Spectrophotometric Determination of Rhenium with N-(4-Methoxy-phenyl)-α-thiopicolinamide and Evaluation of the Stability Constant of the Complex Involved Therein

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Rhenium reacts with N-(4-methoxy-phenyl)-α-thiopicolinamide to form a stable reddish brown complex on reduction with stannous chloride in 1.08 M to 1.32 M hydrochloric acid medium and the metal can be estimated by extractive photometry in chloroform medium. The system obeys Beer's law from 1-12 ppm at 430 nm. The molar absorptivity is 7.43×10^3 and the Sandell's sensitivity is 0.025 μg cm^{-2}. The metal forms a 1 : 2 complex (metal to ligand) with the ligand. Stability constant (log K) of the Re-complex has been evaluated by the Leden (7.60) and Rossotti and Rossotti (7.99) methods.

O F the existing spectrophotometric methods of determination of rhenium, those utilizing thiocyanate, some sulphur bearing organic reagents[1-4], and some oximes are of particular importance in analytical chemistry.

The present work describes the use of extractive photometric determination of rhenium with N-(4-methoxy-phenyl)-α-thiopicolinamide. Rhenium forms a reddish brown complex in 1.08-1.32 M HCl medium in presence of $SnCl_2$. The metal forms 1 : 2 complex as determined by Job's and molar ratio methods. The equilibrium constant has been evaluated by extending Leden's and Rossotti-Rossotti's method by graphical extrapolation using spectrophotometric data.

Experimental

A Hilger Uvispek spectrophotometer with 10 mm quartz transmission cells was used.

The standard rhenium(VII) solution was prepared by dissolving an accurately weighed quantity of potassium perrhenate (Johnson Matthey) in double distilled water. The solution was standardised by nitron method.

A 0.05% (w/v) solution of N-(4-methoxy-phenyl)-α-thiopicolinamide was prepared in absolute ethanol.

0.6694 M solution of stannous chloride (G. R., E. Merck) was prepared in 1 M hydrochloric acid.

Standard solutions of diverse ions were prepared from their chloride or sulphate, or from sodium, potassium or ammonium salts. All other chemicals were of AR grade. Double distilled water was used for preparing the solutions.

Recommended procedure : 5 ml of 0.05% (w/v) reagent solution in absolute ethanol was added to a standard solution of perrhenate (0.75 ml of 0.25 mg/ml rhenium) in a beaker followed by 2.5 ml of 0.6694 M stannous chloride solution and hydrochloric acid to maintain the final acidity between 1.08-1.32 M. At subsequent measurements, final acidity was maintained at 1.2 M with HCl. The solution was diluted to 25 ml with the addition of measured quantity of water and ethanol in the ratio of 1 : 1. The mixture was warmed for 5 min at 60-70°, cooled and transferred to a separatory funnel. The mixture was then shaken with 12 ml of chloroform for 5 min. The settled chloroform layer was collected. The aqueous phase was washed twice, each time with 5 ml of chloroform. The combined extract and washings were dried over anhydrous sodium sulphate and transferred to 25 ml volumetric flask and diluted up to the mark with chloroform. This order was maintained throughout this work. A reagent blank without the addition of rhenium was also run. Absorbance of the complex against reagent blank and also that of the reagent against chloroform blank was measured at various wavelengths. The complex showed maximum absorbance at 430 nm.

Results and Discussion

The full colour development of the complex was obtained after heating for 5 min at 60°-70°.

The colour intensity remained constant for 5 hr and the period of complete extraction in chloroform was 5 min.

4 ml of 0.05% reagent solution in absolute ethanol was quite enough for the full colour development of 10 ppm of rhenium.

Addition of more reagent did not produce any adverse effect on the colour system. For subsequent measurements 5 ml of the reagent solution was used. For maximum colour development, 1.08-1.32 M HCl medium was required.

It has been observed that 1.5 ml of 0.6694 M stannous chloride solution was sufficient for full colour development though a higher concentration of the latter had no adverse effect. A 0.6694 M $SnCl_2$ solution was however always used.

Validity of Beer's law, relative error, sensitivity and molar absorptivity : Test solutions with different concentrations of rhenium were prepared by the recommended procedure. The system adheres to Beer's law from 1-12 ppm.

The Ringbom's[5] optimal concentration range for measurement was found to be from 3.72 11.5 ppm.

The relative error per 2% absolute photometric error[6] was found to be 2.72.

