

SPECTROPHOTOMETRIC STUDY OF THE REACTION OF ALIZARIN GREEN SERIES DYES WITH URANYL IONS IN THE PRESENCE OF CATIONOID SURFACTANTS

Jiří ŠIMEK^a, Nguyen Truong SON^b and Eduard RUŽIČKA^a

^a Department of Analytical and Organic Chemistry, Palacký University, 771 46 Olomouc, Czechoslovakia and

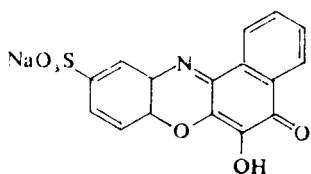
^b Institute for Agriculture, Hanoi, Vietnam Socialist Republic

Received January 17th, 1984

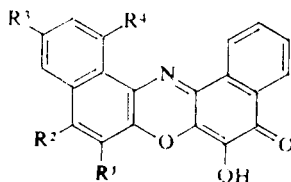
The coordination properties of alizarin green series dyes with uranyl ions were studied in the presence of cationoid surfactants (cetylpyridinium bromide, carbethoxypentadecyltrimethylammonium bromide). Ternary complexes of the composition $UO_2L_2S_2$, $UO_2L_2S_4$, $UO_2L_2S_6$, and $UO_2L_3S_9$, where L is dye and S is surfactant, are formed in weakly acid solutions. The formation constants of the complexes were established and a procedure was worked out for the direct photometric determination of uranium.

Dyes of alizarin green series (sulpho derivatives of phenoxazine dyes) have been applied, in the presence of cationoid surfactants, to the direct photometric determination of cetyltrimethylammonium¹, vanadium²⁻⁴, iron⁵, or iridium⁶, or as metalochromic indicators for the chelometric determination of vanadium³, bismuth⁷, zirconium, thorium⁸ and lanthanoids⁹.

In this work the coordination properties are studied for five dyes of alizarin green series, *viz.* compounds I–V, in the presence of the cationoid surfactants cetylpyridinium bromide (CPy⁺) and carbethoxypentadecyltrimethylammonium bromide, (Septonex, Sep⁺).



I



II–V

- II, R² = SO₃Na, R¹ = R³ = R⁴ = H
 III, R² = R³ = SO₃Na, R¹ = R⁴ = H
 IV, R³ = R⁴ = SO₃Na, R¹ = R² = H
 V, R¹ = R³ = SO₃Na, R² = R⁴ = H

EXPERIMENTAL

Reagents and Instruments

Solutions of dyes I–V in concentrations of 0.4 and 1.0 mmol l⁻¹ were obtained by dissolving the corresponding amounts of their sodium salts in water. The purity of the dyes was tested by paper chromatography, elemental analysis, and thin layer chromatography^{10,11}; their concentration in the solutions was determined by photometric titration with vanadate in the presence of CPy⁺ and Sep⁺.

Stock solutions of the cationoid surfactants were prepared by dissolving the solid chemicals in water; their concentration was determined titrimetrically by the method of Uno and co-workers¹² and Cross¹³. The stock solution of uranyl ions ($c = 10 \text{ mmol l}^{-1}$) was prepared by dissolving $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2 \text{ H}_2\text{O}$ in water; uranium in it was determined gravimetrically as oxinate¹⁴.

The pH of the solutions was held at a constant value by using 0.1M-HCl and acetate buffers. The ionic strength was adjusted to $I = 0.01$ with 1M-KCl or with a calculated amount of buffer. All the chemicals used were of reagent grade purity.

The absorbances of the solutions were measured on Specord UV-VIS (Carl Zeiss, Jena) and SP 1800 (Pye Unicam, Cambridge) spectrophotometers in 10, 20, and 50 mm cells, the pH was determined on a PHM 4d pH-meter (Radiometer, Copenhagen) fitted with a glass and a saturated calomel electrode (accuracy ± 0.02 pH units). NBS standards (0.05M potassium hydrogenphthalate and 0.05M potassium tetraoxalate) were used for calibration.

