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 (*e*) 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 $2.12 \times 10^5 \, \mathrm{l\,mol^{-1}cm^{-1}}$ 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 earlier [1] and its structure is as given in chart 1.
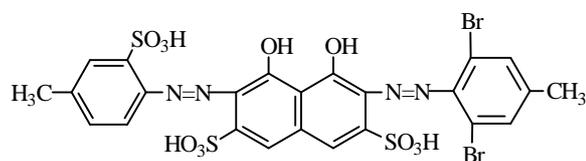

Chart 1.

This reagent was earlier used in the determination of trace amounts of some metals [2]. 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

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 solutions [3–6]. 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 $3 \cdot 91 \times 10^{14}$ and $2 \cdot 34 \times 10^{28}$ and the real (not apparent) absorptivities were between $8 \cdot 85 \times 10^{4}$ and $2 \cdot 12 \times 10^{5} \, 1 \, mol^{-1} \, cm^{-1}$ at 640 nm. The spectral correction technique was more acceptable in principle and simpler in operation than classical methods such as molar ratio [7], continuous variation [8], equilibrium movement [9] 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 $1 \cdot 00 \, g/l$ (oxide content) were provided by the National Geological Testing and Instrumentation Centre. Standard solutions of these, $0 \cdot 100 \, mmol/1$, were prepared by diluting the stock solutions with $0 \cdot 32 \, mmol/l$ nitric acid. DBMMSA (purified and provided by Changke Reagent Institute of Shanghai, China) solution, $1 \cdot 00 \, mmol/l$, 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 $0 \cdot 3$ **n**S/cm was prepared and used in this work.

2.2 *Recommended procedures*

RE (III) $0 \cdot 100$ **m**mol 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 $1 \cdot 00 \, mmol/l$ 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

$$a = \frac{e_{ML_g}^{l_1}}{e_{ML_g}^{l_2}} = \frac{A_a'}{A_a},$$

and

$$b = \frac{e_L^{l_2}}{e_L^{l_1}} = \frac{A_0}{A_0'}.$$

Here, the terms ΔA and $\Delta A'$ are absorbances of the reaction solution at 640 (l_2) and 530 nm (l_1) against the reagent blank respectively. The coefficients, a and b are the correction factors. The symbols, $e_{ML_g}^{l_1}$, $e_{ML_g}^{\lambda_2}$, $e_L^{l_1}$ and $e_L^{l_2}$ 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 methods [10–14] 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, b and 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 (h%) of DBMMSA and the complex ratio (g') of DBMMSA to RE were calculated according to the following equations.

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

where

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

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 (mg/25 ml)	Minimum addition of DBMMSA ($m$mol/25 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 (e) of the complex can be calculated from the following equations:

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

and

$$e_{ML_n}^{l_2} = \frac{A_c}{dC_M(g' + 1 - n)} - \frac{n - g'}{g' + 1 - n} e_{ML_{n-1}}^{l_2}.$$

Here, the symbols, n indicates the nth 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 $m$mol of DBMMSA, 0·100 $m$mol of La(III) with 0·300, 0·400 and 0·600 $m$mol of DBMMSA, 0·100 mg of Ce(III) with 0·300, 0·400 and 0·800 $m$mol of DBMMSA, 0·100 mg of Pr(III) with 0·300, 0·500, 0·700 and 1·00 $m$mol of DBMMSA, 0·100 mg of Sm(III) with 0·300, 0·500, 0·800, 1·00, 1·25 and 2·00 $m$mol of DBMMSA, 0·100 mg of Eu(III) with 0·500, 0·800, 1·25 and 2·00 $m$mol of DBMMSA and 0·100 mg of Gd(III) with 0·800, 1·25, 1·50 and 2·50 $m$mol 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, l mol^{-1} cm^{-1}			
	e_{ML3}	e_{ML4}	e_{ML5}	e_{ML6}
Nd-DBMMSA	$8·85 \times 10^4$			
La-DBMMSA	$9·44 \times 10^4$			
Ce-DBMMSA	$1·10 \times 10^5$			
Pr-DBMMSA	$9·78 \times 10^4$	$1·29 \times 10^5$		
Sm-DBMMSA	$9·77 \times 10^4$	$1·33 \times 10^5$	$1·63 \times 10^5$	$2·12 \times 10^5$
Eu-DBMMSA	$8·74 \times 10^4$	$1·57 \times 10^5$		
Gd-DBMMSA	$8·62 \times 10^4$	$1·38 \times 10^5$		

preparations and determinations of each were carried out and results are shown in table 2. Standard deviations of Ks are listed, which are less than 20% of the average. The cumulative stability constant (K) of RE(DBMMSA)$_n$ was followed: Nd(DBMMSA)$_3$ $3·91 \times 10^{14}$, La(DBMMSA)$_3$ $3·93 \times 10^{14}$, Ce(DBMMSA)$_3$ $2·85 \times 10^{15}$, Pr(DBMMSA)$_4$ $3·47 \times 10^{19}$, Sm(DBMMSA)$_6$ $2·34 \times 10^{28}$, Eu(DBMMSA)$_4$ $9·73 \times 10^{17}$ and Gd(DBMMSA)$_4$ $4·42 \times 10^{17}$ 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, $e_{ML_n}^{l_2}$ of RE(DBMMSA)$_n$ were all between $8·85 \times 10^4$ and $2·12 \times 10^5$ l mol^{-1}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 $3·81 \times 10^4$ l mol^{-1}cm^{-1} at 640 nm (except the Nd complex), all RE(DBMMSA)$_2$ were between 6·13 and $7·60 \times 10^4$ l mol^{-1}cm^{-1} at 640 nm (except the Gd complex) and all RE(DBMMSA)$_3$ were between 8·62 and $11·0 \times 10^4$ l mol^{-1}cm^{-1} at 640 nm.

Acknowledgement

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