  Bull. Chem. Soc. Jpn., 61, 689—692 (1988)

Spectrophotometric Study of Complexation Equilibria between Lanthanoids(III) and 2-(5-Bromo-2-pyridylazo)-5-(*N*-propyl-3-sulfopropylamino)phenol

Emiko Ohyoshi
Yatsushiro National College of Technology, Hirayamashinmachi 2627, Yatsushiro, 866
(Received May 6, 1987)

Complex formation (1:1) between lanthanoids(III) and 2-(5-bromo-2-pyridylazo)-5-(*N*-propyl-3-sulfopropylamino)phenol (5-Br-PAPS, HL) has been studied by spectrophotometry at 25 °C and at I=0.1 ($NaNO_3$). The protonated complex MHL is found to exist in equilibrium with the normal complex ML at pH 5—6. The formation constants K_{ML} and K_{MHL} are obtained by a graphical analysis. The K_{ML} values uniformly increase with increasing atomic number except for those in the Gd-Ho region where a distinct decrease is observed. However, there is little variation in the K_{MHL} values with atomic number. A linear relation holds well between log K_{ML} values of 5-Br-PAPS and 4-(2-pyridylazo)resorcinol (PAR) complexes for the elements up to Eu(III), the intercept of which reflects the difference in the basicity of the oxygen atom ortho to the azo group between the two ligands. This is not the case for log K_{MHL} of the two systems.

Recently, a highly sensitive reagent 2-(5-bromo-2-pyridylazo)-5-(*N*-propyl-3-sulfopropylamino)phenol (5-Br-PAPS, HL) has been developed and shown to be useful for spectrophotometric determination of some transition metals.[1-3] It has the same reacting group as 4-(2-pyridylazo)resorcinol (PAR) but has a different substituent in the para position to the azo group. Shibata et al.[4] suggested that the dialkylamino group which is a strongly electron-donating group existing in the para position to the azo group may play an important role in the high molar absorptivity and stability of the metal complex. However, very few studies on the stability of the metal complex with this type of reagent have been reported.

In this paper, the complexation of 5-Br-PAPS with lanthanoids(III) is studied spectrophotometrically and the results are compared with those of the PAR complexes.[5]

Experimental

Materials. All chemicals used were of G. R. grade. 5-Br-PAPS was obtained from Dojindo Chemical Co., and its purity was checked spectrophotometrically by using the standard solution of Zn(II). The molar absorptivity of ZnL_2 (L=5-Br-PAPS) at 553 nm is 1.28×10^5 M^{-1} cm^{-1} (1 M=1 mol dm^{-3}) which agreed with the reported value of 1.3×10^5 M^{-1} cm^{-1}.[1] A weighed quantity of 5-Br-PAPS was dissolved in distilled water to prepare the stock solution of 1.0×10^{-2} M. The lanthanoid(III) nitrate solutions were prepared by dissolving the oxides or nitrates in nitric acid and were standardized by EDTA titration. 2-Morpholinoethanesulfonic acid (MES, Good's buffer reagent) and sodium nitrate were used to maintain the pH at 4.8—6.1 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 5-Br-PAPS ($1.5—2.0\times10^{-5}$ M), to give concentrations of $10^{-4}—3\times10^{-3}$ M. Before and after the addition of the metal for each 50 μl, the absorbance at the peak of 5-Br-PAPS (446 nm) was measured by using a Shimadzu UV-260 spectrophotometer. No precipitation occurred under these experimental conditions.

