

THE REACTION OF UO_2^{2+} WITH CHROMAZUROL S AND THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM IN THE PRESENCE OF SEPTONEX

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This work is concerned with a detailed study of the reaction of UO_2^{2+} with chromazurol S in the presence of cationic tenside Septonex, which was found to be very promising of the group of cationic tensides. From the study were drawn a number of conclusions regarding the effect of the cationic tenside on the reaction of triphenylmethane dyes with salicylic acid groups with metal cations. Optimum conditions for the spectrophotometric determination of uranium with chromazurol S in the presence of Septonex were found.

The reaction of UO_2^{2+} with chromazurol S is among the more marked reactions of this triphenylmethane dye with salicylic acid functional groups, which has already been studied and recommended for the spectrophotometric determination of uranium in pure solutions¹⁻⁴.

In the presence of high molecular weight detergents and macromolecular type substances this reaction becomes analytically interesting and enables highly sensitive spectrophotometric determination of uranium which has, however, limited sensitivity. The following substances have been recommended for the determination of uranium with chromazurol S: polyvinyl alcohol⁵, cetylpyridinium bromide^{6,7}, cetyltrimethylammonium chloride⁸ and gelatine⁹. Evtimova¹⁰ studied the effect of a larger number of cationic detergents on the reaction of UO_2^{2+} with chromazurol S.

The interaction between UO_2^{2+} -chelates and tensides reflects a more complicated reaction mechanism, different from the reaction in media lacking tenside and which strongly affects the conditions for the spectrophotometric method.

This work deals with study of the reaction of UO_2^{2+} with chromazurol S in the presence of Septonex (*p*-ethoxycarbonylpentadecyltrimethylammonium bromide) which was found to be most useful for UO_2^{2+} of a large number of tested cationic tensides. A sensitive method for the spectrophotometric determination of uranium in the presence of this tenside was optimized.

EXPERIMENTAL AND RESULTS

Chemicals and Solutions

The standard solution of 0.173M uranyl nitrate in dilute nitric acid with pH 0.9 was standardized gravimetrically *via* the 8-hydroxyquinolate and was diluted with distilled water. Chromazurol S

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(the sodium salt of 3"-sulpho-2",6"-dichloro-3,3'-dimethyl-4-hydroxyfuchson-5,5'-dicarbonic acid), from the firm Geigy, Basel, contained several coloured components, primarily chromazurol B (the unsulphonated analogue of chromazurol S) in amounts of up to 10%. In the purification 3 g of the sodium salt of chromazurol S were dissolved in 55 ml of redistilled water, the solution was acidified with several drops of conc. HCl of semiconductor purity so that a precipitate was not formed and chromazurol B was extracted from the acidic aqueous solution into ether saturated with HCl (phase volume ratio 1 : 1) and then ether without HCl; the extraction was repeated five times to disappearance of the yellow colouration of the ether phase. The aqueous phase was then precipitated by dropwise additions of conc. HCl of semiconductor purity; the precipitated acidic form of chromazurol S was collected on an S3 sintered glass filter and washed with HCl (1 : 1). After complete removal of solvent it was dried over KOH and equilibrated in the air to a constant weight. The content of active dye ($C_{23}H_{16}O_9S_2Cl_2 \cdot 2H_2O$, m.w. 575) was calculated from the carbon content found by elemental analysis of the substance (92.25% active component as the dihydrate of free chromazurol S acid). The reagent purity was controlled by TLC on Silufol^R impregnated with 0.05M-EDTA and using a solvent mixture of n-butanol-acetic acid-water (7 : 1 : 3) or isopropanol-25% ammonia-water (8 : 1 : 2).

The stock reagent solution ($c_L = 5 \cdot 10^{-4}M$) was prepared by dissolving the pure substance in 2.6M-NH₃ and the solution was adjusted with 1M-HNO₃ to pH 8.5 and diluted to a precise volume (c. 250 ml) with distilled water. A solution prepared in this way is stable for at least 10 days.

The following chemicals were also used: Zephiramine (benzyltrimethyltetradecylammonium chloride, $C_{23}H_{42}ClN$, m.w. 368.0), from the firm Dojindo Co., Japan; stock solution $4.0 \cdot 10^{-2}M$, in 95% ethanol; cetylpyridinium bromide ($C_{21}H_{38}BrN$, m.w. 384.4) from the firm Lachema, Brno, stock solution $2.0 \cdot 10^{-2}M$ in 20% (v/v) ethanol; cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$, m.w. 364.4) from the firm Lachema, Brno, stock solution $2.0 \cdot 10^{-2}M$ in ethanol; Septonex (1-ethoxycarbonylpentadecyltrimethylammonium bromide ($C_{21}H_{44}BrNO_2$, m.w. 422.5) of Czechoslovak Pharmacoepia 3 purity from Slovafarma, Hlohovec. The commercial preparation was purified by dissolving in the smallest amount of hot ethanol (about 20 ml) and the solution was added dropwise into 200 ml of ethyl ether. The precipitated plates of pure tenside were collected on an S4 sintered glass filter and dried. The Septonex concentration in the pure preparation was controlled by potentiometric argentometric titration of the bromide and the curve was evaluated by the Gran method. The ethanolic stock solution concentration was $4 \cdot 10^{-2}M$.

Ajatin (benzyltrimethyl laurylammonium bromide, $C_{21}H_{38}BrN$, m.w. 384.4), Spofa, Prague. The commercial solution was concentrated and cooled to 5–8°C; after several weeks tenside crystals were precipitated out, filtered off from the mother liquor, dried and stored over silica gel. The stock solution contained 10^{-2} – $10^{-3}M$ of the substance in water.

Solvasol O (lauryl alcohol with 4.7 mol of ethylene oxide, m.w. 393.4), from the W. Pieck factory, Nováky Czechoslovakia). The substance was dissolved in hot ethanol (1 g in 1 ml 95% ethanol), the solution was briefly boiled with purified active charcoal and filtered on a S4 sintered glass filter; the solution was concentrated at 45°C in a vacuum evaporator and left to crystallize in a cold place. The substance was filtered off and dried over P₂O₅ *in vacuo*.

Polyvinyl alcohol (Moviol 50/80), Farbwerke Höchst, GFR contained 12% unhydrolyzed acetate groups. Polyvinylpyrrolidone (m.w. 24500), pharm. pure, from Koch Light Lab., Ltd., Colnbrook, Bucks, England; a 0.5% stock solution was employed. Sodium lauryl sulphate ($C_{12}H_{25}NaO_4S$, m.w. 288.4) from the firm BDH Ltd., Poole, England. KNO₃, *p.a.*, Lachema, was recrystallized twice after removal of traces of heavy metals by the method of Biederman¹¹; HNO₃, HCl, ammonia were of *p.a.* purity; NaOH *p.a.*, Lachema, Fe(III) and other metallic impurities were removed after standing for a prolonged time in a 50% aqueous solution in a closed

PE vessel and rapid filtration of the solution through an S4 sintered glass filter under nitrogen.

The buffers employed were in equimolar mixtures with HNO_3 and the final concentration of the base in the stock solution was 1M: Tris(tris(hydroxymethyl)aminomethane) ($\text{p}K_a$ 8.10); triethanolamine ($\text{p}K_a$ 7.90); hexamethylenetetraamine ($\text{p}K_a$ 5.13); α -picoline ($\text{p}K_a$ 6.02), redistilled; pyridine ($\text{p}K_a$ 5.18), redistilled; Tris- and hexamethylenetetraamine were recrystallized 2–3 times from water.

Masking solution: 0.25M stock solution of Mg^{2+} -chelate of cyclohexanediaminetetraacetic acid (CDTA) was prepared by dissolving 43.3 g of CDTA in 240 ml of redistilled water containing 10 g NaOH. An amount of 38.5 g $\text{Mg}(\text{NO}_3)_2$ in 200 ml water was added to this solution. After adjusting the pH to 7.5 the solution was diluted to 500 ml with distilled water and filtered.

All the other chemicals employed were analytically pure or recrystallized.

Instruments

Umicam SP-500 spectrophotometer, Superscan Varian recording spectrophotometer, PHM-4 pH-meter, Radiometer, Copenhagen, with a G 200B glass electrode, calibrated with aqueous NBS buffers and 0.1M-HCl solutions in the pH range 1–10 and s.c.e. reference electrode, K 401 Radiometer, were used.

Method of pH Measurement

In the presence of tenside the electrode response shifts to higher pH values in the pH region $\text{pH} > 7$ and to lower pH values in the region $\text{pH} < 7$ after short use (after two or three days). Simultaneously, the period required for electrode potential equilibration increases. Poisoning of the glass electrode appears as a variable pH value in quiescent solution and during stirring of the solution with a magnetic stirrer (positive pH change of about 0.15–0.25 units). With repeated turning on and off of the stirrer, the pH of the quiescent solution shifts to higher values without stabilization at a defined value. These undesirable phenomena can be prevented by careful wiping of the bulb of the glass electrode with tissue paper and washing both electrodes (glass and s.c.e.) with hot ethanol. The uranium–chromazurol S-tenside complex adsorbed on the electrodes can be decomposed by 1M- HNO_3 or dissolved in hot dimethylformamide. The measurement is carried out with slow diffusion of the saturated KCl solution from the s.c.e. into the measured solution.

Method of Studying Complexes in Solution

The reaction mechanism was studied spectrophotometrically. The absorbance-pH curves and concentration dependences of the absorbance at constant pH were interpreted using the earlier derived slope-intercept transformations^{12–15} and by graphical logarithmic transformations of the equilibrium constant (DSILT) for solutions with excess cation, excess reagent or for equimolar solutions in the presence of the tenside. The basic transformations used are listed in Table I.

The method of continuous variations and mole ratios and the absorption curves independence on the pH or on the concentrations of the components yielded supplementary data.

The Kankare¹⁶ program segmented and adjusted for use with a Tesla 200 computer (ref.¹⁷) was used for matrix analysis of the absorption curves of the reagent in the presence and absence of tenside and in dependence on the pH. The concentration of all forms of the reagent, the molar absorption coefficients of all absorbing forms of the reagent for all the λ values employed and the dissociation constants of the reagent were calculated for all the pH values at which the absorption curves of the reagent were measured. On the basis of this data distribution diagrams

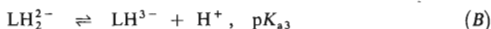
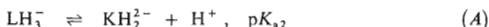
can be drawn up for the individual forms of the reagent and absorption curves for the individual absorbing components.

The critical micelle concentration of the tenside, CMC, was found conductometrically from the shape of the dependence $A = f(\sqrt{c})$ and from measurement of the surface tension by drop weighing. The CMC value found for Septonex was $c_D = 0.9 \cdot 10^{-3} \text{ M}$ (from conductance measurements) or $1.6 \cdot 10^{-3} \text{ M}$ (from surface tension) in aqueous solutions at $I \rightarrow 0$. In further work the tenside concentration employed was generally greater than the CMC value. The ternary UO_2^{2+} -chromazurol S-Septonex complex is formed even at submicellar concentrations of the tenside; however, the solution absorbance is unstable and the complex is readily precipitated from solution.

