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FLOW INJECTION STUDY OF EUROPIUM(III)-BENZOYLTRIFLUOROACETONE-TRIOCTYLPHOSPHINE OXIDE SYSTEM IN MICELLAR SOLUTION

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Abstract

Complex formation of europium(III) with benzoyltrifluoroacetone(BFA) and trioctylphoshine oxide(TOPO) in micellar solution has been studied by a flow injection analysis(FIA) and a stopped-flow FIA. A flow injection spectrofluorimetric method has been developed for the determination of europium(III) as its ternary complex with BFA and TOPO in micellar solution of nona(oxyethylene) dodecyl ether(BL-9EX). This procedure is a satisfactory of the determination of the europium(III) ion in the range 2 X 10^{-7} - 10^{-5} mol dm^{-3}. The ligand exchange reactions of europium(III) complex with BFA-TOPO by aminopolycarboxylic acids were investigated by a stopped-flow FIA. The exchange rates for the reactions were found to be a first order rate law with respect to the concentration of Eu(III) complex.

The synergistic solvent extraction of lanthanoid ions has been widely investigated by using β-diketone chelating agents.[1-6] Methods for determination, extraction constant, and separation factor etc., have been reported. Taketatsu et al. found that europium(III), samarium(III) and terbium(III) ternary complexes with β-diketone in the presence of trioctyl-phosphine oxide(TOPO) are readily soluble in an aqueous solution containing nonionic surfactant and that the strong fluorescence originating from the ternary complexes can be applied to the determination of lanthanoid ions.[7-9] The other ternary complexes of lanthanoid(III)-β-diketone-certain substituted ammonium cation or neutral ligand have also been investigated.[10-12]

The technique based on solubilising complex in nonionic surfactant has been applied to the flow injection analysis(FIA) of europium(III)[13-15], samarium(III)[15] and teribium(III).[16] These spectrofluorimetric determination methods of lanthanoid ions using thenoyltrifluoroacetone(TTA) as a β-diketone have been studied extensively. The preliminary experimental study indicates that the relative fluorescence intensities of europium(III)- β-diketone (TTA, Benzoyltrifluoroacetone(BFA) and pivaloyltrifluoroacetone (PTA))-TOPO complexes in micellar solution are larger than those of other europium(III)-β-diketone-TOPO complexes.[9]

The purposes of the work were to develope a flow-injection method for the determination of europium(III) based on solubulising its ternary complex with BFA and TOPO in micellar solution. A stopped-flow FIA was adopted to the ligand exchange reaction of europium(III) complex with BFA and TOPO by a chelating agent(ethylenediamine-N,N,N',N'-tetraacetic acid(EDTA),diethylene triamine-,N,N,N',N'',N''-pentaacetic acid(DTPA) or trans-1,2-diamino-cyclohexane-N,N,N',N'-tetraacetic acid(CyDTA)) in micellar solution.

Experimental

Reagents

Stock solutions of lanthanoid ions were prepared by dissolving 99.9% pure oxides in dilute hydrochloric acid and standardised by titration with EDTA. Stock solutions of mixed ligands(BFA and TOPO) were prepared by dissolving the reagents(Dojin) in 0.5% m/V aqueous solution of surfactant (BL-9EX,nona(oxyethylene) dodecyl ether; Nikko Chemical Co.) and the pH of the solutions was adjusted by the addition of acetate buffer. All other chemicals used were of analytical-reagent grade.

Apparatus

FIA and stopped-flow FIA systems were the same as those described in a previous paper.[13] It consisted of a reciprocating pump with two channels (plunger type , Kyowaseimitu KHU-W-62), six way sample injection valve, a spectrofluorimeter (UVIDIC 610, Japanspectroscopic Co.) with a flow cell(32 μl) . The fluorescence was measured at apparent excitation and emission wave lengths of 355 and 596 nm, respectively. A simplest line FIA system[17,18] was used for a stopped-flow FIA. A switching valve in Ref. 13 was switched to lead the carrier solution to waste and to stop the sample zone in the flow cell during the measurement.

Results and Discussion

The formation of a complex of europium(III) with β-diketone and TOPO in a micellar solution of non-ionic surfactant has been investigated[7-9] and the following equilibrium was postulated

$$Eu^{3+}_{(b)} + 3HX_{(b)} + 2TOPO_{(m)} = Eu(X)_3(TOPO)_{2(m)} + 3H^+_{(b)}$$

where HX is β-diketone and the subscripts(b) and (m) refer to mutually equili- brated bulk and micellar phases, respectively. The fluorescence intensity for europium(III) -β-diketone complex gave constant over the pH range of 3-5. The pH of 3.5 was selected because of the preventing lanthanoid ions from hydrolysis.

Effect of flow rate, coil length and reagent concentration.

The flow rates of the reagent and the carrier solution were studied. The peak height increased with increasing flow rate and maximum peaks were observed at 1.0 ml/min. The flow rate of 1.0 ml/min was chosen for subsequent work.