Results and Discussion

Absorption Spectra of the Reagent (HL^-) and the Complexes. The absorption spectra of the reagent were studied at various pH adjusted with a dilute nitric acid or sodium hydroxide solution. Three species of the reagent, H_2L (λ_{max}=466 nm, pH<2.5), HL^- (λ_{max}=446 nm, pH 4—9), and L^{2-} (λ_{max}=512 nm, pH>11) are involved in its acid-base equilibria. The protonation constants of HL^- and L^{2-}, $K^H_{H_2L}=[H_2L]/([HL^-][H^+])$ and $K^H_{HL}=[HL^-]/([L^{2-}][H^+])$, were determined by the method of Schwarzenbach.[6] The values of 2.78±0.05 and 10.56±0.03 were obtained for log $K^H_{H_2L}$ and log K^H_{HL}, respectively at 25 °C and I=0.1. According to these values and the known acidity constants of analogous azo dyes,[4] $K^H_{H_2L}$ and K^H_{HL} refer to the protonation of the amino group and of the phenolic oxygen, respectively.

Under the conditions where the metal is in large excess over the ligand, the absorption spectra of the complexes had two maxima at 533 and 566 nm for all the lanthanoids(III). Their apparent molar absorptivities which were different for different lanthanoids(III) at constant pH increased with increasing pH and reached the limiting values of $4.6—5.0\times10^4$ M^{-1} cm^{-1} at 533 nm and of $5.5—6.0\times10^4$ M^{-1} cm^{-1} at 566 nm. The reagent 5-Br-PAPS is shown to be almost twice as sensitive as PAR[5] for the determination of lanthanoids(III).

Determination of the Complex Formation Constant. The formation of the 1:1 complex, ML, has been studied by measuring the absorbance of the ligand, L, in the absence (A_o) and the presence (A) of the metal, M, under conditions where $C_M \gg C_L$ (C_M and C_L are the total concentrations of M and L) and pH=constant.[7] The complex formation constant so obtained may be regarded as the conditional

formation constant, $K_{ML'}$, as defined by Eq. 1, by considering any side reactions.

$$K_{ML'} = [ML']/([M'][L']) \quad (1)$$

where [ML'], [M'], and [L'] represent all forms of the metal complexes, the uncomplexed metal and the uncomplexed ligand, respectively. The expressions for C_L and A are then given as follows:

$$C_L = [ML'] + [L'] \quad (2)$$

$$A = \varepsilon_{ML'}[ML'] + \varepsilon_{L'}[L'] \quad (3)$$

where $\varepsilon_{ML'}$ and $\varepsilon_{L'}$ are the apparent molar absorptivity of ML' and L', respectively. Combining Eqs. 1, 2, and 3, and substituting A_0 for $\varepsilon_{L'}C_L$ and C_M for [M] (since $C_M \gg C_L$) in the resulting equation, we obtain

$$K_{ML'} - \frac{\varepsilon_{ML'}K_{ML'}}{\varepsilon_{L'}}\frac{A_0}{A} = (A_0/A - 1)/C_M. \quad (4)$$

From Eq. 4, a linear relation between $(A_0/A-1)/C_M$ and A_0/A should be obtained at a constant pH, the intercept of which yields the $K_{ML'}$ value. This value can be related to the formation constant K_{ML} by means of the side reaction coefficient, α, viz.

$$K_{ML'} = K_{ML}\alpha_{ML}/(\alpha_M\alpha_L) \quad (5)$$

where α_{ML}=[ML']/[ML], α_M=[M']/[M], and α_L=[L']/[L].

From the measured absorbance decreases at the peak of 5-Br-PAPS (446 nm) with increasing metal concentrations at a constant pH, we plotted the relation expressed by Eq. 4. Figure 1 shows the plots obtained at pH 5.51 for different lanthanoids(III). This linear relation was shown to be independent of C_L. The experimental data showed no detectable difference in the plots for Yb(III) and Lu(III) (line 1), and for Tb(III) through Ho(III) (line 6), respectively. Similar plots were obtained at different pH values as exemplified for the Eu(III)-5-Br-PAPS system in Fig. 2. As seen in Figs. 1 and 2, the $K_{ML'}$ values given as the intercept increase with either increasing atomic number (though a discontinuity is shown in the Gd-Ho region) or pH. From the pH dependency of $K_{ML'}$, the side reactions are considered to be the protonation of L and the formation of the MHL complex. The α coefficients for these reactions, α_L and α_{ML} are given by