Some Acid-Base Equilibria of Chromazurol S in the Presence of Septonex

The absorption curves of chromazurol S in the presence of Septonex and in dependence on the pH corresponding to the transitions $\text{LH}_3 \rightarrow \text{LH}_2$ and $\text{LH}_2 \rightarrow \text{LH}$ (Fig. 1, 2) have sharp isosbestic points and a marked plateau at 580 nm, which is characteristic of the ion associate $\text{LH}_2^{2-} \cdot 2 \text{ D}^+$ (ref.¹⁵). The long wavelength maximum in the spectrum of the associate reflects the polarization of the phenolic hydroxyl bond of the reagent in the $\text{LH}_2^{2-} \cdot 2 \text{ D}^+$ ion associate with the tenside. This maximum is close to that of the L^{4-} form in aqueous solutions without tenside ($\lambda_{\text{max}} 598$).

Of the five acid-base equilibria of the reagent¹⁸, only the equilibria of the carboxyl protons were evaluated:



which are established in the pH region corresponding to the formation of the complex with UO_2^{2+} . The absorption curves were measured at the critical micelle concentration of Septonex ($c_D = 1.6 \cdot 10^{-3} \text{ M}$) and at two concentrations of chromazurol S and interpreted using the KANKARE program for calculation of the molar absorption coefficients at various wavelengths and dissociation constants of the reagent. Simultaneously, the pH curves for the λ_{max} of LH_3^- , LH_2^{2-} and LH^{3-} were evaluated for a single reagent concentration and four tenside concentrations so that $c_D/c_L \geq 10$, where the turbidity by the ion associate of chromazurol S with Septonex is not formed. The resultant concentration of ethanol in solution was 4%. The values of $\text{p}K_{a2}$, $\text{p}K_{a3}$, λ_{max} and the molar absorption coefficient for some wavelengths are given in Tables II and III.

In the presence of the tenside at its critical micelle concentration, protonation of LH^{3-} occurs more readily and dissociation of LH_2^{2-} is more difficult at higher pH values than in solutions without tenside. The H_2L^{2-} form is preferred in the presence of the tenside, as the stable ion associate $\text{LH}_2^{2-} \cdot 2 \text{ D}^+$ with the cationic tenside is formed¹⁵. The dissociation of H_3L is shifted to more acid media and the

dissociation of H_2L to more alkaline media. The absorbance-pH curve of the reagent in the presence of the tenside is measured from acid to alkaline regions is not the same as that measured from alkaline to acid medium. The $\text{p}K_{\text{a}3}$ value obtained on transition from alkaline to acid medium is smaller than that measured in the opposite direction, as LH_2 dissociates more readily, similarly as in solutions without

TABLE I

Basic Use of Slope-Intercept Transformations for Equilibrium Constants

Equilibrium: $m\text{M} + n\text{H}_1\text{L} + p\text{D} \rightleftharpoons \text{M}_m\text{L}_n\text{H}_z\text{D}_p + q\text{H}$

Solutions with excess $c_{\text{M}} (c_{\text{D}} = \text{const})$:

$$c_{\text{L}}/A = n/\varepsilon_1 + \frac{Z(A - A_{\text{L}})(Z\varepsilon_1 - n\varepsilon_{\text{L}})^{n-1} [\text{H}]^q}{A(\varepsilon_1 c_{\text{L}} - nA)^{n-1} c_{\text{M}}^m \varepsilon_1} \quad (1)$$

$$A = \varepsilon_1 c_{\text{L}}/n - \frac{Z(A - A_{\text{L}})(Z\varepsilon_1 - n\varepsilon_{\text{L}})^{n-1} [\text{H}]^q}{(\varepsilon_1 c_{\text{L}} - nA)^{n-1} c_{\text{M}}^m n^* \beta} \quad (2)$$

$Z = 1 + ([\text{H}]/K_{\text{a}})^{\pm 1}$ (reaction of the dissociated reagent form (+),

$Z A_{\text{L}} = \varepsilon_{\text{L}} c_{\text{L}}$ (undissociated reagent form (-))

$c_{\text{L}} = \varepsilon_{\text{L}(x)} + \varepsilon_{\text{L}(x-1)} K_{\text{a}}/[\text{H}]$

$$\log \frac{Z(A - A_{\text{L}})}{(\varepsilon_1 c_{\text{L}} - nA)^n} + (n-1) \log (Z\varepsilon_1 - n\varepsilon_{\text{L}}) = m \log c_{\text{M}} + q \text{pH} + \log * \beta \quad (3)$$

Solutions with excess c_{L} :

$$c_{\text{M}}/(A - A_{\text{L}}) = m/\varepsilon_1 + \frac{[\text{H}]^q Z^n \varepsilon_1^{m-2}}{[\varepsilon_1 c_{\text{M}} - m(A - A_{\text{L}})]^{m-1} * \beta c_{\text{L}}^n} \quad (4)$$

$$A - A_{\text{L}} = \varepsilon_1 c_{\text{M}}/m - \frac{(A - A_{\text{L}}) [\text{H}]^q Z^n \varepsilon_1^{m-1}}{[\varepsilon_1 c_{\text{M}} - m(A - A_{\text{L}})]^{m-1} * \beta c_{\text{L}}^n} \quad (5)$$

$$\log \frac{(A - A_{\text{L}}) Z^n}{[\varepsilon_1 c_{\text{M}} - m(A - A_{\text{L}})]^m} = \log * \beta + n \log c_{\text{L}} + q \text{pH} - (m-1) \log \varepsilon_1 \quad (6)$$

$$c_{\text{M}}/\Delta A = \frac{1}{\varepsilon - n\varepsilon_{\text{L}}/Z} + \frac{1}{(c_{\text{L}} - \Delta A/(\varepsilon - n\varepsilon_{\text{L}}/Z))} \text{const.} \quad (7)$$

$$\begin{aligned} \log \frac{\Delta A}{c_{\text{M}} - \Delta A/(\varepsilon - n\varepsilon_{\text{L}}/Z)} &= \log x + q \text{pH} = \\ &= n \log \left(c_{\text{L}} - \frac{n \Delta A}{\varepsilon - n\varepsilon_{\text{L}}/Z} \right) + \log (\varepsilon - n\varepsilon_{\text{L}}/Z) - n \log Z. \end{aligned} \quad (8)$$

tenside. The associate is formed less readily, appearing as hysteresis in the absorbance-pH curve in the presence of the tenside. The distribution diagram of the reagent in solutions with and without Septonex is given in Fig. 3.

The process of proton dissociation from the reagent molecule in the presence of tenside according to the assumed scheme¹⁸ leads to structure (1), which does not, however, exclude structure (2) in the presence of tenside, which corresponds better to the behaviour of the system with UO_2^{2+} and tenside.

The absorbance of the reagent solutions at 612 nm and the time dependence of the absorbance are dependent on the method of preparation of the Septonex solutions and on the content and type of solvent. After addition of an aqueous solution of Septonex the absorbance of the reagent decreases with time and becomes constant after 4 days at pH 5 and $c_D = 1.6 \cdot 10^{-3} \text{M}$. The absolute absorbance values change in dependence

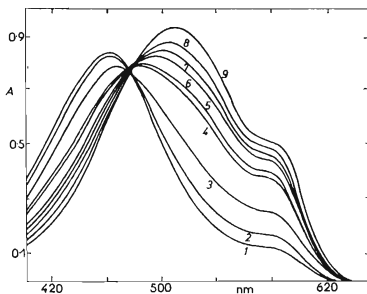


FIG. 1

Absorption Curves in the Chromazurol S-Septonex System in Dependence on the pH ($\text{LH}_3^- \rightarrow \text{LH}_2^{2-}$ Transition)

pH: 1 0.85; 0.90; 2 1.20; 3 1.30; 4 1.47; 5 1.60; 6 1.77; 7 1.90; 8 2.08; 9 2.90. $c_L = 4.47 \cdot 10^{-5} \text{M}$; $c_{\text{EDTA}} = 6 \cdot 10^{-4} \text{M}$, $c_D 1.6 \cdot 10^{-3} \text{M}$.

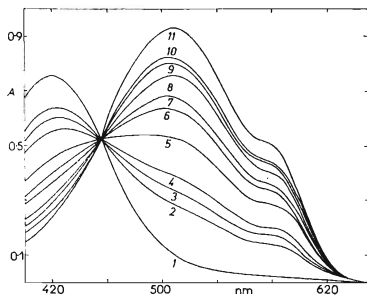
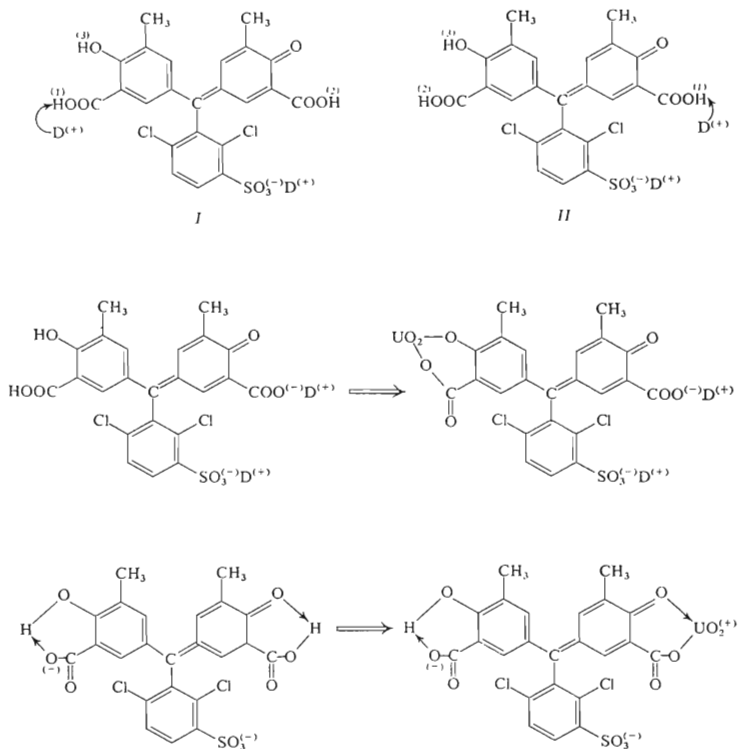


FIG. 2

Absorption Curves in the Chromazurol X-Septonex System in Dependence on the pH ($\text{LH}_2^{2-} \rightarrow \text{LH}^{3-}$ Transition)

pH: 1 1.864; 2 6.04; 3 5.87; 4 5.73; 5 5.48; 6 5.24; 7 4.84; 8 5.11; 9 4.67; 10 4.51; 11 3.71, $c_L = 4.47 \cdot 10^{-5} \text{M}$; $c_{\text{EDTA}} = 6.04 \cdot 10^{-4} \text{M}$, $c_D 1.6 \cdot 10^{-3} \text{M}$.

on the solvent employed (water, ethanol or dimethylformamide) and its content in the Septonex solution. At pH 8 older aqueous solutions of Septonex with chromazurol S exhibit lower absorbance than freshly prepared Septonex solutions. A stock solution of Septonex in 95% ethanol was employed for greater reproducibility of measurements.