Data Evaluation

The composition of the ternary complexes was determined by the analysis of the concentration curves 1–4 (where c_{UO_2} , c_{L} , and c_{S} are the total analytical concentrations of uranyl ions, dye, and surfactant, respectively)

$$A = f(c_{\text{UO}_2})_{c_{\text{L}}, c_{\text{S}}, \text{pH}} \quad c_{\text{S}} > c_{\text{L}}, c_{\text{UO}_2} \quad (1)$$

$$A = f(c_{\text{L}})_{c_{\text{UO}_2}, c_{\text{S}}, \text{pH}} \quad c_{\text{S}} > c_{\text{L}}, c_{\text{UO}_2} \quad (2)$$

$$A = f(x)_{c_{\text{O}}, c_{\text{S}}, \text{pH}} \quad c_{\text{S}} > c_{\text{O}} \quad (3)$$

(where $c_{\text{O}} = c_{\text{UO}_2} + c_{\text{L}} = \text{const}$, $x = c_{\text{UO}_2}/(c_{\text{UO}_2} + c_{\text{L}})$), and

$$A = f(c_{\text{S}})_{c_{\text{UO}_2}, c_{\text{L}}, \text{pH}} \quad (4)$$

by the molar ratios method¹⁵ and the Job continuous variations method¹⁶. The stability constants of the ternary complexes were calculated from the concentration curves (1)–(4) and the pH curve

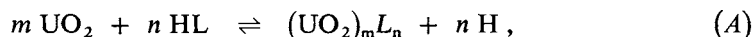
$$A = f(\text{pH})_{c_{\text{UO}_2}, c_{\text{L}}, c_{\text{S}}}, \quad c_{\text{S}} > c_{\text{L}}, c_{\text{UO}_2} \quad (5)$$

and the composition and the stability constants of the UO_2 -L binary complexes were defined by means of the Ketelaar transformation¹⁷ of the dependence

$$A = f(c_{\text{UO}_2})_{c_{\text{L}}, \text{pH}} \quad (6)$$

RESULTS AND DISCUSSION

The dyes give coloured products with uranyl ions in weakly acid solutions. The binary complexes formed exhibit absorption maxima at 586–608 nm. The absorption curves (6) display a single isosbestic point (λ_{iso} 546 nm, $c_L = 40 \mu\text{mol l}^{-1}$, pH 5.05–5.56, 5.84, dye *IV*; λ_{iso} 559 nm, pH 4.69; λ_{iso} 557 nm, pH 5.27, dye *II*). The UO_2 -dye binary complexes are not very stable. Their composition and stability constants were determined *via* the Ketelaar transformation¹⁷. Assume that the reaction can be described by equation (A) (charges are omitted for simplicity),



characterized by the equilibrium constant

$$*\beta_{mn} = [(\text{UO}_2)_m \text{L}_n][\text{H}]^n / \{[\text{UO}_2]^m [\text{HL}]^n\} \quad (7)$$

which can be transformed to

$$c_L/\Delta A = n/\Delta\varepsilon + [\text{H}]^n / \{*\beta_{mn} \Delta\varepsilon(c_{\text{UO}_2} - m \Delta A/\Delta\varepsilon) \Delta A^{n-1}\}^{1/n}, \quad (8)$$

where $\Delta A = A - A_0$, $A_0 = \bar{\varepsilon}_L c_L$, $A = \bar{\varepsilon}_L [\text{L}'] + \varepsilon_C [(\text{UO}_2)_m \text{L}_n]$, and $\Delta\varepsilon = \varepsilon_C - n\bar{\varepsilon}_L$, ε_C is the molar absorptivity of the complex, $\bar{\varepsilon}_L$ is the mean molar absorptivity of all the dye species, and $[\text{L}']$ is the conditional concentration of dye, $[\text{L}'] = [\text{HL}] + [\text{L}]$.

Within the region of $4 < \text{pH} < \text{pK}_a - 1.5$, $\bar{\varepsilon}_L$ can be replaced²¹ by ε_{HL} and $[\text{L}']$ by $[\text{HL}]$. Transformation (8) of the concentration curves (6) for dyes *II* and *IV*, where the uranyl ion concentration was varied over the range of $c_{\text{UO}_2} = (0-75) c_L$ with $c_L = 16$ or $40 \mu\text{mol l}^{-1}$, showed that the equation is linear for $m = n = 1$ only, hence, the complex formed has the $\text{UO}_2 : \text{L}$ ratio 1 : 1. The stability constants were calculated for this complex by Eq. (8) (Table I). Dyes *I*, *III*, and *V* also form a single complex with the $\text{UO}_2 : \text{L}$ ratio 1 : 1 (ref.¹).