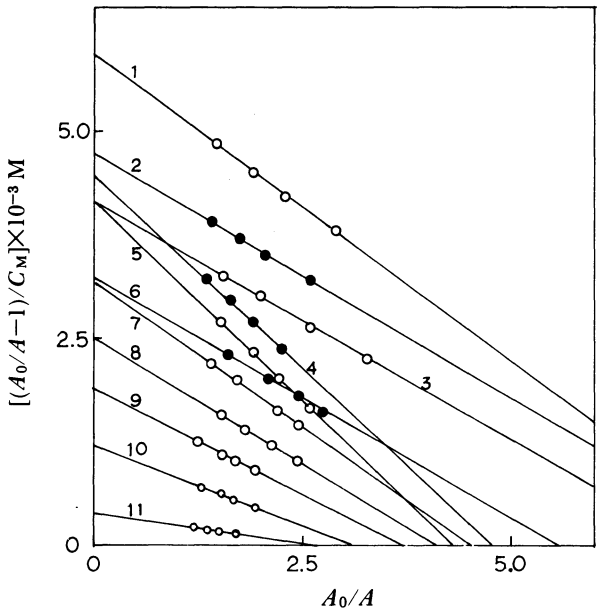

Fig. 1. Plots according to Eq. 4 at a constant pH of 5.51 for the system of 5-Br-PAPS and lanthanoids-(III). 1) Lu, Tb; 2) Tm; 3) Er; 4) Eu; 5) Sm; 6) Ho, Dy, Tb; 7) Gd; 8) Nd; 9) Pr; 10) Ce; and 11) La.

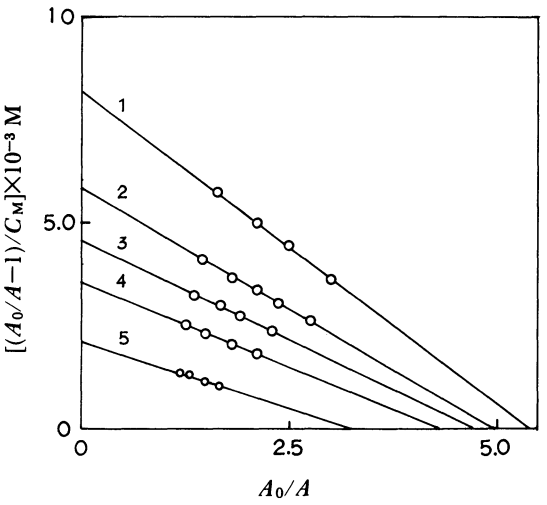

Fig. 2. Plots according to Eq. 4 at different pH values for the Eu(III)-5-Br-PAPS system. pH: 1) 5.81, 2) 5.65, 3) 5.51, 4) 5.40, and 5) 5.12.

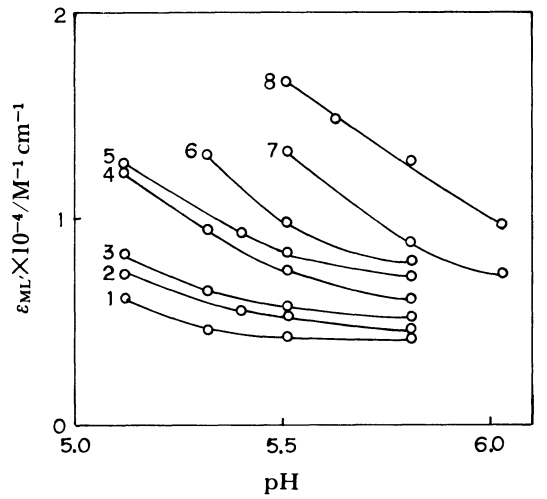

Fig. 3. Plots of the apparent molar absorptivity of ML', $\varepsilon_{ML'}$, at 446 nm vs. pH for the system of 5-Br-PAPS and lanthanoids(III). 1) Yb, 2) Tm, 3) Er, 4) Ho, 5) Eu, 6) Pr, 7) Ce, and 8) La.

