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Formation Constants of Lanthanoid(III) Complexes with 4-(2-Thiazolylazo)resorcinol

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Synopsis. The formation constants of the protonated (MHR) and normal (MR) complexes (1:1) of lanthanoids(III) with 4-(2-thiazolylazo)resorcinol (TAR, H_2R) have been determined spectrophotometrically by estimation of the free ligand. The MR complexes of TAR were less stable than the corresponding 4-(2-pyridylazo)resorcinol (PAR) complexes, but the relative stabilities were reversed for the MHR complexes.

4-(2-Thiazolylazo)resorcinol (TAR) gives intensely colored complexes with most metals and is widely used in analytical chemistry.[1] Shimizu and Momo reported that TAR is the most useful reagent for determination of Sc(III).[2] It is of interest to study complexation of lanthanoids(III) with TAR. As described previously, the method[3] developed for determination of complex formation constants by estimation of the free ligand was applicable to study the lanthanoid(III)-4-(2-pyridylazo)resorcinol (PAR) complexes.[4] In the present work, the method[3] was applied to the lanthanoid(III)-TAR system and the results were compared with those of the lanthanoid(III)-PAR system.[4]

Experimental

Materials. All chemicals used were of G.R. grade. TAR was obtained from Dojindo Chemical Co., and its purity was checked by using thin-layer chromatography.[5] A weighed quantity of TAR was dissolved in a small volume of 1.0 M (1 M=1 mol dm^{-3}) NaOH and the solution was diluted with distilled water to prepare the stock solution of 2.0×10^{-3} M. The lanthanoid(III) nitrate solutions except for Ce(III) were prepared by dissolving the calculated amounts of the respective oxides in nitric acid. The cerium(III) nitrate solution was prepared by dissolving $Ce(NO_3)_3\cdot2(NH_4NO_3)\cdot4H_2O$ in 10^{-2} M HNO_3 and the concentration was determined by EDTA titration. Hexamine and sodium nitrate were used to maintain the pH at 5—6.3 and the ionic strength at 0.1, respectively.

Procedure. The metal solution was added in small aliquots, 50 μl each, using a microliter pipet to a 10 ml of the buffered solution of TAR (1.5—2.0×10^{-5} M), to give the concentrations of 10^{-4}—5×10^{-3} M. Before and after the addition of the metal for each 50 μl, the absorbance at the peak of TAR (420 or 440 nm) was measured by using a Shimadzu UV 200s spectrophotometer. No precipitation occurred under these experimental conditions.

Results and Discussion

As described previously,[3] metal complexes of TAR (H_2R), MHR, and MR, can indirectly be estimated by utilizing the ligand absorption peak. The absorbance at the free ligand peak measured in the absence (A_0) and the presence (A) of the metal under conditions where $C_M \gg C_R$ (C_M and C_R are the total concentrations of the metal and the ligand), *i.e.*, formation of the 1:1 complexes, MHR and MR, is assumed, can be related to their formation constants, K_{MHR} and K_{MR}, as follows (the charges are omitted for simplicity):

$$C_R = [MHR] + [MR] + [R'] \tag{1}$$

$$A = \varepsilon_{MHR}[MHR] + \varepsilon_{MR}[MR] + \varepsilon_{R'}[R'], \tag{2}$$

where R′ is the free ligand not combined with metal, and ε_{MHR}, ε_{MR}, and $\varepsilon_{R'}$ are the molar extinction coefficient of MHR, MR, and R′ at the free ligand peak, respectively. With the formation constants, $K_{MHR}=[MHR]/([M][HR])$ and $K_{MR}=[MR]/([M][R])$, the acid dissociation constants of H_2R, $K_1=[H][HR]/[H_2R]$ and $K_2=[H][R]/[HR]$, and α coefficient,[6] $\alpha_R=[R'][R]$, Eqs. 1 and 2 can be brought into the following expressions:

$$\begin{aligned}[M](K_{MHR}K_1[H]+K_{MR}K_1K_2)/(\alpha_R K_1K_2)\\ = C_R/[R'] - 1,\end{aligned} \tag{3}$$

$$\begin{aligned}A/\varepsilon_{R'} = [R']\{1+(\varepsilon_{MHR}K_{MHR}K_1[H]\\ +\varepsilon_{MR}K_{MR}K_1K_2)[M]/(\varepsilon_{R'}\alpha_R K_1K_2)\}.\end{aligned} \tag{4}$$

Combining Eq. 3 with Eq. 4, and substituting C_M for [M] (since $C_M \gg C_R$) and A_o for $C_R\varepsilon_R$, we obtain

$$\frac{K_{MHR}K_1[H]+K_{MR}K_1K_2}{\alpha_R K_1K_2} - \frac{\varepsilon_{MHR}K_{MHR}K_1[H]+\varepsilon_{MR}K_{MR}K_1K_2}{\varepsilon_{R'}\alpha_R K_1K_2} \times\frac{A_o}{A} = (A_o/A-1)/C_M. \tag{5}$$

From Eq. 5, a linear relation between $(A_o/A-1)/C_M$ and A_o/A should be obtained at a constant pH where $\varepsilon_{R'}$ remains constant. The product of the intercept of the y axis ($y=(A_o/A-1)/C_M$), y_o, at a fixed pH and $\alpha_R K_1K_2$ is given as a function of [H]:

$$y_o \times \alpha_R K_1K_2 = K_{MHR}K_1[H] + K_{MR}K_1K_2 \tag{6}$$

According to Eq. 6, a linear plot of the left-hand side of Eq. 6 *vs.* [H] should be obtained in a pH range where no hydrolysis of metal ion occurs. From the slope and the intercept of the line, both K_{MHR} and K_{MR} can be determined.