In the presence of cationoid surfactants, the formation of UO_2 -L-S ternary complexes was observed. Their λ_{max} and ε_{max} values are given in Table II. The absorption curves (1) for constant concentrations of dye, $c_L = 16-80 \mu\text{mol l}^{-1}$, and tenside, $c_S = (5-100) c_L$, and variable concentrations of uranyl ions, $c_{\text{UO}_2} = (0-5) c_L$, display a single isosbestic point over the pH 3.5–5.5 range for dyes *I-IV*. For dye *V*, a single isosbestic point is observed in the regions of pH 3.0–4.6 and pH 5.3–7.0, whereas two isosbestic points, $\lambda_{\text{iso},1}$ 552 nm ($c_{\text{UO}_2} \leq c_L/3$) and $\lambda_{\text{iso},2}$ 546 nm ($c_{\text{UO}_2} > c_L/3$), are found in the pH 4.8–5.2 range.

The molar ratios method revealed the formation of a single complex with the $\text{UO}_2 : \text{L}$ ratio 1 : 2 over the entire region for dyes *I-IV*; for each, 5–7 titrations

were performed within the pH 3.5–5.5 range. The Job method of continuous variations of equimolar solutions of dye and uranyl ions ($c_0 = 40 \mu\text{mol l}^{-1}$, $c_S = 0.8 \text{ mmol l}^{-1}$, pH 4.66, 4.81) provided the same result. For dye V, the $\text{UO}_2 : \text{L} = 1 : 3$ complex formation was found by the molar ratios method over the pH 5.2–7.0 region ($c_L = 16\text{--}80 \mu\text{mol l}^{-1}$, $c_S = (5\text{--}50) c_L$, c_{UO_2} , 6 titrations), by the analysis of the concentration curves (2) ($c_{\text{UO}_2} = 14 \mu\text{mol l}^{-1}$, $c_S = 0.4 \text{ mmol l}^{-1}$, pH 5.29), as by the Job analysis of the concentration curves (3) ($c_0 = 40 \mu\text{mol l}^{-1}$, $c_S = 0.4 \text{ mmol l}^{-1}$, pH 5.93). Over the pH 4.8–5.3 range, however, the Job method indicates two complexes with the $\text{UO}_2 : \text{L}$ ratios 1 : 2 and 1 : 3 ($c_0 = 40$ or $80 \mu\text{mol l}^{-1}$, $c_S = 0.4$ or 1 mmol l^{-1} , pH 4.96 or 5.30). At lower pH values (pH 3.8–4.6), the Ketelaar transformation of dependence (1) ($c_L = 16$ and $40 \mu\text{mol l}^{-1}$, $c_S = 40$ and $80 \mu\text{mol l}^{-1}$, $c_{\text{UO}_2} = (0\text{--}25) c_L$, pH 3.98, 4.28, 4.64) and of dependence (2) ($c_{\text{UO}_2} = 12 \mu\text{mol l}^{-1}$, $c_S = 0.8 \text{ mmol l}^{-1}$, $c_L = (0\text{--}15) c_L$, pH 4.11) revealed the formation of a single complex with the $\text{UO}_2 : \text{L}$ ratio 1 : 2.

TABLE I

Spectral characteristics and conditional stability constants of the uranyl-dye complexes. Acetate buffer, $I\ 0.01$, $t = 25^\circ\text{C}$

Dye	pH	λ_{max} nm	ε_{max} $\text{l mol}^{-1} \text{ cm}^{-1}$	λ_{iso} nm	$\log \beta_1^a$
<i>I</i>	4.66	554	7 250	516	3.02 ± 0.01
	5.55	554	6 900	516	3.53 ± 0.06
	5.97	554	6 760	515	3.39 ± 0.06
<i>II</i>	3.58	616	10 870	568	2.88 ± 0.05
	4.11	615	10 920	563	3.35 ± 0.04
	4.69	612	10 880	559	3.79 ± 0.06
	5.27	609	10 830	557	3.97 ± 0.04
<i>III</i>	4.48	576	5 780	550	3.44 ± 0.05
	5.07	576	5 800	550	3.95 ± 0.05
	5.86	576	5 300	548	4.06 ± 0.03
<i>IV</i>	4.67	576	9 650	547	3.31 ± 0.03
	5.05	576	9 630	547	3.66 ± 0.05
	5.56	576		547	3.77 ± 0.07
	5.84	576	9 500	546	3.96 ± 0.06

^a Calculated from concentration curves (6) by transformation (8); $c_L = 40 \mu\text{mol l}^{-1}$, average of 8–10 values, converted to the logarithmic scale, confidence interval for $\alpha = 0.05$.