$$\alpha_L = [L']/[L] = ([L] + [HL])/[L] = 1 + K^H_{HL}[H] \quad (6)$$

$$\alpha_{ML'} = [ML']/[ML] = ([ML] + [MHL])/[ML] = 1 + K^H_{MLH}[H] \quad (7)$$

where K^H_{HL}=[HL]/([H][L]) and K^H_{MLH}=[MHL]/([ML][H]). The relation between $K_{ML'}$ and α_L (Eqs. 5 and 6) coincides with the observed dependence of $K_{ML'}$ on pH, confirming that the former side reaction occurs. However, no such confirmation is given for the latter. This was found to occur by studying the dependence of the apparent molar absorptivity of ML', $\varepsilon_{ML'}$ on pH (Fig. 3). To calculate the $\varepsilon_{ML'}$ values we used the intercept of the A_o/A axis of the plot of Eq. 4 which equals $\varepsilon_{L'}/\varepsilon_{ML'}$. With increasing pH the $\varepsilon_{ML'}$ values for different lanthanoids initially decrease showing the presence of MHL and ML, and tend to reach the limiting values (ε_{ML}) different for different lanthanoids where only one component, ML exists. In the acidic media used in this study there are no hydroxo complexes.[8] No complexes with buffer ions were also found by studying the effect of buffer concentrations on the $K_{ML'}$ values. Thus,

$$\alpha_M \simeq 1. \quad (8)$$

Substituting Eqs. 6, 7, and 8 into Eq. 5, we obtain

$$K_{ML'}(1 + K^H_{HL}[H]) = K_{ML}(1 + K^H_{MLH}[H]) \quad (9)$$

With the formation constant of MHL, K_{MHL}=[MHL]/[M][HL])=$K_{ML}K^H_{MLH}/K^H_{HL}$, Eq. 9 is rewritten in the form

$$K_{ML'}(1 + K^H_{HL}[H]) = K_{ML} + K_{MHL}K^H_{HL}[H] \quad (10)$$

According to Eq. 10, a plot of the left-hand side of Eq. 10 against [H] by using values of $K_{ML'}$ obtained at constant pH yields K_{ML} as the intercept and K_{MHL} as the slope/K^H_{HL} ratio.

The results of the plots of Eq. 10 are linear with intercepts (Fig. 4), indicating the presence of both MHL and ML complexes in this pH range for all the lanthanoids(III). The formation constants K_{MHL} and K_{ML} calculated from the slope and the intercept of the plots in Fig. 4 by applying the least squares method are listed in Table 1 together with the corresponding values of the PAR complexes for comparison. It is noted that the difference in K_{ML} is greater than that in K_{MHL} for different elements. Comparison of the 5-Br-PAPS and PAR systems shows both the MHL and the ML complexes of 5-Br-PAPS to be less stable than those of PAR.

For the ML complexes, 5-Br-PAPS and PAR show a similar coordination trend to the lanthanoids(III) except for several elements heavier than Gd(III). It is seen from Fig. 5 that for the elements up to Eu(III) the

