

Investigation of properties of rare earth complexes with dibromo-*p*-methyl-methylsulfonazo by spectral correction technique

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Abstract. The reactions were sensitive between seven rare earth (RE) metals Nd(III), La(III), Ce(III), Pr(III), Sm(III), Eu(III) and Gd(III) and dibromo-*p*-methyl-methylsulfonazo (DBMMSA) in acidic solution. The spectral correction method has been applied in the determination of properties of RE complexes instead of ordinary spectrophotometry. Composition ratios, real molar absorptivities (ϵ) and stepwise stability constants (K) of each of the RE complexes were determined easily because the method eliminated the absorption influence of excess of ligand on complex. Results showed that the cumulative K values of the complexes were between 3.91×10^{14} and 2.34×10^{28} and the real (not apparent) absorptivity between 8.85×10^4 and $2.12 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 640 nm.

Keywords. Spectral correction technique; rare earth; dibromo-*p*-methyl-methylsulfonazo (DBMMSA).

1. Introduction

The synthesis of the ligand dibromo-*p*-methyl-methylsulfonazo (DBMMSA) was reported earlier¹ and its structure is as given in chart 1.

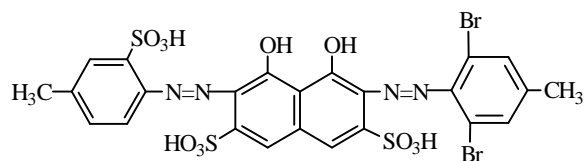


Chart 1.

This reagent was earlier used in the determination of trace amounts of some metals². However, the updated investigation showed that the free DBMMSA absorbs at the peak wavelength of the complex formed and so ordinary spectrophotometry may not work

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with high precision and good accuracy. The new technique, the spectral correction method, is the first to eliminate the absorption influence of the excess of ligand and give the real absorption of the complex formed. It has been applied extensively in the determination of many complex solutions³⁻⁶. In the present report, the reactions between REs(III) and DBMMSA in acidic solution were studied in detail. Seven rare earth metals (Nd(III), La(III), Ce(III), Pr(III), Sm(III), Eu(III) and Gd(III)) were observed to react sensitively with DBMMSA and to form blue complexes with composition ratios between 3 and 6. Determination of the real absorptivities (K) and stepwise stability constants (e) of the complexes was also carried out. Results showed that the cumulative K values of the complexes were between 3.91×10^{14} and 2.34×10^{28} and the real (not apparent) absorptivities were between 8.85×10^4 and $2.12 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 640 nm. The spectral correction technique was more acceptable in principle and simpler in operation than classical methods such as molar ratio⁷, continuous variation⁸, equilibrium movement⁹ etc.

2. Experimental

2.1 Apparatus and reagents

Absorption spectra were recorded on a UV-VIS 265 spectrophotometer (Shimadzu, Japan) in 10 mm glass cells.

Standard Nd(III), La(III), Ce(III), Pr(III), Sm(III), Eu(III) and Gd(III) stock solutions, all 1.00 g/l (oxide content) were provided by the National Geological Testing and Instrumentation Centre. Standard solutions of these, 0.100 mmol/l, were prepared by diluting the stock solutions with 0.32 mmol/l nitric acid. DBMMSA (purified and provided by Changke Reagent Institute of Shanghai, China) solution, 1.00 mmol/l, was dissolved in non-ionic water and stored in a dark bottle. A solution of 5 mol/l hydrochloric acid was prepared so as to adjust the optimum acidity of the complex solution. Non-ionic water with specific conductivity less than 0.3 $\mu\text{S/cm}$ was prepared and used in this work.

2.2 Recommended procedures

RE (III) 0.100 mmol was taken in a 25 ml volumetric flask. To this about 10 ml distilled water was added, followed by 2 ml of 5 mol/l hydrochloric acid and 1.00 mmol/l DBMMSA. This was diluted to volume and mixed well. After 10 min, the absorbances at 530 and 640 nm were measured against a reagent blank. The real absorbance (A_c) of the complex was calculated according to the following expression,

$$A_c = \frac{\Delta A - b\Delta A'}{1 - ab}$$

where

$$a = \frac{e^{I_1}_{\text{ML}_g}}{e^{I_2}_{\text{ML}_g}} = \frac{A'_a}{A_a},$$

and

$$\mathbf{b} = \frac{\mathbf{e}_L^{I_2}}{\mathbf{e}_L^{I_1}} = \frac{A_0}{A_0'}$$

Here, the terms ΔA and $\Delta A'$ are absorbances of the reaction solution at 640 (I_2) and 530 nm (I_1) against the reagent blank respectively. The coefficients, \mathbf{a} and \mathbf{b} are the correction factors. The symbols, $\mathbf{e}_{MLg}^{I_1}$, $\mathbf{e}_{MLg}^{I_2}$, $\mathbf{e}_L^{I_1}$ and $\mathbf{e}_L^{I_2}$ indicate the molar absorptivity of complex ML_g and ligand (L) at 530 and 640 nm respectively.