The molar absorptivity as obtained from Beer's law is 7.43×10^3 at 430 nm and Sandell's sensitivity[7] is 0.025 $\mu g\ cm^{-2}$.

Composition of the complex : The composition of the complex was determined by Job's method of continuous variation[8] and by the mole-ratio method[9]. For Job's method, mixture (12 ml total) of equimolar solutions $(5.37 \times 10^{-4}\ M)$ of the perrhenate and the reagent were treated as in the general procedure. The curve indicated that the complex contained rhenium and the reagent in the ratio 1 : 2. This result was confirmed by the mole-ratio method.

Effect of diverse ions : The effect of diverse ions on the determination of rhenium was studied by adding a definite amount of foreign ion to a solution containing 10 ppm of rhenium and working as under the recommended procedure. The results are shown in Table 1.

as is evident from the values of free ligand concentration calculated for each determination of absorbance.

The successive stability values obtained by considering the degree of complexation are given below :

$$\underset{L \to 0}{Lim}\ \psi_1 = \underset{L \to 0}{Lim}\ \frac{\phi - 1}{L} = \beta_1 = 4.0 \times 10^8$$

The plot of ψ_1 against free ligand concentration gave a straight line of intercept $\beta_1 = 4.0 \times 10^8$ (Fig. 1).
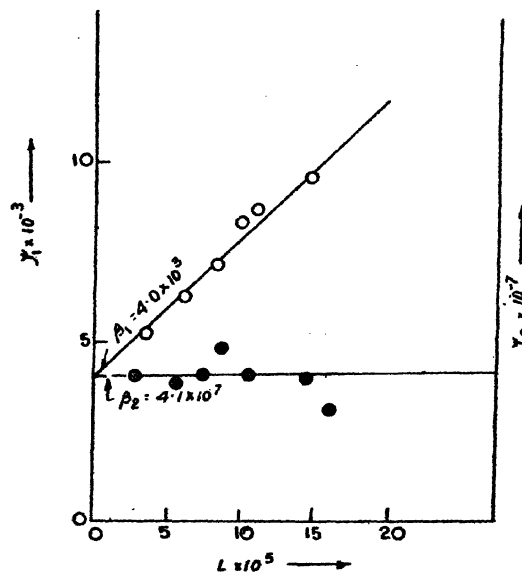

Fig. 1. Leden's method of stability constant. Re - N(4-methoxy-phenyl) α-thiopicolinamide.

Similarly, by substituting the value of β_1 in the following function

$$\underset{L \to 0}{Lim}\ \psi_2 = \underset{L \to 0}{Lim}\ \frac{\psi_1 - \beta_1}{L} = \beta_2 = 4.1 \times 10^7$$

The plot of ψ_2 against free ligand concentration gave a straight line of intercept β_2 (Fig. 1), the overall stability constant. The values of K_1 and K_2 are found to be

$$K_1 = 4.0 \times 10^8\ ;\ K_2 = 1.0 \times 10^4$$

The results are tabulated in Table 2.

TABLE 1—EFFECT OF DIVERSE IONS ; Re=10 ppm

Ions	Amount studied ppm	Ions	Amount studied ppm
U(VI)			
Ti(IV)	400	Cd(II)	400
Mo(VI)	400	Ca(I)	400
W(VI)	60	Ir(III)	Interferes
V(V)	200	Oxalate	400
Pt(IV)	Interferes	EDTA	400
Pd(II)	Interferes	Tartrate	400
Mn(II)	Interferes	Citrate	400
Cu(II) EDTA	400	F⁻	Interferes
Co(II) EDTA	400	SCN⁻	Interferes
Fe(II) Oxalate	400	BO₂⁻	Interferes
Ni(II)	200	SO₄²⁻	400
Zn(II)	400	NO₃⁻	400
	400	PO₄³⁻	400

Stepwise formation constants : -The procedure for evaluation of the stepwise formation constants was examined by proper extension of Leden's method and verified by the method of Rossotti-Rossotti.