REACTION OF $\text{UO}_2(\text{II})$ WITH CHROMAZUROL S IN THE PRESENCE OF SEPTONEX*Solutions with Excess c_M*

Two typical absorption maxima appear on the absorption curves at 594 and 612 nm at constant $\text{pH} > 3.6$ and variable metal cation excess and also at various tenside excesses (Figs. 4, 5). The long wavelength maximum (612 nm) grows markedly at small tenside concentrations; however, in both cases the curves pass through a single isosbestic point at 550 nm. The long wave maximum appears primarily for the UO_2^{2+} complex in solutions with $c_M/c_L \geq 10$ and for a small concentration of tenside, $c_D = 4 \cdot 10^{-4} \text{M}$. At $\text{pH} 4.5$ where associate decomposition does not occur in the tenside concentration interval used, only the ratio of the peaks of the double maximum varies and the spectra pass through a single isosbestic point at 604 nm.

The absorbance-pH curves with various metal cation excesses and in equimolar solutions have analogous course with a single defined plateau for a constant tenside concentration, $c_D = 1.6 \cdot 10^{-3} \text{M}$ (Figs 6, 7). At small tenside concentrations, $c_D = 1.6 \cdot 10^{-4} \text{M}$, $c_D/c_M = 2$, a precipitate is formed at $\text{pH} 3.2$, probably $\text{UO}_2\text{L}^{2-} \cdot 2 \text{D}^+$, where the number of tenside molecules bound to the reagent does not change (Fig. 7). With increasing tenside concentration, the complex formation becomes less easy and the complex is formed in less acid medium; simultaneously, however, the absorbance of the plateau decreases (Fig. 7). The fragment of curve 1 (Fig. 7) after interpretation by the DSILT using transformations (1-3) (Table I) and with extrapolated value $\epsilon = 128000$ for 612 nm indicates a number of dissociated protons equal to $q = 2$ for $m(\text{M}) = 1$ and $n(\text{L}) = 1$ for the reaction of form H_2L according to (C):

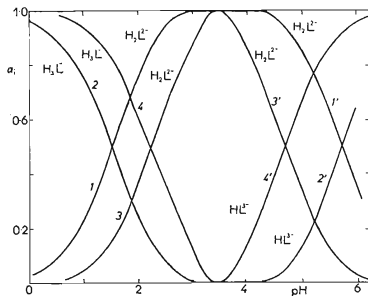
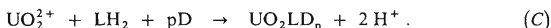


FIG. 3
Distribution Diagrams of Individual Forms of Chromazurol S in the Presence of Septonex (curves 1, 2) and without Septonex (curves 3, 4)

$$\alpha_i = \text{LH}_i/c_L.$$

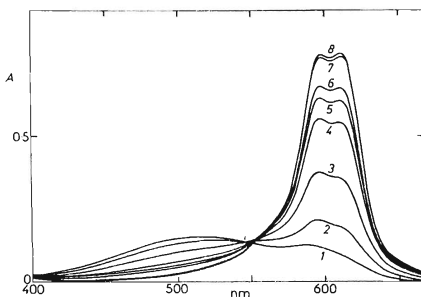


FIG. 4

Absorption Curves in the Chromazurol S- UO_2 -Tenside System in Dependence on the Concentration of UO_2 at pH 3.80

$c_L = 8 \cdot 10^{-6} \text{M}$; $c_D = 1.6 \cdot 10^{-3} \text{M}$; c_M : 1 $4.335 \cdot 10^{-6} \text{M}$; 2 $8.672 \cdot 10^{-6} \text{M}$; 3 $1.734 \cdot 10^{-5} \text{M}$; 4 $3.468 \cdot 10^{-5} \text{M}$; 5 $4.002 \cdot 10^{-5} \text{M}$; 6 $6.936 \cdot 10^{-5} \text{M}$; 7 $2.427 \cdot 10^{-4} \text{M}$; 8 $4.162 \cdot 10^{-4} \text{M}$.

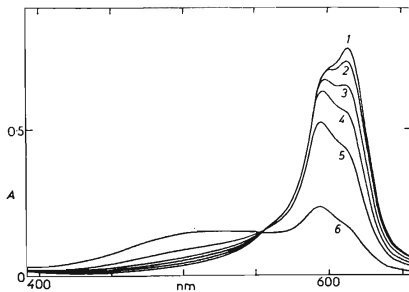


FIG. 5

Absorption Curves in the Chromazurol S- UO_2 -Septonex System in Dependence on the Septonex Concentration

$c_L = 8 \cdot 10^{-6} \text{M}$; $c_M = 8.672 \cdot 10^{-5} \text{M}$; $c_M/c_L = 10.81$; pH 3.60; c_D : 1 $4 \cdot 10^{-4} \text{M}$; 2 $8 \cdot 10^{-4} \text{M}$; 3 $1.6 \cdot 10^{-3} \text{M}$; 4 $8 \cdot 10^{-3} \text{M}$; 5 $1.6 \cdot 10^{-2} \text{M}$; 6 $4.8 \cdot 10^{-2} \text{M}$.

Equilibrium (C) was demonstrated unambiguously for curves of solutions with $c_D = 1.6 \cdot 10^{-3} \text{ M}$ and $c_M = 8.672 \cdot 10^{-5} - 2.167 \cdot 10^{-3} \text{ M}$ (Fig. 6) from $\text{pH} > 2.6$ ($c_M/c_L = 2/7$), from $\text{pH} > 3.0$ (from $c_M/c_L = 54$) and from $\text{pH} > 3.4$ ($c_M/c_L = 10.8$) using transformations (1, 2). Extrapolation of this part of the curves in agreement

TABLE II
Some Dissociation Constants of Chromazurol S in the Presence of Septonex

$c_L \text{ M}$	$c_D \text{ M}$	$\text{p}K_{a3}$	$\text{p}K_{a2}$
$3.47 \cdot 10^{-5}$	—	4.787 ± 0.012^b	2.309 ± 0.001^b
		4.88 ± 0.02^a	2.37 ± 0.01^a
$1.6 \cdot 10^{-5}$	$1.6 \cdot 10^{-3}$	5.479 ± 0.06^b	1.147 ± 0.002^b
$4.47 \cdot 10^{-5}$	$1.6 \cdot 10^{-3}$	5.430 ± 0.008^b	1.261 ± 0.003^b
$8 \cdot 10^{-6}$	$1.6 \cdot 10^{-4}$	5.48^c	
		5.49^d	
	$1.6 \cdot 10^{-3}$	$5.60^c; 5.59^d$	
	$8.0 \cdot 10^{-3}$	$5.63^c; 5.63^d$	
	$8.0 \cdot 10^{-2}$	$5.68^c; 5.67^d$	

^a See ref.⁴; ^b calculated by the KANKARE program; ^c 510 nm; ^d 430 nm.

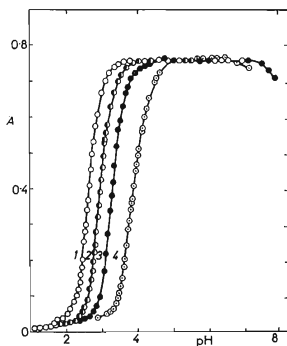


FIG. 6
The Dependence of the Absorbance of a Solution of Chromazurol S with Excess UO_2^{2+} in the Presence of Septonex on pH
 $c_L = 8 \cdot 10^{-6} \text{ M}$; $c_D = 1.6 \cdot 10^{-3} \text{ M}$; c_M :
1 $2.167 \cdot 10^{-3} \text{ M}$; 2 $4.335 \cdot 10^{-4} \text{ M}$; 3 $8.672 \cdot 10^{-5} \text{ M}$; 4 $8.000 \cdot 10^{-6} \text{ M}$; c_M/c_L : 1 270; 2 54;
3 10.8; 4 1.0.

TABLE III
 λ_{max} and Molar Absorption Coefficients for Some Forms of Chromazurol S with and without Septonex

c_L, M	c_D, M	$\lambda_{\text{max}}, \text{nm}$	$\epsilon, \text{mol}^{-1} \text{l cm}^{-1}$	H_3L $\epsilon, \text{mol}^{-1} \text{l cm}^{-1}$	$\lambda_{\text{max}}, \text{nm}$	$\epsilon, \text{mol}^{-1} \text{l cm}^{-1}$	H_2L $\epsilon, \text{mol}^{-1} \text{l cm}^{-1}$	$\lambda_{\text{max}}, \text{nm}$	$\epsilon, \text{mol}^{-1} \text{l cm}^{-1}$	HL
$3 \cdot 47 \cdot 10^{-5}$	—	470	18 800	498	19 500	429; 426	19 000			
$1 \cdot 6 \cdot 10^{-5}$	$1 \cdot 6 \cdot 10^{-3}$	457	21 000	512	21 500	420	16 600			
$4 \cdot 47 \cdot 10^{-5}$	$1 \cdot 6 \cdot 10^{-3}$	458	21 400	512	21 100	420	17 000			
$8 \cdot 0 \cdot 10^{-6}$	$1 \cdot 6 \cdot 10^{-4}$	—	20 800 ^a 460 nm	—	20 915 ^b 510 nm	—	16 820 ^c			
	$1 \cdot 6 \cdot 10^{-3}$	—	—	—	20 727 ^b	—	16 740 ^c			
	$8 \cdot 0 \cdot 10^{-3}$	—	21 960 ^a	—	21 520 ^b	—	17 270 ^c			
	$8 \cdot 0 \cdot 10^{-2}$	—	23 590 ^a	—	22 630 ^b	—	19 030 ^c			

^a 460 nm; ^b 510 nm; ^c 430 nm.

with the experimental plateau yields a lower δ value (612 nm) = 95000–98750 using a continuous measuring technique or measuring solutions in flasks after 10 min. For absorbance values at 612 nm and at pH < 2.6 (curve for solutions with

TABLE IV

Survey of the Molar Absorption Coefficients for the Ternary Complex of UO_2^{2+} with Chromazul S and Septonex (results of analysis of the absorption curves)

