UPDATED ANALYSIS OF GALLIUM CHELATE AND VANADIUM CHELATE SOLUTIONS WITH 4-(2-PYRIDYLAZO)RESORCINOL AND XYLENOL ORANGE

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The characteristic factors of the gallium and vanadium chelates with the ligands 4-(2-pyridylazo)resorcinol (PAR) and xylenol orange (XO) have been determined with the aid of the principle of β -correction, which makes it possible to eliminate the influence of the surplus ligand in the solution of its chelate with methane (which makes calculation easier) and thereby provides a more acceptable method in comparison with others. The real molar coefficients of extinction of the chelates Ga and V with PAR and XO have been determined and a detailed calculation of the stoichiometric ratios of chelates has been made. The results have shown that the chelates formed have the following structure: Ga(PAR), Ga(XO), V(PAR)₂, and V(XO).

Keywords: principle of β -correction, characteristic factors, chelate of gallium, chelate of vanadium, 4-(2-pyridylazo)resorcinol, xylenol orange.

Introduction. The molar ratio [1], equilibrium constant [2], angular coefficient [3], etc. are the characteristic factors of the chelates of metals. In the present communication we carry out a new analysis of the characteristic factors of the chelates formed by gallium, vanadium, and by two ligands (PAR and XO) with the aid of the contemporary analytical method of two wavelengths called the principle of β -correction [4]. This principle is capable of eliminating entirely the interfering influence of the ligand excess, yielding the actual absorption of the chelate. Therefore, it is widely used for determining trace amounts of metals [5–10]. We have determined the effective fraction of ligand complexing, the stoichiometric ratio for the chelates formed, and their actual molar extinction coefficients. The results have shown that the determination of the stoichiometric ratio is easier and more acceptable in the theory than that made by conventional methods. The complexing ratios of the chelates are: Ga:PAR = 1:2, V:PAR = 1:2, Ga:XO = 1:1, and V:XO = 1:1. Their actual molar coefficients of extinction are equal to $(10^{-4} \text{ liter-mole}^{-1} \cdot \text{cm}^{-1} \text{ (at } \lambda, \text{ nm}))$: 5.6 (510), 1.09 (540), 2.64 (510), and 1.69 (510).

Method of β-Correction. The true optical density (A_c) of the solution of the ML_{γ} complex of a metal (M) with a ligand (L) is calculated from the following equation:

$$A_{\rm c} = \frac{\Delta A - \beta \Delta A}{1 - \alpha \beta} \, .$$

Here ΔA and $\Delta A'$ are the optical densities of a mixed solution of ML_{γ} and L measured at the wavelengths λ_2 and λ_1 relative to a pure reagent (only the solution of L); α and β are the correction factors:

$$\alpha = \frac{\varepsilon_{ML_{\gamma}}^{\lambda_{1}}}{\varepsilon_{ML_{\gamma}}^{\lambda_{2}}}, \quad \beta = \frac{\varepsilon_{L}^{\lambda_{2}}}{\varepsilon_{L}^{\lambda_{1}}},$$

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| Metal | Solution of a ligand | | Working wavelength, nm | | |
|----------|-------------------------------|-----------|------------------------|-------------|--|
| | concentration, mmole/liter | added, ml | λ_1 | λ_2 | |
| Gallium | PAR, 2.0 | 1.0 | 380 | 510 | |
| | XO, 1.0 | 2.0 | 410 | 510 | |
| Vanadium | PAR, 2.0 | 1.0 | 385 | 540 | |
| | XO, 1.0 | 2.0 | 410 | 510 | |

TABLE 1. Measurement Conditions for the Solutions of the Ga and V Complexes

TABLE 2. The α and β Parameters and the Form of the Expression for A_c

| Complex | α | β | $A_{\rm c} =$ |
|---------|-------|-------|-----------------------------------|
| Ga-PAR | 0.170 | 0.180 | $\Delta A - 0.180 \Delta A'$ |
| Ga-XO | 0.663 | 0.185 | $1.14(\Delta A - 0.185\Delta A')$ |
| V-PAR | 0.344 | 0.060 | $\Delta A - 0.160 \Delta A'$ |
| V-XO | 0.663 | 0.185 | $1.14(\Delta A - 0.185\Delta A')$ |

where $\varepsilon_{ML_{\gamma}}^{\lambda_1}$, $\varepsilon_{ML_{\gamma}}^{\lambda_2}$, $\varepsilon_{L}^{\lambda_1}$, and $\varepsilon_{L}^{\lambda_2}$ are the molar coefficients of extinction ML_{γ} and L at the wavelengths λ_1 and λ_2 , whose ratio can be calculated after direct investigation of the solutions L and ML_{γ} . The actual implicit molar coefficient of extinction ($\epsilon_{ML_{\gamma}}^{\lambda_2}$) and the amount (γ) of the ligand L needed for the