TABLE II

Equilibrium constants of the UO_2 -dye-surfactant complex formation. Acetate buffer, I 0.01, $t = 25^\circ\text{C}$

c_s mmol l ⁻¹	pH	$\text{p}K'_a$	ϵ_{max}^a	$\log^* \beta_{1,2}$	$\log^* \beta_{1,2,r}$	$\log^* \beta_{1,3}$	$\log^* \beta_{1,3,9}$
<i>I</i> -CPy ⁺ , $r = 2$, $\lambda_{\text{max}} = 594$ nm							
0.5	2.8–4.0 ^b	4.40	17 700	2.17 ± 0.06	8.83 ± 0.06	—	—
0.5	4.2–5.0 ^c	4.46	17 600	2.18 ± 0.02	8.84 ± 0.02	—	—
—	4.43 ^d	—	12 600	1.83	13.19	—	—
<i>I</i> -Sep ⁺ , $r = 4$, $\lambda_{\text{max}} = 596$ nm							
0.5	3.0–4.0 ^b	5.16	17 300	1.98 ± 0.02	16.63 ± 0.02	—	—
1.6	4.65 ^c	4.59	17 300	1.37	12.22	—	—
0.32	4.69 ^c	5.01	17 300	1.98	15.91	—	—
—	4.67 ^d	—	17 100	–0.06	16.55	—	—
0.64	5.31 ^c	4.70	—	1.77	14.31	—	—
<i>II</i> -CPy ⁺ , $r = 4$, $\lambda_{\text{max}} = 598$ nm							
0.5	3.58 ^b	4.88	18 200	2.91 ± 0.04	10.31	—	—
1.0	4.11 ^b	4.79	18 400	3.41 ± 0.02	14.81	—	—
1.0	4.69 ^b	4.79	18 400	3.87 ± 0.05	19.32	—	—
0.5	5.27 ^b	4.88	18 300	4.02 ± 0.05	17.11	—	—
<i>II</i> -Sep ⁺ , $r = 4$, $\lambda_{\text{max}} = 593$ nm							
0.5	2.9–4.0 ^b	4.92	18 400	2.21 ± 0.05	15.87 ± 0.04	—	—
0.5	4.2–5.9 ^c	4.92	18 400	2.23 ± 0.03	15.80 ± 0.06	—	—
—	4.69 ^d	—	18 700	2.03	15.99	—	—
<i>III</i> -CPy ⁺ , $r = 4$, $\lambda_{\text{max}} = 630$ nm							
0.5	2.7–3.7 ^b	4.46	17 500	2.17 ± 0.02	15.46 ± 0.02	—	—
0.25	3.9–5.0 ^c	5.01	17 500	2.15 ± 0.02	16.92 ± 0.02	—	—
—	4.73 ^d	—	17 600	0.90	21.72	—	—
<i>IV</i> -Sep ⁺ , $r = 6$, $\lambda_{\text{max}} = 642$ nm							
0.64	3.3–4.5 ^e	5.01	21 000	2.20 ± 0.07	21.71 ± 0.08	—	—
1.6	4.67 ^c	4.84	—	1.61	17.91	—	—
0.64	4.68 ^c	5.32	20 800	1.99	21.16	—	—
0.80	5.39 ^c	5.10	—	1.47	20.36	—	—

