

Kinetic Studies on Forming Iso-nuclear β -type Chelates of Rare Earths with *p*-Sulphoaminobromophosphonazo

Fei ZHA, Li YUAN, Jin Zhang GAO*, Hui CHEN

Chemistry & Chemical Engineering College, Northwest Normal University, Lanzhou 730070

Abstract: The kinetic behavior of forming the iso-nuclear β -type chelates of rare earth ions (RE^{3+}) with *p*-sulphoaminobromophosphonazo (BPA-pSN) in $ClCH_2COOH-CH_3COONa$ buffer solutions were studied by a spectrophotometric method.

Keywords: β -Type chelates, rare earths, *p*-sulphoaminobromophosphonazo.

Some 2,7-bis(arylozo) derivatives of chromotropic acid can form chelates with rare earth ions in the 700-800 nm region, especially they can form iso-nuclear β -type chelates which have higher molar absorptivities and have been used for the determination of trace amounts of light lanthanides in the presence of heavy lanthanides^{1,2}. Some papers^{3,4} have reported the kinetic behavior of forming homo-nuclear β -type chelates. However, the information about forming iso-nuclear β -type chelates is still sparse. Therefore, we had a kinetic study on the system of rare earth elements with *p*-sulphoaminobromophosphonazo.

All the absorption is measured by means of a U-3400 Spectrophotometer (Hitachi, Japan) on a constant temperature controlled by a model 501 Super Thomostat (Shengzhen, China). The acidity is determined by means of a model pH-S-3C meter (Zhejiang, China).

Only the heavy rare earth ions are able to form homo-nuclear β -type chelates with BPA-pSN, where the maximum absorption peak shifts from 707 nm to 717 nm with the increasing of the atomic number of Tb to Y. However, if the light and the heavy rare earth ion co-exist, they can form iso-nuclear β -type chelates with BPA-pSN which the molar absorptivity is higher than that of homo-nuclear β -type chelates. The information can be also acquired from the spectra that the absorption peaks of the α -type chelates disappear during the process of forming iso-nuclear β -type chelates while the α -type chelates still exist during the process of forming homo-nuclear β -type chelates.

The composition ratio of the homo-nuclear β -type chelates of rare earth ions with BPA-pSN indicates that the metal-to-ligand is 1:2. While the composition ratio of the iso-nuclear β -type chelates of rare earth ions with BPA-pSN is as follows: RE_1 (light rare earth ion): BPA-pSN : RE_2 (heavy rare earth ions) = 1 : 3 : 1.

The reaction order of rare earth ions with BPA-pSN in $ClCH_2COOH-CH_3COONa$ buffer solutions (pH = 3.70 \pm 0.1) at the temperature of 298 \pm 0.2 K was determined

by a graphical method. The results showed that forming homo-nuclear β -type chelates is a second-order reaction and forming iso-nuclear β -type chelates is a first-order reaction.

Using the same graphical method, the investigation results are listed in **Table 1**. It shows that the reaction rate of forming homo-nuclear β -type chelates increase with the increasing of the atomic number from Tb to Y (except for the Er-BPA-pSN system).

Table 1. The rate constants for forming homo-nuclear β -type chelates

RE ³⁺ ion	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
$k \cdot 10^5 \text{ (m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}\text{)}$	0.32	0.55	1.49	4.36	0.99	2.16	3.75	35.28

Selecting a requested amount of Yb³⁺ ion as a matrix ion, adding the light rare earth ion respectively, the rate constants of forming iso-nuclear β -type chelates were also investigated by the above method. The results listed in **Table 2**. It shows that the reaction rate of forming iso-nuclear β -type chelates increase with the increasing of the atomic number of La to Gd. The results were also listed in **Table 2** when Eu³⁺ ion as a matrix ion and the heavy rare earth ions are correspondingly changed. Except for the Eu-Lu system, the rate constant also increases with the increasing of the atomic number from Tb to Y.

Table 2. The rate constants for forming iso-nuclear β -type chelates

Yb-RE	La	Ce	Pr	Nd	Sm	Eu	Gd	
$k \cdot 10^3 \text{ (S}^{-1}\text{)}$	0.14	0.32	0.48	0.56	0.70	0.98	0.57	
Eu-RE	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
$k \cdot 10^3 \text{ (S}^{-1}\text{)}$	0.46	0.62	0.70	0.72	0.75	0.92	0.42	1.78

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