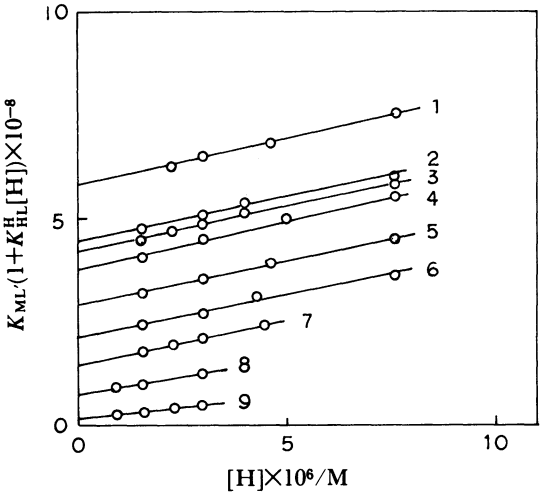

Fig. 4. Plots according to Eq. 10 for the system of 5-Br-PAPS and lanthanoids(III). 1) Lu, Yb; 2) Tm; 3) Eu; 4) Er, Sm; 5) Ho, Dy, Tb, Gd; 6) Nd; 7) Pr; 8) Ce; and 9) La.

Table 1. Formation Constants, K_{MHL} and K_{ML}, for 5-Br-PAPS and PAR Complexes of Lanthanoids(III) I=0.1 ($NaNO_3$), 25 °C

Element	5-Br-PAPS		PAR[5,7]	
	log K_{MHL}	log K_{ML}	log K_{MHL}	log K_{ML}
La	2.38	7.22	3.18	8.91
Ce	2.60	7.90	3.78	9.61
Pr	2.77	8.16	3.95	9.78
Nd	2.74	8.33	4.07	10.02
Sm	2.80	8.58	4.28	10.25
Eu	2.76	8.63	4.28	10.25
Gd	2.79	8.46	4.28	10.25
Tb	2.79	8.46	4.28	10.25
Dy	2.79	8.46	4.29	10.36
Ho	2.79	8.46	4.29	10.47
Er	2.80	8.58	4.31	10.52
Tm	2.76	8.65	4.34	10.57
Yb	2.79	8.77	4.39	10.70
Lu	2.79	8.77	4.39	10.70

The relative errors of K_{MHL} and K_{ML} are 8—12% and 4—8%, respectively.

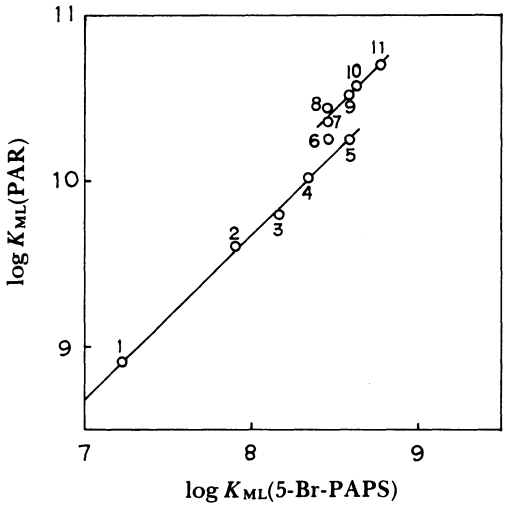

Fig. 5. Relationship between log K_{ML} values of 5-Br-PAPS and PAR complexes with lanthanoids(III). 1) La; 2) Ce; 3) Pr; 4) Nd; 5) Sm, Eu; 6) Gd, Tb; 7) Dy; 8) Ho; 9) Er; 10) Tm; and 11) Yb, Lu.

linear relationship holds well between log K_{ML} values of 5-Br-PAPS and PAR complexes with the slope of unity and the intercept of 1.7 which reflects the difference in the basicity of the ortho-oxygen atom to the azo group between the two ligands (log K^{H}_{HL}=12.30 for PAR[9] and log K^{H}_{HL}=10.56 for 5-Br-PAPS). This is not the case for log K_{MHL} of the two systems. A recent study,[10] showed that such a linear relation has been obtained between log K_{MHL} as well as log K_{ML} for the lanthanoid(III) complexes with a pair of ligands, PAR and 4-(2-thiazolylazo)resorcinol (TAR), both of which have a *p*- and an *o*-hydroxyl group. These facts suggest that the effect of the difference in character between 5-Br-PAPS and PAR on the formation of MHL is much larger than that on the formation of ML. These two ligands have a different functional group in the para position to the azo group, the dipropylamino group (5-Br-PAPS) or the hydroxyl group (PAR), and thus have one dissociable proton (5-Br-PAPS) or two (PAR), respectively.