TABLE II
(Continued)

c_S mmol l ⁻¹	pH	pK' _a	ϵ_{\max}^a	$\log^* \beta_{1,2}$	$\log^* \beta_{1,2,r}$	$\log^* \beta_{1,3}$	$\log^* \beta_{1,3,9}$
<i>V</i> -Cpy ⁺ , $r = 6$, $\lambda_{\max} = 610$ nm							
0.5	3.6–4.7 ^b	6.08	21 000	0.58 ± 0.10	21.38 ± 0.09	—	—
0.8	4.1–4.75 ^c	6.09	21 000	0.59 ± 0.03	19.43 ± 0.02	0.33	30.90
0.5	5.24 ^c	6.26	29 100	—	—	0.33	30.90
0.5	5.87 ^c	6.26	29 200	—	—	–0.34	30.32
<i>V</i> -Sep ⁺ , $r = 6$, $\lambda_{\max} = 610$ nm							
0.4	3.9–4.8 ^a	6.73	20 500	1.36 ± 0.02	22.42 ± 0.02	—	—
0.4	5.50 ^c	6.98	28 700	—	—	–0.28	31.37
0.4	6.13 ^c	6.98	—	—	—	–1.86	29.86
0.8	6.16 ^c	6.74	—	—	—	–2.21	26.63
2.0	6.16 ^c	7.61	28 600	—	—	–3.25	21.23

^a In 1 mol⁻¹ cm⁻¹; ^b calculated from pH curves (5), $c_L = c_{\text{UO}_2} = 16 \mu\text{mol l}^{-1}$, average of 8–10 values converted to the logarithmic scale, confidence interval for $\alpha = 0.05$, KCl + HCl system; ^c calculated from concentration curves (1), $c_L = 40 \mu\text{mol l}^{-1}$; ^d calculated from concentration curves (4), $c_L = 40 \mu\text{mol l}^{-1}$, $c_{\text{UO}_2} = 0.1 \text{ mmol l}^{-1}$; ^e calculated from pH curves (5), $c_L = 40 \mu\text{mol l}^{-1}$, $c_{\text{UO}_2} = 0.1 \text{ mmol l}^{-1}$, average of 8–10 values converted to the logarithmic scale, confidence interval for $\alpha = 0.05$, KCl + HCl system.

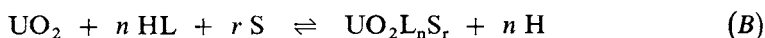
In the titration (4), the absorption curves for dyes *I*–*IV* exhibit a single isosbestic point, whereas those for dye *V* show two isosbestic points ($\lambda_{\text{iso},1}$ 560 nm, $\lambda_{\text{iso},2}$ 546 nm; $c_L = 16 \mu\text{mol l}^{-1}$, $c_{\text{UO}_2} = 4.0 \mu\text{mol l}^{-1}$, 0.2 mmol l⁻¹, pH 4.80, 6.16). The molar ratios method indicates the formation of L : S = 1 : 1 complexes (*I*, CPy⁺), 1 : 2 complexes (*I*, Sep⁺; *II*, CPy⁺, Sep⁺; *III*, CPy⁺, Sep⁺), 1 : 3 complexes (*IV*, CPy⁺, Sep⁺), 1 : 1 and 1 : 3 complexes (*V*, CPy⁺, Sep⁺), and of UO₂ : S = 1 : 2 complexes (*I*, CPy⁺), 1 : 4 complexes (*I*, Sep⁺; *II*, CPy⁺, Sep⁺; *III*, CPy⁺, Sep⁺), 1 : 6 complexes (*IV*, Sep⁺), and 1 : 9 complexes for dye *V* (pH > 5.3). The measurements were carried out with dye concentrations $c_L = 16$ – $40 \mu\text{mol l}^{-1}$ and uranyl ion concentrations $c_{\text{UO}_2} < c_L/2$ or $c_L/3$, or $c_{\text{UO}_2} = (1$ – $15) c_L$; the surfactant concentration was varied over the concentration region $c_S = (0$ – $50) c_L$. Five to seven titrations were performed over the pH 4.4–6.2 region for each dye.