$\epsilon, \text{mol}^{-1} \text{l cm}^{-1}$		Conditions
598 nm	612 nm	
100 200; 100 900	98 750; 95 000	$A = f(\text{pH}); c_L = 8.0 \cdot 10^{-6} \text{M}; c_M = 8.672 \cdot 10^{-5}$ to $2.167 \cdot 10^{-3} \text{M}; c_D = 1.6 \cdot 10^{-3} \text{M}$
—	12 800	$c_M = 8.672 \cdot 10^{-5} \text{M}; c_L = 8.0 \cdot 10^{-6} \text{M}$ $c_D = 1.6 \cdot 10^{-4} \text{M}$
100 200; 100 900	98 750; 95 000	$c_D = 1.6 \cdot 10^{-3} \text{M}$
108 100	92 500	$c_D = 8.0 \cdot 10^{-3} \text{M}$
109 700	87 500	$c_D = 8.0 \cdot 10^{-2} \text{M}$
109 700	86 250	$c_L = 8.0 \cdot 10^{-6} \text{M}; c_D = 8.0 \cdot 10^{-2} \text{M}$
109 100	87 500	$c_M = 8.672 \cdot 10^{-5} \text{M}$ $c_M = 2.167 \cdot 10^{-3} \text{M}$
101 500	98 800	$c_L = 8.0 \cdot 10^{-6} \text{M}; c_D = 1.6 \cdot 10^{-3} \text{M}$ $c_M = 8.672 \cdot 10^{-5} \text{M} - 3.47 \cdot 10^{-3} \text{M}$
101 500	94 400	$A = f(c_M); \text{pH } 2.90$ $\text{pH } 3.20$
	101 500 ^a ; 112 500	$A = f(\text{pH}); c_M = 8 \cdot 10^{-6} \text{M}; c_D = 1.6 \cdot 10^{-3} \text{M}$
	100 000 ^a ; 112 500	$c_L = 6 \cdot 10^{-5} \text{M}$
	101 000 ^a ; 112 500	$c_L = 8 \cdot 10^{-5} \text{M}$ $c_L = 1.2 \cdot 10^{-5} \text{M}$
	131 000	$c_M = 8.0 \cdot 10^{-6} \text{M}; c_L = 1.6 \cdot 10^{-5} \text{M}$
	125 000	$c_D = 4.0 \cdot 10^{-4} \text{M}$
	119 000	$c_D = 1.6 \cdot 10^{-3} \text{M}$ $c_D = 1.6 \cdot 10^{-2} \text{M}$
	101 500	$A = f(c_L); \text{excess reagent}$
	108 000	$c_D = 1.6 \cdot 10^{-3} \text{M}; \text{pH } 3.60$
	106 100	$\text{pH } 4.20$
	102 700	$\text{pH } 7.00$ $\text{pH } 7.00; c_D = 1.6 \cdot 10^{-2} \text{M}$

^a Extrapolated from transformations (4) and (5).

$c_M/c_L = 271$), at $\text{pH} < 3.0$ for solutions with $c_M/c_L = 54$ and at $\text{pH} < 3.4$ for solutions with $c_M/c_L = 10.8$, DSILT indicates, according to (1, 2), dissociation of three protons assuming reaction of H_2L^{2-} or four protons assuming reaction of HL^{3-} and for limiting value $\varepsilon = 98750$. If formation of a dimer of the M_2L_2 type was assumed, then transformations (1) came closest to linearity for $n = 2$, $m = 2$ and $q = 4$. The logarithmic dependence (3) has two sections under the same conditions with $q = 3$ for $\text{pH} < 3$ and $q = 2$ for $\text{pH} \geq 3$, if the solution contains the critical micelle concentration of tenside ($c_D = 1.6 \cdot 10^{-3}\text{M}$) and at 612 nm, assuming formation of the mononuclear complex. Assuming $n = 2$ in the complex, transformation (3) has a constant slope for $q = 4$. A value of $q < 3$ is not attained at $\text{pH} < 2.9$ even after substituting higher values of the molar absorption coefficient into transformation (3) (e.g. $\varepsilon = 128000$ from the curve for the solution with $c_D = 1.6 \cdot 10^{-4}\text{M}$). In evaluation of the absorbance data for 598 nm, analysis of the absorbance-pH curves under the same conditions using transformations (1)–(3) yielded an effective number of dissociated protons, $q = 3$ over the whole pH range.

In the presence of a large tenside excess ($c_D = 8 \cdot 10^{-2}\text{M}$), a 1 : 1 complex is formed with dissociation of two protons ($m = 1$, $n = 1$, $q = 2$) for both concentrations,

TABLE V

Conditional Equilibrium Constant for the Equilibrium $\text{M} + \text{H}_2\text{L} + p\text{D} \rightleftharpoons \text{MLD}_p + 2\text{H}^+$ in Septonex Medium

$\log * \beta$	Conditions
–2.14	$c_D = 1.6 \cdot 10^{-4}\text{M}$; $c_L = 8 \cdot 10^{-6}\text{M}$
–2.62; –2.58 ^a ; –2.54 ^b ; –2.65 ^a ; –2.53 ^d	$c_D = 1.6 \cdot 10^{-3}\text{M}$
–2.92	$c_D = 8 \cdot 10^{-3}\text{M}$
–3.68; –3.82 ^b	$c_D = 8 \cdot 10^{-2}\text{M}$ (excess UO_2^{2+}): $A = f(\text{pH})$; $A = f(c_M)$
–2.18 ^e ; –2.12 ^f	$c_M = 8 \cdot 10^{-6}\text{M}$; $c_D = 1.6 \cdot 10^{-3}\text{M}$; $c_L = 6 \cdot 10^{-5}\text{M}$
–1.94 ^e ; –2.04 ^f	$c_L = 8 \cdot 10^{-5}\text{M}$
–1.88 ^e ; –1.92 ^f	$c_L = 1.2 \cdot 10^{-4}\text{M}$
–1.80 ^f ; –1.95 ^g ; –1.97 ^h	$c_L = 1.6 \cdot 10^{-4}$
–2.85 ⁱ ; –2.60 ^j	$c_M = 4.335 \cdot 10^{-6}\text{M}$; $c_D = 1.6 \cdot 10^{-3}\text{M}$ (excess c_L): $A = f(\text{pH})$; $A = f(c_L)$

^a $c_M = 4.335 \cdot 10^{-4}\text{M}$; ^b $c_M = 2.167 \cdot 10^{-3}\text{M}$; ^c $\text{pH} 2.92$; ^d 3.20 ; ^e 612 nm ; ^f 630 nm ; ^g 640 nm ; ^h 650 nm ; ⁱ $\text{pH} 3.9$; ^j $\text{pH} 3.6$.

$c_M = 8.672 \cdot 10^{-5} M$ and $2.167 \cdot 10^{-3} M$ for $pH > 3.9$ or $pH > 3.2$, with extrapolated values $\epsilon = 86250$ and 87500 at 612 nm. However, logarithmic dependence (3) is not linear over the whole region of complex formation assuming formation of the mono-

TABLE VI
The Effect of Tensides on the Reaction of UO_2^{2+} with Chromazurol S

Tenside	c_D, M	c_L, M	pH	λ_{max}, nm	$\epsilon, mol^{-1} l cm^{-1}$
Zephyramine	$8 \cdot 10^{-3}$	$8 \cdot 10^{-5}$	4.8 (≤ 5.0)	627	94 000
Cetyltrimethyl- ammonium bromide	$8 \cdot 10^{-4}$	$8 \cdot 10^{-5}$	6.0 (≤ 6.5)	612	95 900 (615 nm) 86 000 (625 nm)
Cetylpyridinium bromide	$8 \cdot 10^{-4}$	$8 \cdot 10^{-5}$	5.5 (≤ 5.7)	626 655	85 500
Ajatin	$8 \cdot 10^{-4}$	$2 \cdot 10^{-5}$	5.0	624	72 000
Septonex	$1.6 \cdot 10^{-3}$	$8 \cdot 10^{-5}$	7.4 (7.2)	612 (598)	111 300
Slovasol O	0.04%	$2 \cdot 10^{-5}$	5.0	615	43 000
Polyoxyethylen- lauryl ether	0.024%	$2 \cdot 10^{-5}$	5.0	630	59 000
Polyvinylpyrrolidon	0.5%	$8 \cdot 10^{-5}$	5.0—5.1	615	69 800
Polyvinyl alcohol	0.2%	$1 \cdot 10^{-4}$	6.8—6.9	600	84 000
No tenside	—	$(5-10) \cdot 10^{-5}$	5.0	582	23 650

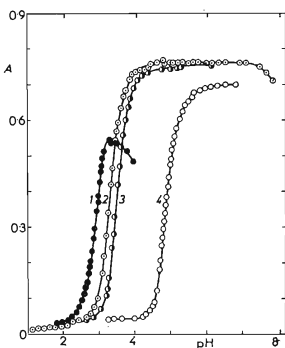


FIG. 7

The Dependence of the Absorbance of a Chromazurol Solution Containing Excess UO_2^{2+} on the pH in the Presence of Various Concentrations of Septonex

$c_L = 8 \cdot 10^{-6} M$; $c_M = 8.672 \cdot 10^{-5} M$; c_D :
1 $1.6 \cdot 10^{-4} M$; 2 $1.6 \cdot 10^{-3} M$; 3 $8 \cdot 10^{-3} M$;
4 $8 \cdot 10^{-2} M$.

nuclear complex. The course becomes linear with slope $q = 4$ only when assuming $n = 2$ and a limiting value of ϵ twice as large.

The curve of the concentration dependences $\Delta A = f(c_M)$ in solutions with a constant ligand concentration ($c_L = 8.0 \cdot 10^{-6} \text{M}$) at 598 nm, 612 nm and pH 3.20 confirm the ratio of the components in the ternary complex, $\text{UO}_2 : \text{L} = 1 : 1$ in the whole range of c_M concentrations. At pH 2.90 and small metal concentrations a complex with a smaller effective molar absorbance for the given concentration of tenside in solution appears, resulting in higher values of $m = 1.5$ from transformation (3) for $c_M 7 \cdot 10^{-4} \text{M}$ (Table IV).

Effect of Tenside Concentration

The critical micelle concentration is suitable for optimal formation of the UO_2 complex in a solution with excess UO_2^{2+} ($c_M = 4.335 \cdot 10^{-4} \text{M}$ and $c_L = 8.024 \cdot 10^{-6} \text{M}$) at pH 2.70. With increasing supercritical concentration of tenside the absorbance decreases rapidly at 594 and 612 nm, corresponding to complex dissociation in time. At pH 3.50 the absorbance change and thus complex dissociation is less marked for $c_D = 10^{-1.3} - 10^{-2.9} \text{M}$. This decomposition is controlled by addition of one tenside molecule to the ternary complex in the range $c_D = 10^{-1.3} - 10^{-2.7} \text{M}$. At pH > 4 the solution absorbance is constant up to $c_D = 10^{-2} \text{M}$ and then decreases.

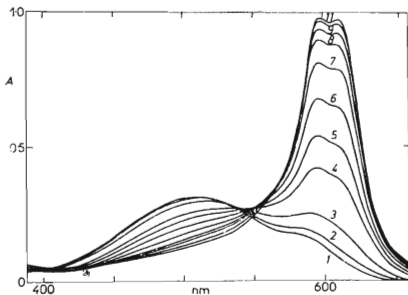


FIG. 8

Absorption Curves of UO_2 Solutions with Small Excesses of Chromazurol S in Dependence on the pH in the Presence of Septonex

$c_L = 1.6 \cdot 10^{-5} \text{M}$; $c_M = 8 \cdot 10^{-6} \text{M}$; $c_D = 1.6 \cdot 10^{-3} \text{M}$; $c_L/c_M = 2$; pH: 1 3.02; 2 2.30; 3 3.50; 4 3.74; 5 3.86; 6 4.00; 7 4.20; 8 4.43; 9 4.63; 10 5.00; 11 6.37.

