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Formation Constants of Eu(III)–Carboxylates Determined by Ion-selective Liquid Membrane Electrode

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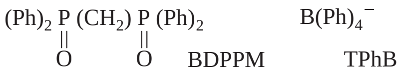
A trivalent metal ion-selective electrode (ISE) consisting of bis(diphenylphosphoryl)methane as an ionophore was developed for the determination of formation constants with organic ligands. The ISE prepared exhibited Nernstian response to the concentration of Eu^{3+} in the test solutions. Even in the presence of carboxylic acids such as malonic acid in samples, the obtained potential values were found to be stable and reproducible during the measurement time. The present formation constants of Eu with carboxylates were in good agreement with the reported values.

In aqueous solution, the chemistry of trivalent metal ions is dominated by hydrolysis and complexation with several organic and inorganic ligands. The predominant species in various environmental systems can be described thermodynamically with the help of certain parameters such as the formation constants and the solubility products. Many researchers have determined the formation constants of trivalent metal ions with organic ligands by pH titration, spectrophotometry, conductimetry, solvent extraction, and so on. Potentiometric titration by using ion-selective electrode (ISE) has been also a quite conventional approach in order to directly measure the activity of free (uncomplexed) metal ion because of its easy, rapid, accurate, and low-cost method of analysis. Though a few ion-selective electrodes have been developed for the potentiometric determination of trivalent lanthanide and actinide ions,[1–4] no application to determine the formation constant has been reported. Kitatsuji et al. have developed the present liquid membrane electrode for trivalent plutonium and evaluated electrochemically the basis of sensitivity and selectivity.[5] The ISE exhibited usable ranges of working concentration and pH, fair response time toward Pu^{3+}, and interference effects of different actinide ions such as Pu^{4+}, $UO_2{}^{2+}$, and $NpO_2{}^{+}$.

SSE1	Inner solution	Liquid membrane (NB)	Test solution	SSE2
Ag|AgCl 0.1M LiCl	10^{-3}M Eu^{3+} pH 2 (HCl)	10^{-3}M $Eu(BDPPM)_3$・3TPhB +10^{-2}M BDPPM	*x*M Eu^{3+} *I* = 0.1, 0.01 (NaCl)	Ag|AgCl 0.1M LiCl


$(Ph)_2\underset{\substack{\|\\ O}}{P}(CH_2)\underset{\substack{\|\\ O}}{P}(Ph)_2$ BDPPM $\qquad B(Ph)_4{}^-$ TPhB

Scheme 1. The ISE cell configuration.

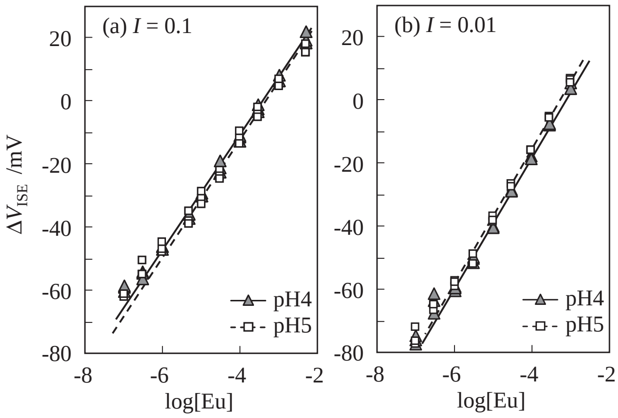


Figure 1. ISE response of Eu test solutions of pH 4 and 5 at (a) *I* = 0.1 M and (b) *I* = 0.01 M (NaCl).

Prior to the titration to determine the formation constants of lanthanide(III) with artificial and simple carboxylic ligands, the applicability of the present ISE is demonstrated. A fresh nitrobenzene (NB) solution containing Eu(III)–bis(diphenylphosphinyl)methane (BDPPM) complex was prepared by an ion-pair solvent extraction with sodium tetraphenylborate (TPhB) according to the procedure for plutonium(III) reported previously.[5] The concentrations of the extracted species $Eu(BDPPM)_3$・3TPhB and BDPPM were 1×10^{-3} and 1×10^{-2} M, respectively. All other chemicals used were of reagent grade. As shown in Scheme 1, the inner solution of ISE was 1×10^{-3} M Eu^{3+} at pH 2, and the identical supporting electrolyte 0.1 M LiCl was adopted in the inner solution for the silver–silver chloride electrode (SSE1) and reference electrode as SSE2. The Eu-ISE measurements were performed with an automatic potentiometric titrator (AT-510, Kyoto Electronics) equipped with a polypropylene vessel in water bath, a magnetic stirrer, and N_2 gas purge system. The regular test solutions were kept at the ionic strength (0.1 M, NaCl) and pH thorough the titration experiment. The pH combination electrode was calibrated to measure the hydrogen ion concentration ($[H^+] = 10^{-pHc}$) according to the reference method.[6] The potential, denoted as ISE potential (ΔV_{ISE}), generated between SSE1 and SSE2 after the potential attained a constant was measured. The ΔV_{ISE} is plotted against the concentration of Eu^{3+} in the test solution in Figure 1. A slope of 20 mV/decade in Figure 1 agrees with the theoretical Nernstian response corresponding to the reversible transfer of Eu^{3+} similar to Pu^{3+}. The ISE potential was roughly in accordance with that for Pu^{3+} by using Pu-ISE using BDPPM.[5] It indicates that BDPPM is a highly sensitive ionophore for the trivalent ion of lanthanide and actinide series, while the interference by a coexisting trivalent ion might have occurred. The result of response of the ISE with test solution at