coordination of the metal M in a reaction can be written in the form

$$\epsilon_{\mathrm{ML}_{\gamma}}^{\lambda_{2}} = \frac{A_{\mathrm{c}}}{\delta C_{\mathrm{M}}}, \quad \eta = \frac{A_{\mathrm{c}} - \Delta A}{A_{0}}, \quad \gamma = \eta \frac{C}{C_{\mathrm{M}}}, \tag{1}$$

where η is the fraction of the reacted ligand, C_M is the molar concentration (mole/liter) of the metal M in the original solution, δ is the thickness of the cell, $C_{\rm L}$ is the molar concentration (mole/liter) of the ligand L in the original solution, and A_0 is the absorption of the pure reagent (only L) measured at the wavelength λ_2 relative to water.

Experimental. The absorption spectra have been written on a 722 spectrophotometer (Shanghai Third Analytical Instruments, China) in 1-cm cells. The standard 0.1-g/liter solution of gallium was obtained by dissolving 0.1 g of gallium (Shanghai Chemicals, China) in 20 ml of a 5-mole/liter hydrochloric acid and diluting with distilled water up to 1000 ml. Further dilution gave a 10-mg/liter solution of gallium. The standard 0.1-g/liter solution of vanadium was obtained by dissolving 0.2296 g of ammonium metavandate (Shanghai Chemicals) in 5 ml of a 10-mole/liter hydrochloric acid and dilution with distilled water up to 1000 ml. Further dilution of 10 ml of it up to 1000 ml yields a 1.0-mg/liter solution of V(V). To prepare chelates, use was made of the solutions, in distilled water, of 2 mmole/liter PAR (Shanghai Reagents, China) and 1 mmole/liter of XO (Shanghai 3rd Reagents, China). To provide the necessary conditions for complexing, an acetate buffer solution with pH 5 was used.

Recommended Procedure. The standard gallium in the amount of 50 μ g and 8 μ g of standard vanadium are placed in a 25-ml measuring bottle. Thereafter, 2 ml of the buffer solution are added and then solutions of PAR and XO in the amounts indicated in the table are added to the solution obtained. Dilution is made to the mark and then it is carefully mixed. After standing for 10 min the optical densities are measured at two wavelengths of the relatively pure reagent, as is shown in Table 1.

Results and Discussion. The absorption spectra of the solutions of PAR, XO, and of their Ga- and V-complexes are presented in Fig. 1. From curves 3 and 3', two wavelengths are selected at which the difference in the op-



Fig. 1. Absorption spectra of the solutions of PAR (a) and XO (b) and of their chelates with Ga (III) and V (V): a) 0.08 mg/liter PAR relative to water (1, 1'); Ga-PAR chelate (2) and V-PAR chelate (2') relative to water; solution of the chelate containing 2.00 mg/liter of Ga chelate and 0.08 mg/liter of PAR relative to a pure reagent (3); solution of the chelate containing 0.32 mg/liter of V and 0.08 mg/liter of PAR relative to the pure reagent (3'); b) 0.08 mg/liter of XO relative to water (1, 1'); Ga-XO chelate (2) and V-XO chelate (2') relative to water; solution of the chelate containing 2.00 mg/liter of Ga and 0.08 mg/liter of Ga and 0.08 mg/liter of XO relative to a pure reagent (3); solution of the chelate containing 0.32 mg/liter of Ga and 0.08 mg/liter of XO relative to a pure reagent (3); solution of the chelate containing 0.32 mg/liter of Ga and 0.08 mg/liter of XO relative to a pure reagent (3); solution of the chelate containing 0.32 mg/liter of XO relative to a pure reagent (3); solution of the chelate containing 0.32 mg/liter of SO relative to a pure reagent (3); solution of the chelate containing 0.32 mg/liter of Ga and 0.08 mg/liter of XO relative to a pure reagent (3); solution of the chelate containing 0.32 mg/liter of XO relative to a pure reagent (3); solution of the chelate containing 0.32 mg/liter of XO relative to a pure reagent (3); solution of the chelate containing 0.32 mg/liter of XO relative to a pure reagent (3); solution of the chelate containing 0.32 mg/liter of V and 0.08 mg/liter of XO relative to a pure reagents (3').