When the complexation of PAR occurs at pH values lower than either values of log $K^{H}_{H_2L}$=5.50 (para) or log K^{H}_{HL}=12.30 (ortho),[9] it is assumed that protons are released preferentially from the *o*-hydroxyl group. This means that PAR reacts in the thermodynamically unfavored form, *HL$^-$ where *H denotes the para proton for which the dissociation constant is not known. Corcini et al.[11] proposed to use $1/K^{H}_{HL}$ (ortho) as an approximation. On the other hand, 5-Br-PAPS used in this study has only the proton (ortho) dissociable, existing as HL in the pH range studied. The lanthanoid ion thus reacts with HL to form the MHL complex in which the ortho proton does not dissociate. This type of coordination has been reported for the complexes of Be(II),[12] Cu(II),[13] and lanthanoids(III)[14] with 5-sulfosalicylic acid. Hence, the phenolic oxygen would weakly bond either to the proton or to the metal ion. This is consistent with the observation that the absorption bands due to the MHL complex overlap each of the peaks assigned to the HL (proton–ortho-oxygen bond) species and the ML (metal–ortho-oxygen bond) species. This was found by studying changes in the apparent molar absorptivity, $\varepsilon_{ML'}$ at each peak with pH, i.e., $\varepsilon_{ML'}$ at 446 nm (HL) decreased (Fig. 3) but those at 533 and 566 nm (ML) increased with increasing pH. Similarly, the absorption spectra of the PAR complexes of this type (MHL) showed the two maxima at 410 and 495 nm each of which is very close to that of HL at 415 nm and to that of ML at 505 nm.[5] From these facts, the structure of the MHL complexes of the PAR system might be similar to that of the 5-Br-PAPS system, i.e., PAR normally ionizes the para proton first on complexation. It may be reasonable to infer that the para phenolate ion O$^-$ enhances the negative charge on the azo nitrogen; this would make the stability of MHL for the PAR complexes larger and more different from metal to metal than that for the 5-Br-PAPS complexes.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education (No. 60540383).

References

1) T. Makino, M. Saito, D. Horiguchi and K. Kina, *Clin. Chim. Acta*, **120**, 127 (1982).
2) Y. Shijo and K. Sakai, *Bunseki Kagaku*, **33**, E 435 (1984).
3) Y. Shijo and K. Sakai, *Bull. Chem. Soc. Jpn.*, **59**, 1455 (1986).
4) S. Shibata, M. Furukawa, and K. Toei, *Anal. Chim. Acta*, **66**, 397 (1973).
5) E. Ohyoshi, *Talanta*, **31**, 1129 (1984).
6) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 678 (1948).
7) E. Ohyoshi, *Anal. Chem.*, **55**, 2404 (1983).
8) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes, and Supplement No. 1," The Chemical Society, London (1971).
9) W. J. Geary, G. Nickless, and F. H. Pollard, *Anal. Chim. Acta*, **27**, 71 (1962).
10) E. Ohyoshi, *Polyhedron*, **5**, 1165 (1986).
11) A. Corsini, I. Mai-Ling Yih, Q. Fernando, and H. Freiser, *Anal. Chem.*, **34**, 1090 (1962).
12) J. Schubert and A. Lindenbaum, *J. Biol. Chem.*, **208**, 359 (1954).
13) S. E. Turner and R. C. Anderson, *J. Am. Chem. Soc.*, **71**, 912 (1949).
14) N. V. Thakur, S. M. Jogdeo, and C. R. Kanekar, *J. Inorg. Nucl. Chem.*, **28**, 2297 (1966); C. R. Karekar, N. V. Thakur, and S. M. Jogdeo, *Bull. Chem. Soc. Jpn.*, **41**, 759 (1968).