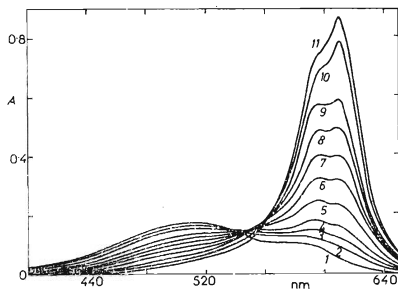


FIG. 9

Absorption Curves of UO_2 Solutions with Equimolar Concentrations of Chromazurol S in Dependence on the pH in the Presence of Septonex

$c_M = c_L = 8.675 \cdot 10^{-6} \text{ M}$; $c_D = 8 \cdot 10^{-4} \text{ M}$; pH: 1 2.90; 2 3.29; 3 3.39; 4 3.49; 5 3.59; 6 3.70; 7 3.80; 8 3.90; 9 4.02; 10 4.20; 11 4.30.

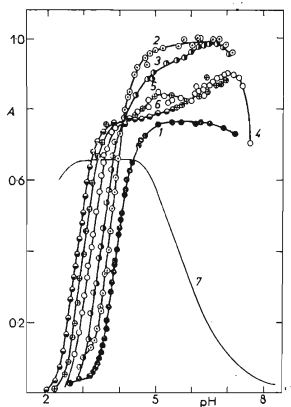


FIG. 10

Dependence of the Absorption of a UO_2^{2+} Solution with Various Reagent Excesses in the Presence of Septonex

$\Delta A = A - A_L$; $c_M = 8.0 \cdot 10^{-6} \text{ M}$; $c_D = 1.6 \cdot 10^{-3} \text{ M}$; c_L : Curve 1 $8.0 \cdot 10^{-6} \text{ M}$; 2 $1.6 \cdot 10^{-5} \text{ M}$; 3 $3.2 \cdot 10^{-5} \text{ M}$; 4 $6.0 \cdot 10^{-5} \text{ M}$; 5 $8.0 \cdot 10^{-5} \text{ M}$; 6 $1.2 \cdot 10^{-4} \text{ M}$; 7 $1.3 \cdot 10^{-4} \text{ M}$ (without OU_2^{2+}); c_L/c_M : 1 1.0; 2 2.0; 3 4.0; 4 7.5; 5 10.0; 6 15.0.

At pH 3.5 the ascending part of the dependence $A = f(c_D)$ could also be analyzed for $c_D = 10^{-4} - 10^{-2} \text{M}$, corresponding to formation of the ternary complex from the binary complex of UO_2^{2+} with chromazurol S. The number of bound molecules of tenside is $s = 2$. The slope of the dependence of the conditional equilibrium constant $\log \beta_2 (\text{MLD}_p + 2 \text{H}^+ \rightarrow \text{M} + \text{H}_2\text{L} + \text{pD})$ on $\log c_D$ in terms of transformation (3) and calculated for various concentrations of c_D and c_M (Table V) corresponds rather to interaction of one mole of tenside with two moles of ML or one mole of M_2L_2 . At pH 4.50 the absorption curves, in dependence on increasing tenside concentration, ($c_D = 4 \cdot 10^{-4} - 1.6 \cdot 10^{-2} \text{M}$ for $c_M = 8.672 \cdot 10^{-5} \text{M}$ and $c_L = 8 \cdot 10^{-6} \text{M}$) pass through a single isosbestic point at 604 nm and λ_{max} 612 nm is shifted to λ_{max} 594 nm.

Solutions with Excess Reagent

The absorption spectra of solutions of UO_2^{2+} with excess reagent, ($c_L/c_M = 2$ ($c_D = 1.6 \cdot 10^{-3} \text{M}$, $c_M = 8 \cdot 10^{-6} \text{M}$, $c_L = 1.6 \cdot 10^{-5} \text{M}$)) are analogous to the spectra of solutions with excess cation. In addition to the maximum of the ternary complex $\lambda_{\text{max}} = 594 \text{ nm}$ in solutions with critical micelle concentration of the tenside at pH 3.5, a second maximum appears at 612 nm with increasing pH. There is not a single equilibrium in solution in dependence on the pH (Fig. 8, 9). The long wavelength maximum also disappears with increasing concentration of tenside; at pH 6.0 lies a sharp transition between the complexes with λ_{max} 612 nm and λ_{max} 594 nm with increasing tenside concentration. At pH 4.0 gradual decomposition of the ternary complex with λ_{max} 612 nm to the associate of the reagent with the tenside was observed with increasing tenside concentration; this transition is characterized by a sharp isosbestic point at 547 nm.

The absorbance-pH curves (Fig. 10) at 592–640 nm exhibit two clear complexation regions in solutions with tenside CMC. At pH < 3 and increasing ligand concentration the formation region for the first complex is shifted to lower pH values; at pH > 4 the formation region for the second complex appears. The highest absorbance is attained at a stoichiometric ratio of $c_L/c_M = 2$; with increasing reagent excess the second formation region is suppressed and simultaneously shifted to higher pH values in dependence on the wavelength. In the first formation region of the absorbance-pH curves for solution with $c_M = 8 \cdot 10^{-6} \text{M}$ and $c_L = 6 \cdot 10^{-5} \text{M}$ to $1.2 \cdot 10^{-4} \text{M}$ and at 612–650 nm the presence of the UO_2LD_p complex was again unambiguously demonstrated at pH < 4 in terms of equilibrium (C) ($m = 1$, $n = 1$, $q = 2$), using transformations ((4)–(6)). The limiting values of ϵ_{612} for the first formation region at pH < 4 are in agreement with the ϵ_{612} values obtained by analysis of the pH absorbance curves for solutions with excess metal and for equimolar solutions ($c_D = 1.6 \cdot 10^{-3} \text{M}$). The shape of the second ascending branch at pH > 4 and 612–650 nm is dependent on the reagent concentration, on time and on the order of component mixing. With increasing reagent concentration the absorbance

in this part of the curve decreases and the second formation region is shifted to higher pH values (Fig. 10). In addition, a shift in the absorbance-pH curves to higher pH values accompanied by a gradual decrease in the plateau value with increasing tenside concentration in the interval $c_D = 4 \cdot 10^{-4} - 1.6 \cdot 10^{-2} \text{ M}$ and at the optimal stoichiometric ratio ($c_L/c_M = 2$, $c_M = 8.0 \cdot 10^{-6} \text{ M}$) was demonstrated. The highest absorbance value was attained for $c_D = 4.0 \cdot 10^{-4} \text{ M}$ ($\epsilon_{612} = 131\,250$). The formation of the highly absorbing complex at $\text{pH} > 4$ with $\lambda_{\text{max}} 612 \text{ nm}$ is thus suppressed both by increasing reagent excess and tenside excess.

The $A = f(c_L)$ dependences for solutions with excess reagent have various shapes for various pH values and various tenside concentrations. At $\text{pH} \geq 5$ and at higher tenside concentrations the formation of the ternary complex with UO_2^{2+} becomes less easy, is shifted to higher concentrations of reagent and the conditional values of the molar absorption coefficients obtained from the limiting values of the absorbance for large reagent excess are lower. Graphical analysis of the dependences using transformations (7), (8) at $\text{pH} 3.6 - 3.9$ and $c_D = 1.6 \cdot 10^{-3} \text{ M}$ and at $598 - 612 \text{ nm}$

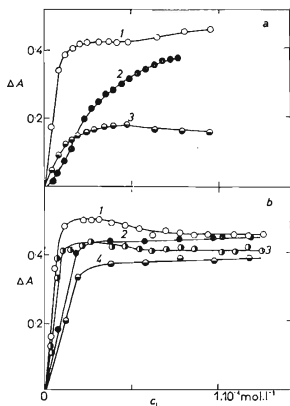


FIG. 11

Dependence of the Absorbance of the Concentration of Reagent in Excess in the Presence of Septonex ($\Delta A = A - A_L$)

a) $c_M = 4.335 \cdot 10^{-6} \text{ M}$, $c_D = 1.6 \cdot 10^{-3} \text{ M}$; 1 $\text{pH} 4.2$, 612 nm ; 2 $\text{pH} 3.6$, 612 nm ; 3 $\text{pH} 4.2$, 640 nm ; b) $c_M = 4.335 \cdot 10^{-6} \text{ M}$, $\text{pH} 7.0$; 1 612 nm , $c_D = 1.6 \cdot 10^{-3} \text{ M}$; 2 612 nm , $c_D = 1.6 \cdot 10^{-2} \text{ M}$; 3 620 nm , $c_D = 1.6 \cdot 10^{-3} \text{ M}$; 4 620 nm , $c_D = 1.6 \cdot 10^{-2} \text{ M}$.

indicate reliably formation of a complex with $M : L = 1 : 1$ and the molar absorption coefficients extrapolated from the transformation limiting values agree with the maximum values found from the absorbance-pH curves of the solutions with excess reagent, $\epsilon = 122000 - 125000$. The decrease in the absorbance at 630–640 nm also reflects partial decomposition of this ternary complex in solutions with large reagent excesses (Table VI). At $\text{pH} \geq 7$, the stepwise formation of two complexes in solutions with $c_D = 1.6 \cdot 10^{-3} \text{M}$ and with large reagent excesses ($c_L/c_M \geq 14$) is indicated, with different characteristics at 612 and 630–640 nm (Fig. 11). The formation of the second complex is suppressed at a larger tenside excess ($c_D = 1.6 \cdot 10^{-2} \text{M}$) and the absorbance decreases in a broad concentration range.

Results in Nearly-Equimolar Solutions

The curves for isomolar series for $c_0 = 1.60 \cdot 10^{-5} - 1.73 \cdot 10^{-5} \text{M}$ and $c_D = 1.6 \cdot 10^{-3} \text{M} - 9.5 \cdot 10^{-4}$ at $\text{pH} 4.0, 5.2$, and 6.0 indicate a mixture of complexes. At 612 nm the complex with $M : L = 1 : 1$ predominates, at 630–640 nm the complex with $M : L = 1 : 2$ is chiefly present. In the presence of higher tenside concentrations ($c_D = 1.6 \cdot 10^{-2} \text{M}$) the formation of the higher complex with $M : L = 1 : 2$ is suppressed. In the presence of 0.05M triethanolamine, $c_0 = 1.734 \cdot 10^{-5} \text{M}$, $\text{pH} 6.0 - 7.0$, $c_D = 1.6 \cdot 10^{-3} \text{M}$ and for 590–620 nm, the maximum appears for $x_L = 0.57 - 0.58$ after 5 min. (Theoretical positions are $x_L = 0.50$ for the complex with $M : L = 1 : 1$ and $x_L = 0.67$ for the complex with $M : L = 1 : 2$). The absorbance of the solutions decreases with time and the maximum of the curves is shifted in one hour to $x_L = 0.68$.