Fig. 2. Effect of PAR (a) and XO (b) on the optical densities of the solutions of the Ga and V chelates: a) solution of PAR, $\lambda_{reg} = 380$ (1) and 385 nm (1') relative to water; a chelated solution containing 200 mg/liter of Ga at 510 (3) and 380 nm (4) relative to a pure reagent; a chelated solution containing 0.32 mg/liter of V at 540 (3') and 385 nm (4') relative to a pure reagent; b) a solution of XO at 510 nm relative to water (1, 1'); a chelated solution containing 0.32 mg/liter of V at 540 (3') and 385 nm (4') relative to a pure reagent; 2 and 2' show the values of A_c calculated from curves 3, 4 and 3', 4', respectively.

tical densities is at maximum, i.e., the maximum and minimum of the curve. The working wavelengths are given in Table 1. The values of β are calculated from curves 1 and 1' and those of α , from curves 2 and 2' (Table 2).

Influence of the concentrations of PAR and XO. Figure 2 illustrates the influence of the addition of PAR and XO on the optical densities of the solutions. Curves 2, 3 and 2', 3' yield that $A_c > \Delta A$. This confirms that the method of the spectrophotometric β -correction has a higher sensitivity than the method of one wavelength. The stoichiometric ratio of the chelates cannot be exactly determined by the conventional method of the molar ratio proceeding from

| Concentration of the ion of a | Addition of ligand | λ ₂ , nm | Molar coefficient of extinction, 10^4 liter mole ⁻¹ cm ⁻¹ | | η, % | γ | 100 – ŋ, % |
|-------------------------------|--------------------|---------------------|---|----------------|------|---|------------|
| metal, mg/liter | solution, in | | ε _a | ε _p | | | |
| Ga(III), 2.00 | PAR, 1.0 | 510 | 4.78 | 5.61 | 70 | 2 | 30 |
| | XO, 2.0 | 510 | 0.86 | 1.09 | 38 | 1 | 62 |
| V(V), 0.32 | PAR, 1.0 | 540 | 2.13 | 2.64 | 15 | 2 | 85 |
| | XO, 2.0 | 510 | 1.44 | 1.69 | 6.5 | 1 | 93.5 |

TABLE 3. Determination of ε , η , and γ

TABLE 4. Accuracy of Determination of A_c and ΔA

| Solution of a metal complex, mg/liter | λ_2 , nm | A _c | ΔΑ | RSD, % | |
|---------------------------------------|------------------|----------------|-------|----------------|------------|
| | | | | A _c | ΔA |
| PAR-Ga (2.00) | 510 | 1.610 | 1.300 | 1.4 | 3.1 |
| XO-Ga (2.00) | 510 | 0.312 | 0.244 | 1.4 | 2.8 |
| PAR-V (0.32) | 540 | 0.166 | 0.136 | 2.5 | 3.3 |
| XO-V (0.32) | 510 | 0.106 | 0.092 | 2.1 | 2.6 |

Note. A_c and ΔA were obtained by averaging six values.





curves 3 and 3', since their inflection points are indistinct. The value of ε_p was calculated from curve 2. The results obtained are presented in Table 3. It is found that $\varepsilon_p < \varepsilon_a$, thus confirming once again the high sensitivity of the β -correction method in comparison with the conventional method.

Determination of η and γ . Proceeding from Eq. (1) and provided that $M_{Ga2} = 0.717 \mu mole$ (50 µg), $M_{V2} = 0.157 \mu mole$, $M_{PAR1} = 2 \text{ mmole/liter}$, and $M_{XO1} = 1 \text{ mmole/liter}$, we calculated the values of η and γ of the solution of each chelate from curves 1, 4, or 1', 4' (Fig. 2a) or from 2, 3, and 4 or 2', 3', and 4' (Fig. 2b). The results are shown in Fig. 3. It is seen from curves 2 and 4 that the value of γ remains constant on addition of more than 1 ml of the solution of ligand and that $\gamma \approx 2$ for PAR and $\gamma = 1$ for XO. Consequently, the formulas of the chelates obtained have the following form: Ga(PAR)₂, Ga(XO), V(PAR)₂, and V(XO). On addition of the recommended amounts of solutions of PAR and XO, the values of η of the solutions of chelates containing 2.00 mg/liter of Ga and 0.32 mg/liter of V were calculated (Table 3). The excess of the PAR and XO ligands amounted to 30–90%. Consequently, the excess of the PAR and XO ligands does not hinder exact determination of the optical densities of the Ga and V

chelates with PAR and XO. In other words, the spectrophotometry of one wavelength is not suitable for the determination of the molar coefficient of the extinction of chelates because of the appreciable interfering influence of ligands.

Using the results of 10 repeated measurements carried out in accordance with the procedure, namely, 0.32 mg/liter of V and 2.00 mg/liter of Ga, Table 4 presents relative standard deviations (RSD) of the values of A_c and ΔA . It is seen that these deviations are smaller for A_c than for ΔA . This indicates that the method of spectrophotometric β -correction is more accurate than the conventional one.

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