In fact, the spectra correction method is also a dual-wavelength spectrophotometric method. However, it is different from the other conventional dual-wavelength methods¹⁰⁻¹⁴ in theory and operation.

3. Results and discussion

3.1 Absorption spectra

The absorption spectra of all rare earth metal (III) complexes with DBMMSA have the same or similar bending shapes but different absorptivities. In this section, Nd(III) was used as an example in the selection of the optimum operation conditions. Two wavelengths were selected such that the difference in absorbances was the maximum: 530 (valley absorption) and 640 nm (peak absorption). From the spectral curves, \mathbf{b} and \mathbf{a} were calculated to be 0.132 and 0.422 respectively. The real absorption of RE-DBMMSA complex at 640 nm was calculated by the equation: $A_c = 1.06 (\Delta A - 0.132 \Delta A')$.

3.2 Effect of addition of DBMMSA solution

By varying the addition of 1.00 mmol/l DBMMSA, the absorption of the RE-DBMMSA reaction solution was measured. The effective fraction ($\mathbf{h}\%$) of DBMMSA and the complex ratio (\mathbf{g}') of DBMMSA to RE were calculated according to the following equations.

$$\mathbf{g}' = \mathbf{h} \times (C_L/C_M),$$

where

$$\mathbf{h} = (A_c - \Delta A)/A_0.$$

The terms, C_M and C_L indicated the concentrations (mol/l) of RE and DBMMSA in the beginning respectively. A_0' represented the absorption of the blank reagent at 530 nm against water. From their curves, the final RE complexes were expressed as follows: Nd(DBMMSA)₃, La(DBMMSA)₃, Ce(DBMMSA)₃, Pr(DBMMSA)₄, Sm(DBMMSA)₆, Eu(DBMMSA)₄ and Gd(DBMMSA)₄. The combined and free DBMMSA in their RE reaction solutions were shown in table 1 where the complex ratio approached or reached the final constant 2. We observed that the excess of DBMMSA took up about 80% of the total addition of DBMMSA in Nd(III) solution, 71% in La(III) solution, 71% in Ce(III) solution, 74% in Pr(III) solution, 75% in Sm(III) solution, 85% in Eu(III) solution and 87% in Gd(III) solution respectively. Therefore, over 70% of the total addition of DBMMSA did not join the combination with RE. Undoubtedly, such high DBMMSA-free concentration did affect the measurement of real absorption of RE-DBMMSA complexes.

Table 1. The effective percentage and the excess of DBMMSA in its RE solutions when the complexation ratio of DBMMSA to RE approaches the maximum.

| RE addition ($\text{mg}/25 \text{ ml}$) | Minimum addition of DBMMSA ($\text{mmol}/25 \text{ ml}$) | Combination of DBMMSA ($h\%$) | Excess of DBMMSA (%) |
|---|--|---------------------------------|----------------------|
| Nd(III) 0.100 | 1.50 | 20 | 80 |
| La(III) 0.100 | 1.00 | 29 | 71 |
| Ce(III) 0.100 | 1.00 | 29 | 71 |
| Pr(III) 0.100 | 1.50 | 26 | 74 |
| Sm(III) 0.100 | 2.00 | 25 | 75 |
| Eu(III) 0.100 | 2.50 | 15 | 85 |
| Gd(III) 0.100 | 3.00 | 13 | 87 |

3.3 Effect of pH and reaction time

By varying the acidity of the solution, the absorption of the Nd-DBMMSA solution was measured. We observed that the sensitivity of the RE-DBMMSA reaction reached the maximum in acidic solution. Therefore, all determinations were made in acidic solution. The effect of reaction time on the real absorption of Nd-DBMMSA complex showed that the reaction between RE and DBMMSA was complete in 10 minutes.