The results thus give evidence of the formation of UO₂L₂S₂ (*I*, CPy⁺), UO₂L₂S₄ (*I*, Sep⁺; *II*, CPy⁺, Sep⁺; *III*, CPy⁺, Sep⁺), UO₂L₂S₆ (*IV*, CPy⁺, Sep⁺; *V*, CPy⁺, Sep⁺, pH < 4.8), and UO₂L₃S₉ (*V*, CPy⁺, Sep⁺, pH > 5.3) complexes. The presence

of surfactant allows for the formation of ternary complexes where the coordination number of uranium is higher than in binary complexes. Since the spectrum of the first complex formed in the reaction of dye *V* in the presence of surfactant, with the $L : S = 1 : 1$ ratio, approaches closely that of the UO_2L binary complex, the former complex can be assumed to be UO_2LS where the surfactant molecule is localized in the position with the highest electron density, *i.e.*, in position 5 or 6, where a carboxy and a hydroxy groups are present in the *ortho* position in the dye molecule¹⁸.

In the $UO_2L_2S_4$ (*I*, Sep^+ ; *II*, CPy^+ , Sep^+), $UO_2L_2S_6$ (*IV*, CPy^+ , Sep^+ ; *V*, CPy^+ , Sep^+), and $UO_2L_3S_9$ (*V*, CPy^+ , Sep^+) complexes the number of the bonded surfactant molecules is higher than the number of sulpho groups in the molecule of the dye; it can be assumed that a molecule of surfactant is localized on the chelating grouping of the carboxy and hydroxy groups in positions 5 and 6 while the remaining surfactant molecules are bonded to the sulpho groups. The bonding of the surfactant to the chelating grouping affects the π -electron distribution over the dye molecule, in contrast to the bonding to the sulpho group which, isolated from the π -electron system, does not affect it appreciably. Thus the coincidence of the peak positions in the electronic spectra of the ternary and binary complexes gives evidence of the surfactant bonding to a sulpho group, whereas different positions of the peaks are indicative of bonding to the chelating grouping. In terms of this hypothesis, in the $UO_2L_2S_2$ complex (*I*, CPy^+) the tenside is bonded to the chelating grouping, and in the $UO_2L_2S_4$ complex (*III*, CPy^+) one of the sulpho groups is unoccupied.

The $UO_2L_nS_r$ ternary complex formation ($n = 2, 3$; $r = 4, 9$) can be described by equation (B) (charges are again omitted),



characterized by the equilibrium constant

$$*\beta_{1nr} = [UO_2L_nS_r][H]^n / \{[UO_2][HL]^n[S]^r\} \quad (9)$$

or by the equilibrium constant in the binary complex formalism,

$$*\beta_{1n} = [UO_2L_n][H]^n / \{[UO_2][HL]^n\} \quad (10)$$

Eq. (9) can be transformed to the form

$$\log \frac{(A - A_0)(A_{\max} - A_0)^{n+r}}{\{npA_{\max} - A - (np - 1)A_0\}(A_{\max} - A)^n \{nqA_{\max} - rA - (nq - r)A_0\}^r} = \\ = \log *\beta_{1nr} + (n + r) \log c_L + n \text{pH} + n \log \left\{ \frac{[H]}{(K'_a + [H])} \right\} \quad (11)$$

or

$$\log \frac{(A - A_0) \{A_{\max} - (n/w) A_0\}^{n+r}}{\{A_{\max} - A + (1 - n/w) A_0\} (wA_{\text{urax}} - nA)^n \{zA_{\max} - rA + (nq - nz/w) A_0\}^r} =$$

$$= \log {}^* \beta'_{1nr} + (n + r) \log c_{\text{UO}_2} + n \text{pH} + n \log \left\{ \frac{[\text{H}]}{K'_a + [\text{H}]} \right\}, \quad (12)$$

where $A_{\max} = \varepsilon_C c_L / n$ (for $p = c_M / c_L \geq 1/n$) or $A_{\max} = \varepsilon_C c_M$ (for $w = c_L / c_{\text{UO}_2} \geq n$), $A_0 = \bar{\varepsilon}_L c_L$, $q = c_S / c_L$, $z = c_S / c_{\text{UO}_2}$, $\bar{\varepsilon}_L$ is the average molar absorptivity of the ternary complex, K'_a is the dissociation constant corresponding to the deprotonisation of the phenolic proton from the dye in the presence of surfactant²¹, and $[L']$ is the conditional concentration of dye in the presence of surfactant.