Leden's method[10] : For evaluation of K_1 and K_2 we have assumed that the equilibrium concentrations of the ligand is equal to total ligand concentration. This assumption is found to be valid

TABLE 2—OVERALL STABILITY CONSTANT AND STEPWISE FORMATION CONSTANT OF THE COMPLEX AT 27°

Methods	Log K_1	Log K_2	Log $K_{overall}$
Leden	3.60	4.00	7.60
Rossotti-Rossotti	3.95	4.04	7.99

Rossotti-Rossotti's method[11] : This method is based on the absorbance of a complex dependent on the total concentrations of ligand and central

group. When only the two complexes are formed, β_1 and β_2 may be calculated from the following equations :

$$\xi = \frac{As - \gamma \epsilon_L[L]}{C_M[L]} = \frac{\epsilon_0 + \epsilon_1 \beta_1[L]}{1 + \beta_1[L]} \qquad \dots \text{(i)}$$

$$\xi = \frac{As - \gamma \epsilon_L[L]}{C_M[L]} = \frac{\epsilon_0 + \epsilon_1 \beta_1[L] + \epsilon_2 \beta_2[L]^2}{1 + \beta_1[L] + \beta_2[L]^2} \qquad \dots \text{(ii)}$$

The plot of ξ against $\dfrac{\xi - \epsilon_0}{L}$ gave a straight line of slope $-\beta_1$ and intercept ϵ_1 for the complex.

The values of β_1 and ϵ_1 are found to be (Fig. 2)
$\beta_1 = 9 \times 10^3$; $\epsilon_1 = 7.5 \times 10^3$.
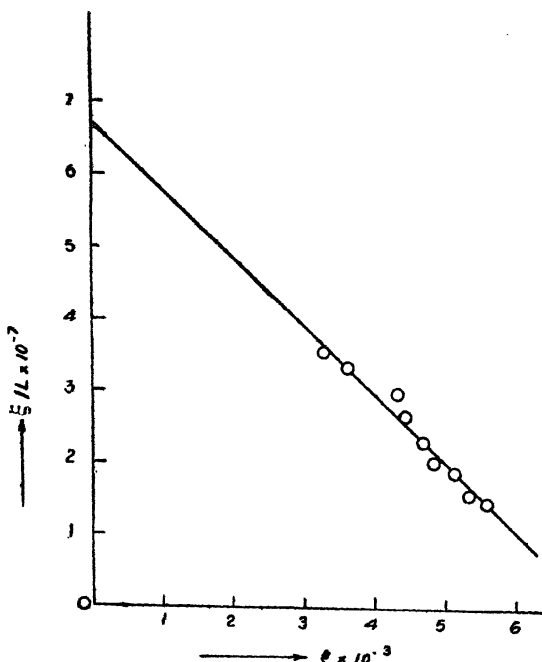
Fig. 2. Rossotti-Rossotti's method of stability constant. Re-N(4-methoxy-phenyl) ∝-thiopicolinamide.

These values of β_1 and ϵ_1 were further substituted in equation (ii) which was solved as below :

$$\frac{\epsilon_0 - \xi}{\xi L} + \frac{\epsilon_1 - \xi}{\xi L} \beta_1 = \beta_2 - \frac{\epsilon_2 \beta_2}{\xi} \qquad \dots \text{(iii)}$$

The plot of $\dfrac{\epsilon_1 - \xi}{\xi L} \beta_1 - \dfrac{1}{L^2}$ against $1/\xi$ gave straight line of slope $-\epsilon_2 \beta_2$ and intercept β_2 for the complex.

The values of β_2 and ϵ_2 are found to be (Fig. 3)
$\beta_2 = 90.0 \times 10^6$; $\epsilon_2 = 4.14 \times 10^3$.

The values of K_1 and K_2 are given below
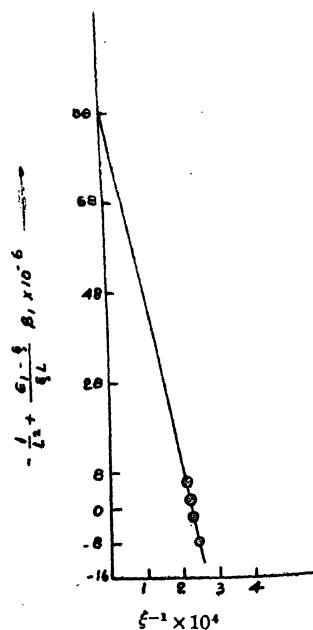$K_1 = 9 \times 10^3$; $K_2 = 1.17 \times 10^5$

Fig. 3. Rossotti-Rossotti method of stability constant. Re-N(4-methoxy-phenyl) ∝-thiopicolinamide complex.

The values of overall stability constant obtained by Leden's method and Rossotti-Rossotti method are summarized in Table 2.

Acknowledgement

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