^{-1}[HL]^{-2}[S]^{-4} \quad (6)$$

If only the complex absorbs at selected wavelengths ( $\lambda$  670 nm) and dye ionization does not occur in the presence of the surfactant within the studied pH interval (pH  $\leq$  3), then the association constant for equilibrium (C) is given by Eq. (6), or, for equimolar solutions of the dye and vanadate, by Eq. (7).

$$*\beta_{2,4} = [H]^2 A(2A_0 - A)^{-1} (1 - A/A_0)^{-2} (p - 2A/A_0)^{-4} c^{-6} \quad (7)$$

where  $A_0$  is the horizontal branch of the pH-curve ( $A = \epsilon lc/2$ ),  $c$  is the dye (vanadate) concentration and  $p$  is the surfactant excess ( $p = c_S/c$ ). With a sufficient surfactant excess, equilibrium constants (8) (8a) can be formulated.

$$*\beta_2 = [H]^2 A(2A_0 - A)^{-1} (1 - A/A_0)^{-2} c^{-2} \quad (8)$$

$$\log A(2A_0 - A)^{-1} (1 - A/A_0)^{-2} = \log *\beta_2 + 2 \text{pH} + 2 \log c \quad (8a)$$

Logarithmic transformation (8a) ( $c_L = c_V$   $1.6 \cdot 10^{-5}M$ ,  $c_S$   $4 \cdot 10^{-4}M$ ) was linear over the whole steep part of the pH curve (pH 2–3), with a slope corresponding to two dissociated protons. Equilibrium constants  $*\beta_{2,4}$  were calculated numerically from relationship (7) ( $c_L = c_V$   $1.6 \cdot 10^{-5}M$ ,  $c_S$   $4 \cdot 10^{-4}M$ ) (Table III).

Conditional stability constants (9) were calculated from the absorbance differences at the equivalence point between the concentration curves, (1a), for the quantitative and the actual reaction ( $c_L$   $2.56 \cdot 10^{-5}M$ ,  $c_S$   $6.4 \cdot 10^{-4}M$ , pH 4.08;  $c_L$   $2.56 \cdot 10^{-5}M$ ,  $c_S$   $4 \cdot 10^{-4}M$ , pH 5.21;  $c_L$   $6.08 \cdot 10^{-5}M$ ,  $c_S$   $4 \cdot 10^{-4}M$ , pH 5.30).

$$\beta'_{2,4} = [VL_2S_4][V]^{-1}[L']^{-2}[S]^{-4} \quad (9)$$

$[L']$  is the dye conditional concentration in the presence of the surfactant ( $[HL] + [L]$ ). Within the pH interval employed, the presence of both acid-base forms

of the dye and simultaneous absorbance by its ionized form must be assumed ((10)(11))

$$A = \varepsilon[\text{VL}_2\text{S}_4] + \varepsilon_L[\text{L}'] \quad (10)$$

$$[\text{VL}_2\text{S}_4] = Y/Y_{\max} c_L/2,$$

where  $Y = \varepsilon[\text{VL}_2\text{S}_4] + \varepsilon_L[\text{L}'] - \varepsilon_L c_L$ ,

$$Y_{\max} = \varepsilon c_L/2 - \varepsilon_L c_L. \quad (11)$$

The constant and molar absorption coefficient values are given in Table III. The presence of the  $\text{VO}_2^+$  form can be assumed in solution at pH 2–3. At higher pH values cation hydrolysis and the polymerization equilibria can play a role, which is manifested as a decrease in the stability of the ternary complex.

*Determination of vanadium.* The stability of the ternary complex permits direct photometric determination of vanadium in a weakly acidic medium in the presence of small excesses of the dye and the surfactant. The colouration is developed instantaneously after mixing the components and remains constant for more than 24 hours in equimolar solutions. The absorbance of the dye – surfactant mixture slowly increases with time; this effects samples with low vanadium contents, e.g. the absorbance increases by 1–2% over 2 hours at  $c_L = 10c_V$ . For this reason it is recommended to always measure the solution absorbance at the same time after mixing the components, using water as a reference. At pH 4–5, 9–90  $\mu\text{g V}$  can be reliably determined in 50 ml. The molar absorption coefficient,  $\varepsilon$ , equals  $22.2 \cdot 10^3$

TABLE III  
Equilibrium Constants of the Vanadium/Dye/Detergent Complex

$\log * \beta_{2,4}$	$I$	pH	$\varepsilon \cdot 10^{-3}(\text{nm})$
$18.25 \pm 0.1^a$	0.01	(2–3)	$15.5 (670)^d$
$15.7^b$	0.1	4.08	$22.2 (630)^d$
$14.3^b$	0.1	5.21	$22.1 (630)^e$
$14.7^b$	0.01	5.30	—
$14.6^{b,c}$	0.01	4.08	—

<sup>a</sup> Calculated from the pH-curve for equimolar solutions. <sup>b</sup>  $* \beta_{2,4}$  recalculated from the conditional constants using the value,  $\text{p}K'_a$  6.09. <sup>c</sup> Calculated from the Job curve for equimolar solutions ( $c_0 8 \cdot 10^{-5}\text{M}$ ,  $c_S > \text{cmc } 1.6 \cdot 10^{-3}\text{M}$ ). <sup>d</sup>  $c_S 1.2 \cdot 10^{-3}\text{M}$ . <sup>e</sup>  $c_S 1.6 \cdot 10^{-3}\text{M}$ .

for a wavelength of  $\lambda$  630 nm. The sensitivity on the Sandell scale is  $0.0026 \mu\text{g}/\text{cm}^2$  for  $\Delta A$  0.001. The coefficient of variation is 0.53% for 6 parallel determinations ( $1.06 \mu\text{g V}/\text{ml}$ ; 95% probability level). The  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{Th}^{4+}$ ,  $\text{ZrO}^{2+}$ ,  $\text{WO}_4^{2-}$ ,  $\text{Sb}^{3+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Sn}^{4+}$  and  $\text{CrO}_4^{2-}$  ions interfere in the determination. Equimolar concentrations of  $\text{Hg}^{2+}$ ,  $\text{Hg}_2^{2+}$ ,  $\text{PtCl}_6^{2-}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Bi}^{3+}$  and  $\text{Au}^{3+}$  ions do not interfere. The presence of the surfactant improves the selectivity of the determination. For example,  $\text{Cu}^{2+}$  ions react with the dye in pure solutions within the recommended pH interval, but their reaction is suppressed in the presence of the surfactant. The determination can still be reliably carried out in the presence of a 10fold excess of  $\text{Pb}^{2+}$ , a 20fold excess of  $\text{La}^{3+}$  and a 50fold excess of  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$  or  $\text{Ag}^+$ . The stability of the dye/surfactant binary complex decreases with increasing ionic strength and large concentrations of electrolytes and buffers may decrease the sensitivity of the determination (Tables II, III). This interference appears only at high concentrations; for example, a 2400fold excess of KCl (0.05M) causes a c. 10% decrease in the absorbance.

*Procedure.* To a 50 ml volumetric flask 10 ml  $10^{-3}\text{M}$  dye solution are added 2.5 ml acetate buffer (pH 4), 15 ml  $4 \cdot 10^{-3}\text{M}$ -CTA<sup>+</sup> solution and the sample containing 9–90  $\mu\text{g V}$ . The mixture is diluted with water to the mark and the absorbance is measured after 10 minutes at 630 nm against water.

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