In the presence of excess surfactant, $c_S = (10 - 50) c_L$, the dependences (11) over the region of pH 3.0–4.5 for dyes I–IV and (12) over the region of pH 3.4–4.6 for dye IV are linear and their slope corresponds to two eliminated protons. The molar absorptivity of $\text{UO}_2\text{L}_2\text{S}_6$ complex was read from the concentration curves (1) (excess surfactant and dye) or from the pH curve (5) (excess uranyl and surfactant). For dye V, the molar absorptivity of $\text{UO}_2\text{L}_2\text{S}_6$ complex was read from the Ketelaar transformation of dependence (1). The equilibrium constants of reaction (B) were calculated numerically *via* Eqs (11) and (12). At higher pH values, the difference between the absorbances of the quantitative and the actual reactions (Eqs (1), (3), (4); refs^{19,20}) or, for dye V at pH > 4.8, the Ketelaar transformation of dependence (1) served for the evaluation of the conditional stability constant β'_{1nr} , or β'_{1n} for the binary complex formation formalism, by Eqs (13), (14):

$$\beta'_{1nr} = [\text{UO}_2\text{L}_n\text{S}_r] / \{[\text{UO}_2][\text{L}']^n[\text{S}]^r\} \quad (13)$$

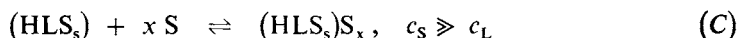
$$\beta'_{1n} = [\text{UO}_2\text{L}_n] / \{[\text{UO}_2][\text{L}']^n\}. \quad (14)$$

These constants were related to the equilibrium constants ${}^* \beta'_{1nr}$ and ${}^* \beta'_{1n}$ as

$${}^* \beta = \beta'([\text{H}] + K'_a)^n. \quad (15)$$

The data are given in Table II.

The decrease in the equilibrium stability constants at higher pH values can be explained by hydrolysis of uranyl ions^{21,22}; the differences in the ${}^* \beta'_{1nr}$ values at different surfactant concentrations may be due to different degrees of association of surfactant; and the decrease in the ${}^* \beta'_{1n}$ values at high surfactant concentrations ($c_S > 10c_L$) can be interpreted⁴ in terms of reactions (C) and (D) counteracting the ternary complex formation:





where s is the number of sulpho groups in the dye molecule.

Determination of Uranium

At pH 4.3–4.8, 4.4–4.9, and 5.2–5.9 for dyes *II*, *III*, and *IV*, respectively, the stability of the complexes is sufficient to enable a direct photometric determination of uranium in excess dye and surfactant. The results for a series of test determinations are given in Table III.

Alkali metal ions, alkaline earth ions, Ce^{3+} ions in a 50-fold excess, lanthanoids in a 50-fold excess, Cd^{2+} , Ni^{2+} , Mn^{2+} , Co^{2+} ions in a 10-fold excess, Cr^{3+} , Pb^{2+} , CrO_4^{2-} , PtCl_6^{2-} , Ag^+ , Zn^{2+} ions in a 5-fold excess, and Y^{3+} , Bi^{3+} , Ti^{4+} , Zr^{4+} , Th^{4+} , Sb^{3+} and Sn^{4+} ions in an equimolar quantity do not interfere; Hg_2^{2+} , Hg^{2+} , Fe^{3+} , Fe^{2+} , Sc^{3+} , Cu^{2+} , Al^{3+} , VO_3^- , MoO_4^{2-} , WO_4^{2-} , Pd^{2+} , In^{3+} , Ga^{3+} , Sn^{2+} , Ti^{3+} , Ce^{4+} , and Au^{3+} ions interfere with the determination.

The selectivity of determination is the same for the dyes examined. Dye *IV* is superior to the others from the sensitivity point of view. The ionic strength of all the solutions should be the same because the absorbance is ionic strength-dependent; over the region of I 0.005–0.015, however, the absorbance changes are negligible. The colour develops instantly on the component mixing and remains steady for several hours. Dye *I* does not suit to the analysis because L–S ionic associates tend to separate from the solution.