In solutions with substoichiometric and stoichiometric concentrations c_M at $c_D = 1.6 \cdot 10^{-3} \text{M}$, $c_L = 8.0 \cdot 10^{-6} \text{M}$ and at $\text{pH} 4.2$, only the complex with $M : L = 1 : 1$ is apparent from the $A = f(c_M)$ curves, at $\text{pH} 6$ also partially the complex with $M : L = 1 : 2$. The near equimolar curves $A = f(c_L)$ in solutions with $c_M = 5 \cdot 10^{-6} \text{M}$, $c_D = 1.6 \cdot 10^{-3} \text{M}$ at $\text{pH} 6.0$ indicate a mixture of ternary complexes with component ratio $M : L = 1 : 1$ and $1 : 2$ ($\epsilon_{612} = 129000$); the plateau is in agreement with that of the absorbance-pH curves for solutions with $c_L/c_M = 2$, $c_M = 8.00 \cdot 10^{-6} \text{M}$, $c_D = 1.6 \cdot 10^{-3} \text{M}$. At $\text{pH} 4.2$ the dependence ends at the limiting value $\epsilon_{612} = 98000$, which is the value extrapolated from the absorbance-pH curves for the solutions with excess metal and corresponds to a ratio of $M : L = 1 : 1$ in the ternary complex. At $\text{pH} 7.0$ the complex decomposes partially.

Results and Explanation of the Reaction Mechanism

In solutions with excess UO_2^{2+} at $\text{pH} 2.6 - 3.4$, the ternary complex UO_2LD_p (ϵ_{max} 612 nm) is formed in dependence on the pH of the solution, on the concentration c_M and for small tenside concentrations in terms of equilibrium (C), with a molar absorption coefficient value dependent on the tenside concentration and pH value.

At subcritical concentrations of tenside this complex is formed even at $\text{pH} < 3$ and at small concentrations of metal cation in excess a complex with a higher value of the molar absorption coefficient. With increasing tenside concentration and at small metal cation concentrations in excess, the formation of the ternary complex is shifted to higher pH values and its gradual decomposition occurs. At $\text{pH} > 2-3$, supercritical concentration of tenside or in the presence of a small excess of metal, another complex is simultaneously formed with λ_{max} 594 nm and with a component ratio of $\text{M} : \text{L} = 1 : 1$. This complex is similar to the UO_2LH complex, which is formed in solutions without tenside and in the presence of excess UO_2^{2+} ($\lambda_{\text{max}} = 592-595$ nm). Simultaneous formation of the M_2L_2 dimer with dissociation of 4 protons and bonded to the tenside micelle is not excluded. At $\text{pH} \leq 3.5$ and at subcritical tenside concentrations, $p = 2$ and apparently corresponds to reaction of the reagent associate $\text{H}_2\text{L}^{2-} \cdot 2\text{D}^+$ with UO_2^{2+} . At $\text{pH} \leq 3$ the ternary complex decomposes with increasing Septonex concentration producing $\text{LH}_2^{2-} \cdot 2\text{D}^+$. The interconversion of the complexes with λ_{max} 612 nm and λ_{max} 594 nm is connected with the reaction of 0.5–1 mol of tenside at $\text{pH} > 3$. The negative effect of higher tenside concentrations on the absorbance of the ternary complex is greatest at $\text{pH} 2-4$ and apparently depends on competing formation of an associate of the reagent with the tenside cation. Acid-base forms of the reagent other than H_2L^{2-} associate much less strongly with the tenside.

In solutions with excess chromazurol at $\text{pH} < 4$, reaction (C) also occurs in dependence on the concentration of reagent and tenside producing ternary complex UO_2LD_p (λ_{max} 612 nm) in solution simultaneously with another complex with $\text{M} : \text{L} = 1 : 1$ and λ_{max} 594 nm. Here also, the ternary complex reacts with a further tenside molecule with dissociation of the bond of the oxygen of the phenol hydroxyl with UO_2^{2+} . At $\text{pH} > 4$ a complex with $\text{UO}_2 : \text{L} = 1 : 2$ is also formed in the presence of a small reagent excess. With increasing chromazurol S concentration in solution the formation of a complex with a higher value of the molar absorption coefficient at 612 nm is shifted to higher values of $\text{pH} 5-7$. The excess tenside prevents formation of a complex with $\text{UO}_2 : \text{L} = 1 : 2$. The highest value of the conditional molar absorption coefficient was obtained for the stoichiometric concentration ratio $c_{\text{M}}/c_{\text{L}} = 1/2$ in solutions with Septonex CMC. In the presence of tensides other than Septonex, a higher complex with $\text{UO}_2 : \text{L} = 1 : 2$ is formed far more readily, *e.g.* in the presence of polyvinyl alcohol at $\text{pH} 6.8-8.0$ (ref.⁵) in the presence of a small excess of various cationic tensides at $\text{pH} 4.25-6.00$ (ref.¹⁰), in the presence of cetyltrimethylammonium chloride at $\text{pH} 4.0-5.5$ (ref.⁸); elsewhere, only a complex with $\text{UO}_2 : \text{L} = 1 : 1$, *e.g.* with cetylpyridinium bromide⁷, was considered.

In the UO_2^{2+} -chromazurol S-Septonex system, competing equilibria between the individual components apparently occur, reflecting the relatively low stability of the ternary complex. The increasing tenside concentration in the supercritical

micelle concentrations has a negative effect on the value of the molar absorption coefficient at 612 nm and shifts the absorption maximum of the complex to 594 nm.

Our experimental results tend to confirm the formation of defined ion associates among UO_2^{2+} , chromazurol S and Septonex, rather than micelle complexes under optimum conditions (see analogous assumptions in other systems²⁰⁻²³). At the stoichiometric tenside concentration, however, a precipitate is readily formed in aqueous solutions, so that a small tenside excess is necessary for stabilization of the ternary complex in solution. In the presence of critical and supercritical micelle concentrations of Septonex, the effect of the micelle in a certain pH region can simulate a certain defined complexation equilibrium. In the formation of the ternary complex with the cationic tenside, the phenol proton is dissociated and bonding of the cation to the limiting quinoid arrangement of the molecule becomes impossible, as this arrangement is protected by the cationic tenside molecule. The polarization effect of the tenside bonded to the carboxyl anion labilizes the phenol proton bond and enhances

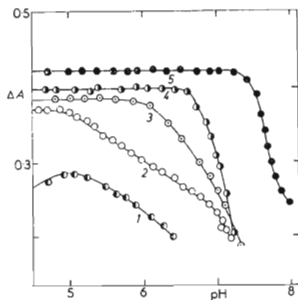


FIG. 12

Dependence of the Absorbance of a UO_2^{2+} Solution with a Small Excess of Chromazurol S in the Presence of Various Tensides

$c_M = 4.335 \cdot 10^{-6} \text{M}$; $c_L = 8 \cdot 10^{-5} \text{M}$; $I 0$; $\Delta A = A - A_L$; 1 polyvinylpyrrolidone, 0.5% solution, 615 nm; 2 zephyramine, $c_D 3.2 \cdot 10^{-3} \text{M}$, 627 nm; 3 cetylpyridinium bromide, $c_D 8 \cdot 10^{-4} \text{M}$, 626 nm; 4 cetyltrimethylammonium bromide, $c_D 4 \cdot 10^{-4} \text{M}$, 615 nm; 5 Septonex, $c_D = 1.6 \cdot 10^{-3} \text{M}$.

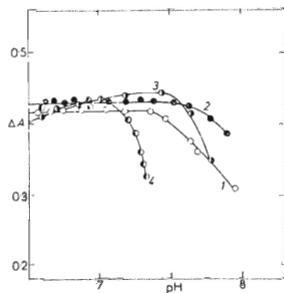


FIG. 13

Dependence of the Absorbance of a UO_2^{2+} Solution with an Excess of Chromazurol S in the Presence of Septonex with Various Buffers

$c_M = 4.335 \cdot 10^{-6} \text{M}$; $c_L = 8 \cdot 10^{-5} \text{M}$; $c_D = 1.6 \cdot 10^{-3} \text{M}$, 612 nm; 0.1M- KNO_3 ; 1 0.1M 2-picoline; 2 0.1M tris(hydroxymethyl)amino-methane; 3 0.1M triethanolamine; 4 without buffer.

the involving of the electron pair on the phenol oxygen in the conjugation of the triphenylmethane skeleton, resulting in an increase in the molar absorption coefficient of the ternary complex.

The conditional values of the equilibrium constant for the principal equilibrium (C) under various conditions are given in Table V.

In aqueous solutions without tenside and in the presence of excess cation, the UO_2LH complex is formed ($\lambda_{\text{max}} = 592-595 \text{ nm}$, $\epsilon = 5.8 \cdot 10^4$ (590 nm)) with dissociation of only one proton at $\text{pH} \leq 4.8$. Simultaneously $(\text{UO}_2)_2\text{L}$ is also formed in the presence of a large excess of UO_2^{2+} ; in both cases the phenol proton is dissociated. In solutions with a small excess of ligand without tenside and for $c_{\text{L}} = 1.01 \cdot 10^{-4} \text{ M}$ $2.00 \cdot 10^{-4} \text{ M}$ and $c_{\text{M}} = 1.734 \cdot 10^{-5} \text{ M}$ a single complex is formed with $\lambda_{\text{max}} 580-582 \text{ nm}$ with composition $\text{M} : \text{L} = 1 : 1$ and with dissociation of a single proton in the reaction of H_2L^{2-} ($\epsilon_{580} = (23.5-23.8) \cdot 10^3$, $\epsilon_{590} = 20.8 \cdot 10^3$, $\epsilon_{600} = (16.7-17.1) \cdot 10^3$). This complex is formed at $I \rightarrow 0$ at $\text{pH} > 3$, attains a maximum concentration at $\text{pH} 4.5-4.8$ and is readily hydrolyzed at $\text{pH} > 5$ ($\log \beta_1^* (\text{M} + \text{H}_2\text{L} \rightleftharpoons \text{MHL} + \text{H}^+) = 0.33-0.18$). The complex decomposes with increasing ionic strength and the conditional molar absorption coefficients found are much lower. The formation of a dimer could not be unambiguously demonstrated in these solutions. Here a bond is probably formed to the unprotonated ketonic oxygen with simultaneous dissociation of the neighbouring carboxyl proton and dissociation of the phenolic proton does not occur.

SPECTROPHOTOMETRIC DETERMINATION OF UO_2^{2+} WITH CHROMAZUROL S⁻ IN THE PRESENCE OF SEPTONEX

The effect of various cationic and nonionic tensides in the system of UO_2^{2+} with chromazurol S is documented in Table VI, Fig. 12 and Fig. 13 for chosen reagent, tenside and pH concentrations. All the cationic and nonionic tensides cause a bathochromic shift in the λ_{max} of the complex of UO_2^{2+} with chromazurol S. The greatest increase in the molar absorption coefficient occurs for cationic tensides, primarily Septonex, in dependence on the concentration of detergent, solution pH and concentration of reagent and UO_2^{2+} . The ternary complex with the tenside is formed even at submicelle tenside concentrations, where the highest values of the molar absorption coefficient are attained; only above the micelle concentration of the tenside is the system sufficiently stable in aqueous solutions or in solutions with added ethanol. The anionic tenside sodium lauryl sulphate does not have a positive effect on the chromazurol S- UO_2^{2+} system. A linear dependence of the increase in the molar absorption coefficient or sensitivity on the length of the carbon chain in the molecule also does not follow from the set of experimental conditions.