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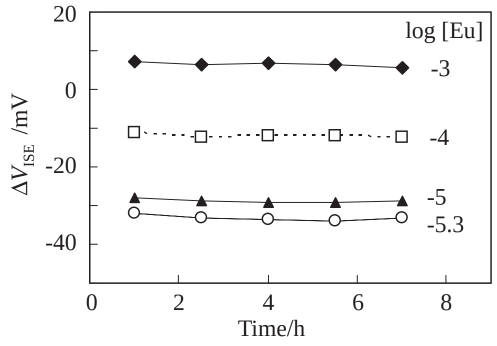

Figure 2. Stability of time dependence of ISE potential for Eu test solutions at pH 5 and $I = 0.1$ M (NaCl).

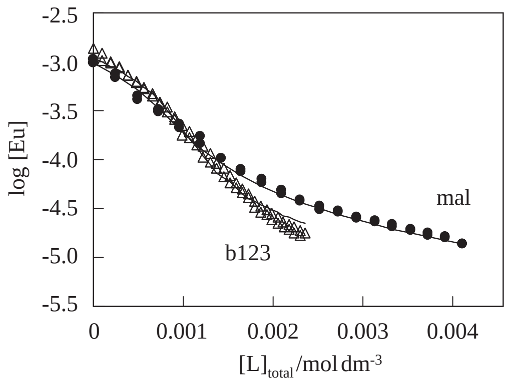

Figure 3. The experimental titration curves for mal and b123 with the fitting curves (solid line). The concentration of titrant solution is 0.05 M for mal and 0.02 M for b123, respectively, and 0.1 M NaOH is used to maintain the pH_c 5. Ionic strength is constant at 0.1.

$I = 0.01$ is also shown in Figure 1. With the lower ionic strength of the test solution, the observed potential shifted lower.

Similar reproducibility of the ISE response was found after one use, i.e., after immersion in the solutions even containing 10^{-3} M organic ligands, malonic acid (mal) and 1,2,3-benzenetricarboxylic acid (b123). The detection limit was below $\log[Eu] = -5$ corresponding to good linearity of response. At europium concentrations of 10^{-3}–5×10^{-6} M, the potential remained stable enough over 6 h and good reproducible readings in several sets of experiments were obtained (Figure 2). In case of drifting the reading electrode potential, the NB solution should be replaced and then calibrated again.

The potentiometric titrations were made at 25 ± 0.5 °C as a function of ligand (mal or b123) concentration, maintaining pH_c 5 and the europium initial concentration of ca. 10^{-3} M. Figure 3 shows that the concentration of free Eu^{3+} in the test solutions decreased with increasing the ligand concentration due to the complexation reaction. The titration plot for each ligand was reproducible. The formation constants, $\beta_{L,i}$ for europium complexes are defined as

$$\beta_{L,i} = [EuL_i]/[Eu^{3+}][L]^i \tag{1}$$

Table 1. Logarithm values of formation constants of 1:1 and 1:2 Eu-complexes, and acid dissociation constants at $I = 0.1$ and 25 °C

	Ligand			
	mal		b123	
	This work	ref	This work	ref
$\log\beta_{L,1}$	4.49 ± 0.02	4.29 ± 0.01[7]	5.11 ± 0.03	5.08 ± 0.01[9]
$\log\beta_{L,2}$	6.69 ± 0.15	6.99[8]	7.78 ± 0.61	—
$\log K_{a1}$		2.65[8]		2.62[8]
$\log K_{a2}$		5.27[8]		3.83[8]
$\log K_{a3}$				5.51[8]

where L is the deprotonated free ligand L^{2-} and L^{3-} for mal and b123, respectively. The complexations with partly deprotonated species such as HL^- were not taken into account for simplicity. In the mal system, for instance, the $\beta_{L,i}$ values ($i = 1, 2$) are determined by a least-squares fitting analysis together with the following mass balances,

$$\begin{aligned}[L]_{total} &= \sum_n [H_nL] + \sum_i i[EuL_i] \\ &= (K_{a1}K_{a2}[H^+]^2 + K_{a2}[H^+] + 1)[L] \\ &\quad + [Eu^{3+}]\sum_i i\beta_i[L]^i \end{aligned} \tag{2}$$

where K_a is the acid dissociation constant (Table 1).

$$[Eu]_{ini} = [Eu^{3+}] + \sum_i [EuL_i] = [Eu^{3+}]\left(1 + \sum_i \beta_i[L]^i\right) \tag{3}$$

The determined values are summarized in Table 1, and good agreements are obtained with the literature values which were determined by other methods such as solvent extraction. The present method was proven to be a simple and feasible technique to monitor the free metal ion concentration and to measure the formation constants of trivalent lanthanide complexes under controlling a given solution condition such as pH and ligand concentration.

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