By measuring the decrease of the absorbance at the peak of TAR (420 nm) with increasing metal concentrations at a constant pH, we plotted the relation expressed by Eq. 5. All the plots obtained at different pH values for different lanthanoids(III) yielded a straight line with a negative slope as expected. Since TAR shows a broad peak (410—440 nm), we tried to plot the data at another wavelength of 440 nm and ascertained the line having the same intercept (the slope is different). Figure 1 shows a typical set of plots at pH 5.50. The experimental data showed no detectable difference in the plots for Yb(III) and Lu(III) (line 1), for Dy(III) through Er(III) (line 3), and for Sm(III)

Table 1. Formation constants, K_{MHR} and K_{MR}, and proton dissociation constants of MHR, K^{H}_{MHR}, for TAR and PAR complexes of lanthanoids(III) $I=0.1$ ($NaNO_3$), 25 °C

Element	TAR			PAR[3,4]		
	$\log K_{MHR}$	$\log K_{MR}$	pK^{H}_{MHR}	$\log K_{MHR}$	$\log K_{MR}$	pK^{H}_{MHR}
La	3.61	6.93	6.12	3.18	8.91	6.57
Ce	4.08	7.44	6.08	3.78	9.61	6.47
Pr	4.27	7.65	6.06	3.95	9.78	6.47
Nd	4.40	7.79	6.05	4.07	10.02	6.35
Sm	4.71	8.10	6.05	4.28	10.25	6.33
Eu	4.71	8.10	6.05	4.28	10.25	6.33
Gd	4.71	8.10	6.05	4.28	10.25	6.33
Tb	4.71	8.10	6.05	4.28	10.25	6.33
Dy	4.71	8.10	6.05	4.29	10.36	6.23
Ho	4.71	8.10	6.05	4.29	10.47	6.12
Er	4.71	8.10	6.05	4.31	10.52	6.09
Tm	4.74	8.34	5.84	4.34	10.57	6.07
Yb	4.77	8.78	5.43	4.39	10.70	5.99
Lu	4.77	8.78	5.43	4.39	10.70	5.99

The relative errors of K_{MHR} and K_{MR} are 5—10% and 8—15% respectively.

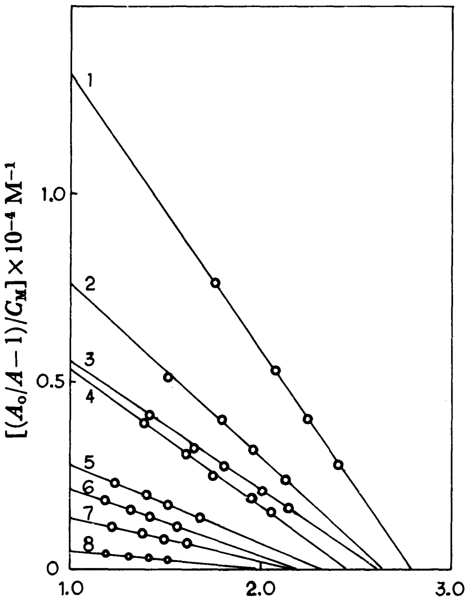

Fig. 1. Plots according to Eq. 5 at a constant pH of 5.50 for the system of TAR and lanthanoids (III). 1) Lu, Yb; 2) Tm; 3) Er, Ho, Dy; 4) Tb, Gd, Eu, Sm; 5) Nd; 6) Pr; 7) Ce; 8) La.

through Tb(III) (line 4), respectively. It is noted that lines 3 and 4 have a slightly different slope but almost the same intercept. This suggests that the degree of complex formation for Sm(III) through Er(III) is very similar to each other.

To determine the formation constants of MHR and MR complexes the relationship expressed by Eq. 6 was plotted for various lanthanoids(III). The values, $K_1=10^{-6.23}$ and $K_2=10^{-9.44}$[7] were used for calculation of $\alpha_R K_1 K_2$. All the plots exhibited straight lines, each of which had an intercept, indicating the presence of both MHR and MR, complexes. Table 1 shows the formation constants of MHR and MR, K_{MHR} and K_{MR}, obtained from the slope and the intercept of the plot of Eq. 6, and the proton dissociation constant of MHR, K^{H}_{MHR}, calculated by: $K^{H}_{MHR}=K_2K_{MR}/K_{MHR}$. The values were obtained by the least squares method. For comparison corresponding values for PAR are included.

In general, TAR forms less stable complexes with metal ions than PAR because of the lower basicity of the thiazole rings. From our results for the lanthanoids(III), this is valid only for the MR complexes. The MHR complexes are more stable than those of PAR. This parallels the protonation constants of the two ligands, HR^- and R^{2-} for TAR[7] ($pK_1=6.23$ and $pK_2=9.44$) and PAR[8] ($pK_1=5.50$ and $pK_2=12.30$). From the variation in the formation constants, K_{MHR} and K_{MR} (Table 1), with the atomic number, it is noticed that there are marked similarities between the coordinating tendencies of TAR and PAR to the lanthanoids(III): 1) The stabilities of MHR and MR complexes increase up to Sm(III); 2) After Sm(III) the K_{MHR} values are very close to each other; 3) The acidity of MHR which parallels the stability order of MR increases with the atomic number.

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