3.4 Determination of stability constant and real absorptivity of complex

The stepwise stability constant (K_n), cumulative stability constant (K) and stepwise absorptivity (ϵ) of the complex can be calculated from the following equations:

$$K_n = \frac{g' + 1 - n}{(n - g')(C_L - g'C_M)},$$

and

$$\epsilon_{ML_n}^{I_2} = \frac{A_c}{dC_M(g' + 1 - n)} - \frac{n - g'}{g' + 1 - n} \epsilon_{ML_{n-1}}^{I_2}.$$

Here, the symbols, n indicates the n th complex and d the thickness of the cell. The complex ratio g' must be kept between $n - 1$ and n by preparing a mixed solution. The following solutions were prepared for the determination of the stepwise stability constants and the stepwise real absorptivities of RE-DBMMSA complexes: 0.100 μmol of Nd(III) with 0.300, 0.600 and 0.800 mmol of DBMMSA, 0.100 mmol of La(III) with 0.300, 0.400 and 0.600 mmol of DBMMSA, 0.100 mg of Ce(III) with 0.300, 0.400 and 0.800 mmol of DBMMSA, 0.100 mg of Pr(III) with 0.300, 0.500, 0.700 and 1.00 mmol of DBMMSA, 0.100 mg of Sm(III) with 0.300, 0.500, 0.800, 1.00, 1.25 and 2.00 mmol of DBMMSA, 0.100 mg of Eu(III) with 0.500, 0.800, 1.25 and 2.00 mmol of DBMMSA and 0.100 mg of Gd(III) with 0.800, 1.25, 1.50 and 2.50 mmol of DBMMSA. Three replicated

Table 2. The determination of the stepwise stability constant and the stepwise real absorptivity of all RE (DBMMSA)_{*n*} at ionic strength 0.1 and temperature 12°C.

| M-L reaction | Stepwise stability constant | | | |
|---|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| | K_3 | K_4 | K_5 | K_6 |
| Nd-BMMSA | $(2.64 \pm 0.29) \times 10^4$ | | | |
| La-DBMMSA | $(6.80 \pm 0.54) \times 10^4$ | | | |
| Ce-DBMMSA | $(1.03 \pm 0.15) \times 10^5$ | | | |
| Pr-DBMMSA | $(1.10 \pm 0.08) \times 10^5$ | $(3.77 \pm 0.66) \times 10^4$ | | |
| Sm-BMMSA | $(9.39 \pm 1.41) \times 10^4$ | $(8.69 \pm 1.22) \times 10^4$ | $(2.44 \pm 0.38) \times 10^4$ | $(3.71 \pm 0.19) \times 10^4$ |
| Eu-DBMMSA | $(3.63 \pm 0.26) \times 10^4$ | $(1.40 \pm 0.18) \times 10^4$ | | |
| Gd-DBMMSA | $(8.77 \pm 1.12) \times 10^3$ | $(7.04 \pm 0.98) \times 10^3$ | | |
| Stepwise absorptivity at 640 nm, $1 \text{ mol}^{-1} \text{ cm}^{-1}$ | | | | |
| | ϵ_{ML3} | ϵ_{ML4} | ϵ_{ML5} | ϵ_{ML6} |
| Nd-DBMMSA | 8.85×10^4 | | | |
| La-DBMMSA | 9.44×10^4 | | | |
| Ce-DBMMSA | 1.10×10^5 | | | |
| Pr-DBMMSA | 9.78×10^4 | 1.29×10^5 | | |
| Sm-DBMMSA | 9.77×10^4 | 1.33×10^5 | 1.63×10^5 | 2.12×10^5 |
| Eu-DBMMSA | 8.74×10^4 | 1.57×10^5 | | |
| Gd-DBMMSA | 8.62×10^4 | 1.38×10^5 | | |

preparations and determinations of each were carried out and results are shown in table 2. Standard deviations of K s are listed, which are less than 20% of the average. The cumulative stability constant (K) of RE(DBMMSA)_{*n*} was followed: Nd(DBMMSA)₃ 3.91×10^{14} , La(DBMMSA)₃ 3.93×10^{14} , Ce(DBMMSA)₃ 2.85×10^{15} , Pr(DBMMSA)₄ 3.47×10^{19} , Sm(DBMMSA)₆ 2.34×10^{28} , Eu(DBMMSA)₄ 9.73×10^{17} and Gd(DBMMSA)₄ 4.42×10^{17} respectively. All these reactions were determined at ionic strength 0.1 mol/l and at a temperature of 12°C. We observed that the cumulative stability constants of complexes increased with the increase of the final complex ratio. The stepwise real absorptivities, $\epsilon_{\text{ML}_n}^{I_2}$ of RE(DBMMSA)_{*n*} were all between 8.85×10^4 and $2.12 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 640 nm (table 2). The greater the complex ratios of RE to DBMMSA, the greater were the absorptivities of the complex. In any rare earth complex, the absorptivity of the next-step complex is always more than that of the last-step complex because the increase of ligand in complex composition enhances the absorption of the complex solution. By contrast, the same step RE complex had similar real absorptivity, for example all RE(DBMMSA) had values between 3.20 and $3.81 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 640 nm (except the Nd complex), all RE(DBMMSA)₂ were between 6.13 and $7.60 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 640 nm (except the Gd complex) and all RE(DBMMSA)₃ were between 8.62 and $11.0 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 640 nm.

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