Under the conditions employed here, Septonex at the micelle concentration exhibited the greatest increase in the molar absorption coefficient; the absorbance

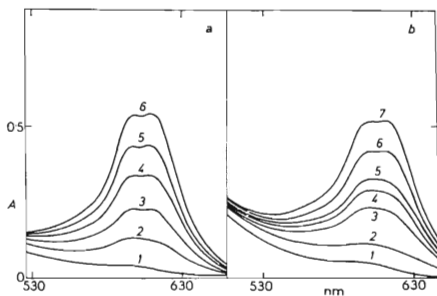


FIG. 14

Absorption Curves of UO_2^{2+} Solutions with Excess Chromazurol S in the Presence of Septonex

$c_L = 8 \cdot 10^{-5} \text{M}$; $c_D = 1.6 \cdot 10^{-3} \text{M}$; a) pH: 7.0, c_M : 1 0; 2 $1.734 \cdot 10^{-6} \text{M}$; 3 $3.468 \cdot 10^{-6} \text{M}$; 4 $5.202 \cdot 10^{-6} \text{M}$; 5 $6.936 \cdot 10^{-6} \text{M}$; 6 $8.672 \cdot 10^{-6} \text{M}$; b) 0.1M triethanolamine, pH 7.4; c_M : 1 0; 2 $0.867 \cdot 10^{-6} \text{M}$; 3 $3.468 \cdot 10^{-6} \text{M}$; 4 $4.335 \cdot 10^{-6} \text{M}$; 5 $5.202 \cdot 10^{-6} \text{M}$; 6 $6.936 \cdot 10^{-6} \text{M}$; 7 $8.672 \cdot 10^{-6} \text{M}$.

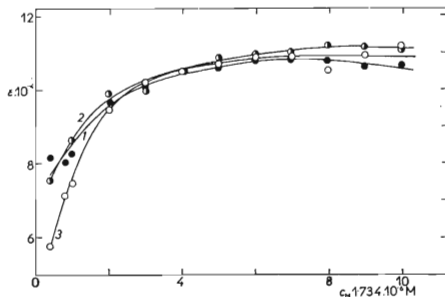


FIG. 15

Conditional Molar Absorption Coefficient in Dependence on the Concentration of UO_2^{2+} in Solutions with Excess Chromazurol S and in the Presence of Septonex at 612 nm

$c_L = 8 \cdot 10^{-5} \text{M}$; $c_D = 1.6 \cdot 10^{-3} \text{M}$; pH 7.4; 0.1M triethanolamine, pH 7.4; 1 0.65M- KNO_3 ; 2 0.1M- KNO_3 ; 3 without KNO_3 .

is constant at pH 4.5–7.1 in solutions with a small reagent excess; this region is further broadened in the presence of the tris(hydroxymethyl)aminomethane or triethanolamine buffers. Use of Septonex at pH 6.9–7.1 is advantageous, as the solution then contains the poorly absorbing HL^{3-} form of the reagent, so that the blank absorbance is small. This form does not yield a stable associate with the tenside. A blue, red-purple or purple colouration is formed at pH 3.0–3.8 in the presence of tetraphenylphosphonium bromide, tetraphenylarsonium chloride, triphenylhexylphosphonium bromide, tetraphenylcarboxymethylphosphonium chloride, n-propylpyridinium bromide or antipyrine; this colouration disappears at pH > 4 and is not reformed on reacidification of the solution. Poorly stable associates with chromazurol S are formed.

Determination of UO_2^{2+} with Chromazurol S in the Presence of Septonex

At pH 6.9–7.0, $c_M = 8.0 \cdot 10^{-6}M$, $c_D = 1.6 \cdot 10^{-3}M$, the effect of excess tenside and reagent is small and the values of the molar absorption coefficient for various

TABLE VII

Calibration Curve $A = f(c_M)$ in Solutions with Excess Chromazurol S, and Septonex in the Presence of Various Buffers

$c_L = 8 \cdot 10^{-5}M$; $c_D = 1.6 \cdot 10^{-3}M$; $0.1M-KNO_3$; $c_M = (0.9-9.0) \cdot 10^{-6}M$; 612 nm; buffer concentration, 0.1M.

Buffer	Optimal pH	$\epsilon \cdot 10^{-5}, \text{mol}^{-1} \text{l cm}^{-1}$	A_{612}^0 ^a	q^b
Hexamethylentetramine	6.0	0.97	0.250	0.248
Tris(hydroxymethyl) aminomethane	6.7	1.06	0.231	0.210
	7.25	1.08	0.170	0.150
2-Picoline	6.0	1.00	0.250	0.251
	6.7	1.09	0.150	0.125
Pyridine	5.2	0.98	0.465	0.460
	6.2	1.02	0.308	0.306
Triethanolamine	7.0	1.06	0.151	0.123
	7.4	1.10	0.083	0.020
No buffer	5.5	1.03	0.300	0.291
	6.9	1.08	0.150	0.136

^a A_{612}^0 is the experimentally determined blank absorbance; q^b , the intercept on the y-axis calculated from linear regression of the values from the linear part of the calibration dependence.

TABLE VIII

The Effect of Masking Agents on the Determination of UO_2^{2+} with Chromazurol S in the Presence of Septonex^a

$c_L = 8 \cdot 10^{-5} \text{M}$; $c_M = 4 \cdot 335 \cdot 10^{-6} \text{M}$; $c_D = 1 \cdot 6 \cdot 10^{-3} \text{M}$; pH 7.4; 0.1M triethanolamine, 0.1M- KNO_3 .

Reagent	c_X, M	$c_X/c_M, \text{M}$
EDTA	$2 \cdot 6 \cdot 10^{-4}$	60
DCTA	$8 \cdot 0 \cdot 10^{-3}$	1 850
Mg(CDTA)	$1 \cdot 3 \cdot 10^{-2}$	3 000
Ca(CDTA)	$5 \cdot 0 \cdot 10^{-3}$	1 150
Ascorbate	$2 \cdot 0 \cdot 10^{-2}$	4 610 ^b
Fluoride	$1 \cdot 0 \cdot 10^{-3}$	230
BF_4^-	$3 \cdot 0 \cdot 10^{-3}$	692
$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$	0.375	87 000 ^c
5-Sulphosalicylate	$4 \cdot 6 \cdot 10^{-4}$	106
Malonate	$2 \cdot 0 \cdot 10^{-3}$	461

^a The c_X concentration data correspond to 2% relative absorbance change; ^b the absorbance was measured within 3 min and decreases rapidly with time; ^c after 20 min the blank changes from yellow to green.

excesses are: c_L/c_M , ϵ_{612} : 2, 125 000; 4, 121 250; 7.5, 112 500; 10, 112 500; 15, 112 500. An average value of $\epsilon = 112 500 \pm 1 300$ with a relative standard deviation of $\pm 1.12\%$ follows from the slope of the calibration dependence for unbuffered solutions with $I = 0.1 \text{M}$ (KNO_3), $c_L = 8 \cdot 10^{-5} \text{M}$, $c_M = 1.734 \cdot 10^{-6} \text{M} - 8.672 \cdot 10^{-6} \text{M}$ ($c_L/c_M = 46.1 - 9.2$) and $c_D = 1.6 \cdot 10^{-3} \text{M}$.

The slope of the $A = f(c_M)$ dependence changes considerably for $c_M < 1.7 \cdot 10^{-6} \text{M}$ and $c_L/c_M > 46$, as a result of the concave shape of the calibration curve for these metal concentrations. The average value in this part of the curve is lower ($\epsilon_{612} = 79 300$). This deformation is actually a result of a larger excess of reagent and tenside as the calibration curve for solutions with $c_L = 8 \cdot 10^{-6} \text{M}$ and $c_M < 1.7 \cdot 10^{-6} \text{M}$ again has a region with $\epsilon_{612} = 7 \cdot 10^4$ from $c_L/c_M > 46$, i.e. $c_M < 8.7 \cdot 10^{-7} \text{M}$. The ϵ value evaluated from the dependence for $c_M = 1.734 \cdot 10^{-7} \text{M}$ to $1.734 \cdot 10^{-6} \text{M}$ in the presence of $c_L = 8 \cdot 10^{-5} \text{M}$ and at pH 7.4 is only 75 600. A dependence of the slope of the calibration curve on c_M has already been observed in the Be^{2+} -chromazurol S-tenside system^{18,19}.

Effect of Buffers

The effect of chosen buffers, 2-picoline, tris(hydroxymethyl)aminomethane and triethanolamine in 0.1M concentrations and in dependence on the pH is depicted in Fig. 13. Compared to unbuffered solution (pH 7.2), the constant absorbance region

is shifted to pH 7.4–7.5 in solutions with critical micelle concentration of Septonex. The following buffers do not interfere in concentrations of $\leq 0.4\text{M}$: triethanolamine (pH 7 and 7.4), tris(hydroxymethyl)aminomethane (pH 6.7 and 7.25), picoline (pH 6.0 and 7.0). Some data for various buffers are given in Table VII. The most suitable buffer is triethanolamine in 0.1M concentration with HNO_3 at $I = 0.1\text{M}(\text{KNO}_3)$, which enables determination even at pH 7.4, where observable hydrolysis of the ternary complex otherwise occurs. The maximal value $\varepsilon_{612} = (1.06 - 1.10) \cdot 10^5$ is constant in the region pH 7.4 \pm 0.1. The calibration curve is also linear here at 612 nm for $c_M = (2.6 - 8.7) \cdot 10^{-6}\text{M}$ in the presence of $c_L = 8.0 \cdot 10^{-5}\text{M}$, $c_D = 1.6 \cdot 10^{-3}\text{M}$ and 0.1M- KNO_3 ($c_L/c_M = 10 - 31$). For $c_L/c_M > 46$ the calibration dependence is curved with an average value of $\varepsilon_{612} = 79300$.

Statistical evaluation of the calibration curve by linear regression for optimal conditions ($c_M = (1.734 - 8.672) \cdot 10^{-6}\text{M}$; $c_L = 8 \cdot 10^{-5}\text{M}$, $c_D = 1.6 \cdot 10^{-3}\text{M}$, 0.1M- KNO_3 , 0.1M triethanolamine, pH 7.4) for seven parallel solutions at each concentration (altogether six concentrations), with the absorbance measured against water without subtraction of the reagent absorbance yielded the following data: optimum concentration range: 0.413–2.064 $\mu\text{g U ml}^{-1}$, λ 612 nm, $\varepsilon = 112000 \pm 504$, blank absorbance (0.013 ± 0.003), $s_{xy(A)} = \pm 0.0071$, $s_{xy(c)} = \pm 0.015 \mu\text{g U ml}^{-1}$, detection limit ($8s_{xy(c)}$) = 0.12 $\mu\text{g U ml}^{-1}$.

The difference between the calculated intercept on the absorbance axis from the linear regression of the linear part of the calibration curve and the measured absorbance of a solution containing only reagent (the experimental blank) is a measure of the curvature of the calibration curve for small metal concentrations (Table VII). The absorption curve for the individual concentration of metal used for the calibration curves exhibit a broad maximum at 590–612 nm; at concentrations $c_M > 5.20 \cdot 10^{-6}\text{M}$, the λ_{max} 612 nm peak becomes more pronounced at pH 7.0–7.4, more in solutions without buffer than in those with buffer. The curvature of the calibration curve in the vicinity of the origin thus depends on the presence of a complex with predominating absorption at 590 nm (Fig. 14).