Procedure. Sample containing 28–380 μg uranium is added to a mixture of 8 ml $1.0 \cdot 10^{-3}\text{M}$ solution of dye *IV*, 5 ml of 0.1M acetate buffer pH 5.3 and 8 ml of $1.0 \cdot 10^{-2}\text{M}$ solution of Sep⁺

TABLE III
Photometric determination of uranium

Dye	c_L^a	c_s^a	Uranium concentration region $\mu\text{g ml}^{-1}$	pH	λ nm	ϵ^b	Sensitivity of determination ^c $\mu\text{g cm}^{-2}$	Relative standard deviation ^d %
<i>II</i>	0.20	0.20	0.50–15.0	4.69	645	27 400	0.011	1.1 (4.41)
<i>III</i>	0.20	0.15	0.76–9.5	4.67	640	21 000	0.013	1.3 (4.75)
<i>IV</i>	0.16	0.16	0.57–7.6	5.35	615	28 500	0.011	1.1 (4.75)

^a In mmol l^{-1} ; ^b in $1 \text{ mol}^{-1} \text{ cm}^{-1}$; ^c for $A = 0.001$; ^d $v = (s/\bar{x}) \cdot 100\%$ for the amount in parentheses in $\mu\text{g ml}^{-1}$, $s = k_n \cdot R$, $n = 6$, $\alpha = 0.05$.

in a 50 ml volumetric flask, and the system is diluted to volume with water. The absorbance is measured at 615 nm against a blank.

The method was tested on ferrouanium and alloy steels. For ferrouanium, the results were analogous to those reported in Table III. For alloy steels the results were poorer which was due to an imperfect separation of the ion to be determined, as found by the analysis of the procedure according to Shewell²³ and Maurice²⁴.

The authors wish to thank Mr. J. Juřina (Lachema, Brno) for providing them with the dyes in sufficient quantities.

REFERENCES

1. Son N. T.: *Thesis*. Palacký University, Olomouc 1975.
2. Lasovský J., Ružička E.: *This Journal* 42, 1941 (1977).
3. Son N. T., Lasovský J., Ružička E., Šimek J., Szotkowská J.: *This Journal* 44, 1568 (1979).
4. Šimek J., Son N. T., Ružička E.: *Chem. Zvesti*, in press.
5. Ružička E., Son N. T.: *This Journal* 43, 1885 (1978).
6. Ružička E., Son N. T.: *Acta Univ. Palacki. Olomuc., Fac. Rerum Natur.* 61/65, 189 (1979/80).
7. Šimek J., Ružička E.: *Acta Univ. Palacki Olomuc., Fac. Rerum Natur.* 49, 183 (1976).
8. Šimek J., Ružička E.: *Acta Univ. Palacki Olomuc., Fac. Rerum Natur.* 73, 89 (1982).
9. Šimek J., Ružička E.: *Acta Univ. Palacki Olomuc., Fac. Rerum Natur.* 61/65, 169 (1979/80).
10. Sedláčková J.: *Thesis*. Palacký University, Olomouc 1975.
11. Juřina J., Ružička E.: Unpublished results.
12. Uno T., Miyajima K., Tsukatani H.: *Yakugaku Zashi* 80, 153 (1960); *Chem. Abstr.* 54, 11 824z (1960).
13. Cross T.: *Analyst (London)* 90, 315 (1965).
14. Patrovský V.: *Analytická chemie vzácných prvků*, p. 126. Published by SNTL, Prague 1956.
15. Joe J. A., Jones A. L.: *Ind. Eng. Chem., Anal. Ed.* 16, 11 (1944).
16. Job P.: *Ann. Chim. (Paris)* 9, 113 (1928).
17. Ketelaar A. A. J., van de Stolpe C., Goudsmit A., Dzcubas W.: *Rec. Trav. Chim. Pays-Bas* 71, 1104 (1952).
18. Pilipenko A. T., Savranskii L. I., Šimek J.: *Talanta* 27, 349 (1980).
19. Sommer L., Jin Tsin Jao: *Chem. Listy* 55, 574 (1961).
20. Nomura T.: *Bull. Chem. Soc. Jap.* 41, 2803 (1968).
21. Šimek J., Son N. T., Ružička E.: *Acta Univ. Palacki. Olomuc., Fac. Rerum Natur.* 79, 185, (1984).
22. Baes Ch. F., jr, Mesmer R. E.: *The Hydrolysis of Cations*, p. 174. Wiley, New York 1976.
23. Shewell C. T.: *Anal. Chem.* 31 (5), 21A (1959).
24. Maurice M. J.: *Fresenius' Z. Anal. Chem.* 158, 271 (1957).

Translated by P. Adámek.