The Effect of Septonex

This effect is negligible in the range $c_D = 10^{-3} - 10^{-2}\text{M}$ under the determination conditions (0.1M triethanolamine, pH 7.4, 0.1M- KNO_3 , $c_L = 8 \cdot 10^{-6}\text{M}$); only a slight decrease in ε_{612} from $1.12 \cdot 10^5$ to $1.07 \cdot 10^5$ and $A_0 = 0.055$ to $A_0 = 0.047$ appears. It is important that the tenside concentration be greater than $c_D = 8 \cdot 10^{-4}\text{M}$ to prevent precipitation of the reagent associate with the reagent.

Effect of Reagent Concentration

For mean concentrations, $c_M = 4.385 \cdot 10^{-6}\text{M}$, pH 7.4 and 0.1M triethanolamine, $c_D = 1.6 \cdot 10^{-3}\text{M}$, the absorbance difference $A - A_L$ is constant up to $c_L = 4.8$.

$\cdot 10^{-5}\text{M}$ ($c_L/c_M = 11$); higher concentrations up to $c_L = 1.28 \cdot 10^{-4}\text{M}$ decrease the absorbance difference only slightly (-9% rel).

Effect of the Ionic Strength

In the interval $\leq 0.5\text{M-KNO}_3$, the absorbance of the solution changes only slightly for $c_L = 8 \cdot 10^{-5}\text{M}$, $c_D = 1.6 \cdot 10^{-3}\text{M}$, $c_M = 4.33 \cdot 10^{-6}\text{M}$, 0.1M triethanolamine, pH 7.4. In the uranium concentration range employed the dependence $(A - A_L) = f(c_M)$ is not ideally linear at any ionic strength realizable with various concentra-

TABLE IX

The Effect of Interfering Ions on the Determination of Uranium with Chromazurol S in the Presence of Septonex at pH 7.4 (0.1M triethanolamine)

$c_L = 8 \cdot 10^{-5}\text{M}$; $c_D = 1.6 \cdot 10^{-3}\text{M}$; $c_M = 4.335 \cdot 10^{-6}\text{M}$; 0.1M-KNO_3 .

Ion	No masking agent		In the presence of 0.03M-Mg-CDTA	
	c_X^a	c_X/c_M	c_X^a	c_X/c_M
Mg^{2+}	$4 \cdot 10^{-2}$	9 230		
Ca^{2+}	$4 \cdot 10^{-2}$	9 230		
Sr^{2+}	$4 \cdot 10^{-2}$	9 230		
Ba^{2+}	$4 \cdot 10^{-2}$	9 230		
Ti(IV)	$1 \cdot 10^{-5}$	2.3^b	$1.6 \cdot 10^{-3}$	369^b
Zn^{2+}	$7 \cdot 10^{-4}$	160	$1 \cdot 10^{-2}$	2 310
Cd^{2+}	$9.6 \cdot 10^{-5}$	22	$9.6 \cdot 10^{-3}$	2 215
Al^{3+}			$1 \cdot 10^{-4}$	23^c
Cu^{2+}			$2 \cdot 10^{-4}$	46
Zr(IV)			$1 \cdot 10^{-4}$	23
Th(IV)			$1 \cdot 10^{-4}$	23
Fe^{3+}			$3 \cdot 10^{-3}$	659
Be^{2+}			$1 \cdot 10^{-4}$	23
Pb^{2+}			$1 \cdot 10^{-2}$	2 310
MoO_4^{2-}	$4 \cdot 10^{-2}$	9 230		
WO_4^{2-}	$4 \cdot 10^{-2}$	9 230 ^d		
SO_4^{2-}	$3 \cdot 10^{-1}$	70 000		
Cl^-	$3 \cdot 10^{-1}$	70 000		
NO_3^-	$5 \cdot 10^{-1}$	115 000		
V(V)	$4 \cdot 10^{-2}$	70 000		
CO_3^{2-}	$4.3 \cdot 10^{-4}$	100		

^a Concentration data correspond to the maximum relative absorbance change, $\pm 2\%$; ^b absorbance is measured within 3 min; ^c solution is first heated; ^d absorbance measured within 10 min.

tions of KNO_3 . With increasing UO_2^{2+} concentration the conditional molar absorption coefficient at 612 nm increases to the maximum value which is $\epsilon_{612} = 121\,000$ ($I = 0$); $\epsilon_{612} = 112\,000$ ($I = 0.1(\text{KNO}_3)$); $\epsilon_{612} = 104\,000$ ($I = 0.65(\text{KNO}_2)$) and is practically constant for $c_M = (1.040 - 1.734) \cdot 10^{-5}\text{M}$ and $I = 0 - 0.1$ (pH 7.4, 0.1M triethanolamine, $c_L = 8 \cdot 10^{-5}\text{M}$). (Fig. 15). The marked deformation of the calibration curves at $c_M = 3.47 \cdot 10^{-6}\text{M}$ decreases with increasing ionic strength (up to $I \leq 0.65$). For $c_M \cdot 10^{-5}\text{M}$, the ionic strength has a marked effect on the time stability of the system. In media with $I = 0.65$ the solution absorbance for the conditions given above is unlimitedly stable in time; at $I = 0.1$ it is stable for 2 h. and in the

TABLE X

The Effect of Ions and Reagents on the Determination of Uranium with Chromazurol S in the Presence of Septonex at pH 5.25 (0.2M 2-picoline buffer)

$c_M = 3.467 \cdot 10^{-6}\text{M}$; $c_L = 8 \cdot 10^{-5}\text{M}$; $c_D = 1.6 \cdot 10^{-3}\text{M}$; 0.1M- KNO_3 ; absorbance measured within 5 min at 612 nm.

Ion or reagent	$c_X, \text{mg} \cdot \text{ml}^{-1} \text{ }^a$	$c_X/c_M, \text{M}$
Mg^{2+}	$9.6 \cdot 10^{-3}$	115
Ca^{2+}	$3.2 \cdot 10^{-2}$	231
Zn^{2+}	$5.4 \cdot 10^{-2}$	240
Pr^{3+}	$1.1 \cdot 10^{-2}$	23
Ni^{2+}	$6.5 \cdot 10^{-4}$	3.1
Cd^{2+}	$3.3 \cdot 10^{-2}$	84
SO_4^{2-}	$9.3 \cdot 10^{-1}$	2 790
ClO_4^-	3.4	10 000
Cl^-	7.0	58 000
CO_3^{2-}	$4.3 \cdot 10^{-1}$	2 050
SCN^-	$1.2 \cdot 10^{-2}$	61
HPO_4^{2-}	$4 \cdot 10^{-2}$	120
Oxalate	$1.7 \cdot 10^{-3}$	5.5
Tartrate	$4 \cdot 10^{-3}$	1 800
Borate		20
Acetate	$3.0 \cdot 10^{-1}$	1 440
Phthalate	$6.9 \cdot 10^{-1}$	1 440
Ascorbate	$1.4 \cdot 10^{-1}$	230
Citrate	$1.2 \cdot 10^{-2}$	19
Sulphosalicylate	$1.8 \cdot 10^{-3}$	2.3
EDTA	$5.3 \cdot 10^{-2}$	52
Ca(EDTA)	$1.3 \cdot 10^{-1}$	115
Mg(EDTA)	$1.1 \cdot 10^{-1}$	100

^a Concentration c_X corresponds to the highest relative absorbance change, $\pm 2\%$.

absence of KNO_3 ($I \rightarrow 0$), the absorbance of the solution decreases with time as soon as the solution is prepared. Apparently the increase in the CMC of the tenside with increasing electrolyte concentration occurs here, decreasing the interfering effect of excess tenside on the ternary complex.

Effect of Masking Agents

All the reagent tested (Table VIII) lead to negative errors. The c_x or c_x/c_M concentrations given in the table result in a systematic error of the absorbance from the theoretical value of -2% rel. An optimal, although not very effective masking agent was a solution of the Mg^{2+} chelate of CDTA (0.03M) with a slight excess of Mg^{2+} ($c_{\text{Mg}}/c_{\text{CDTA}} = 1.2$). The calibration dependence in the presence of $c_L = 8 \cdot 10^{-5}\text{M}$, $c_D = 1.6 \cdot 10^{-3}\text{M}$ ($\epsilon_{612} = 109200$).

Procedure

To a 25 ml volumetric flask are gradually added 1 ml of $4 \cdot 10^{-2}\text{M}$ Septonex solution in 95% ethanol, 5 ml of $4 \cdot 10^{-4}\text{M}$ chromazurol S, 2.5 ml of 1M-KNO_3 , 2.5 ml of 1M triethanolamine buffer (pH 7.4), 3 ml of 0.25M solution of the Mg^{2+} chelate of CDTA and 5–10 ml of sample solution containing less than $5 \mu\text{g ml}^{-1}$ uranium at pH 2.5–3.0; the solution is diluted to the mark. The absorbance at 612 nm is measured immediately and is stable for at least 2 hours. The calibration curve is linear from $0.404 \mu\text{g U ml}^{-1}$.

Effect of Ions

The effect of some cations and anions in the presence and absence of masking agent under optimal conditions is given in Table IX. In the absence of masking agent the following ions interfere strongly: Al^{3+} , Cu^{2+} , Zr(IV) , Th^{4+} , Fe^{3+} and Fe^{2+} after reduction, CrO_4^{2-} , ClO_4^- and H_2O_2 .

THE REACTION OF UO_2^{2+} WITH CHROMAZUROL S IN THE PRESENCE OF SEPTONEX AT pH 5.25

At pH 5.25 in the presence of 0.2M -picoline buffer under the conditions given above, the dependence of A or $A - A_L$ on $f(c_M)$ is linear for the concentration range $c_M = 8.67 \cdot 10^{-7} - 9.54 \cdot 10^{-6}\text{M}$ ($0.206 \mu\text{g ml}^{-1} - 2.27 \mu\text{g ml}^{-1}$), the concave error for small metal concentrations is absent and the limiting absorbance A_0 for $c_M = 0$ is in agreement with the values calculated by linear regression of the measured values. It was found using the STAT program that $\epsilon_{612} = 105230 \pm 162$, $s_{xy(A)} = \pm 0.003$, $s_{xy(c)} = \pm 0.0064 \mu\text{g U ml}^{-1}$, detection limit ($8s_{xy(c)}$) = $0.0051 \mu\text{g ml}^{-1}$.

Here, however, the absorbance is more strongly affected by the ionic strength of the solution and concentration of inert salts (in the absence of 0.1M-KNO_3 the absorbance at 612 nm is 22% lower), and the absorbance of the blank is higher. Ethanol in concentrations of 5–20% does not interfere. The effect of a number of cations is listed

in Table X. The following ions interfere: Al^{3+} , In^{3+} , Ga^{3+} , Be^{2+} , Cu^{2+} , Ti(IV) , Cr^{3+} , Fe^{3+} , Fe^{2+} , Ni^{2+} , Co^{2+} , Zr(IV) , VO^{2+} , oxalate, citrate, so that the procedure at this pH is far less selective.

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