The effect of reaction coil length was tested by the use of 1 - 5 m length while the flow rate was maintained at 1.0 ml/min. The peak heights decreased with increasing coil length. An increase in coil length caused a decrease in peak height because of increasing dispersion. A 1 m coil length was chosen because of the sensitivity and the rapid analysis.

The effect of reagent concentration on europium(III) emission as its ternary complex with BFA and TOPO was studied by varying the concentrations of BFA and TOPO. The peak height increased as the mixed reagent concentration increased up 4 X 10^{-4} mol dm^{-3} at each europium(III) concen- tration and became almost constant above this value. A mixed reagent concentration of 5 X 10^{-4} mol dm^{-3} for BFA and TOPO was chosen for subsequent work.

Determination of europium(III) ion

Samples containing 2 X 10^{-7}-10^{-5} mol dm^{-3} europium(III)(0.15 -1.5 μg/ml) were injected into the carrier stream under the flowing optimum condition; concentrations of BFA and TOPO, 5 X 10^{-4} mol dm^{-3} ; concentration of BL-9EX, 0.5 w/v %; pH 3.5 ; flow rate, 1 ml/min.; coil length, 1m(0.5mm id.).

Typical calibration peaks are shown in Fig 1. The calibration graphs obtained were linear in the range 2 X 10^{-7} - 10^{-5} mol dm^{-3} as shown in Fig. 2. The detection limit of europium(III) in this work is found to be similar to that in TTA-TOPO system. The precision of the method was checked on ten samples containing 6 X 10^{-6} mol dm^{-3} samarium(III). The relative standard deviation was less than 0.7 %.

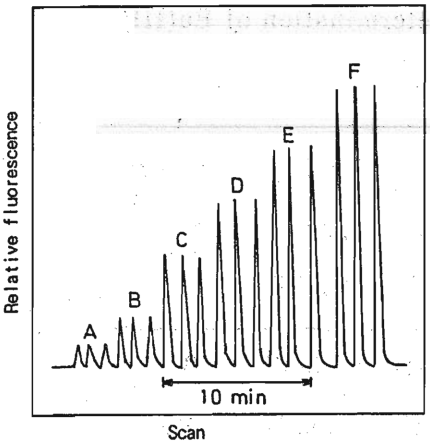

Fig. 1. Peaks obtained for triplicate injection of standard Eu(III) solution. [Eu(III)]:A,1 x 10^{-6};B,2 x10^{-6};C, 4 x 10^{-6};D,6 x 10^{-6};E,8 x 10^{-6};F,10^{-5} mol dm^{-3}

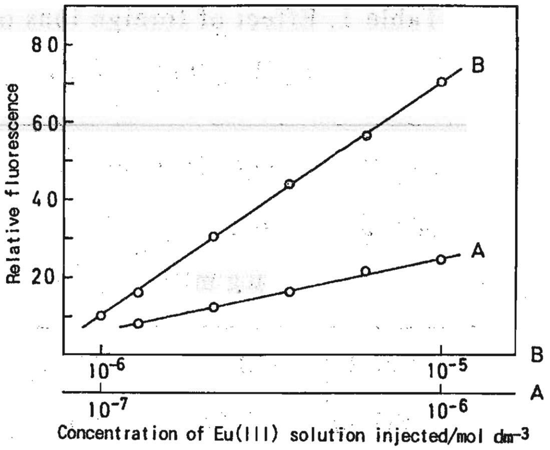

Fig. 2. Typical calibration graphs for the determination of europium(III)

Interferences

The influence of other lanthanoid ions on the determination 0.91 μg/ml was studied and the results are given in Table 1. It was found that five-fold excess amount of Sc, Y, La, Ce(IV), Pr and equi amount of Nd, Gd, Tb, Ho, Er, Tm, Dy, and Lu had no significant effect.

Exchange Reactions

Chelating agents(EDTA,DTPA etc.,) react slowly with lanthanoid(III)-β-diketone-TOPO complex in micellar solution and the fluorecence of complexes disappears gradually.

The exchange reactions of TTA-TOPO from its europium(III) complexes by chelating agents were investigated with a stopped-flow FIA. The effect of chelating agents on the stopped-flow FIA pattern of the system was investigated. Fig. 3 shows a typical example of exchange reaction curves for Eu(III)-TTA-BFA-TOPO-EDTA system. The relative fluorecence for Eu(III)-BFA-TOPO complex was decreased by the addition of EDTA. The decrease of the fluorescence for the complexes could be followed by the stopped-flow FIA.

Table 1. Effect of foreign ions on determination of Eu(III). Eu(III) taken, 0.91 μg ml^{-1}

Ion added	Eu(III) found μg ml^{-1}	Recovery %	Ion added	Eu(III) found μg ml^{-1}	Recovery %
Sc(III)	0.93	102	Tb(III)	0.97	106
Y(III)	0.84	93	Dy(III)	0.87	95
La(III)	0.90	99	Ho(III)	1.06	116
Ce(IV)	0.89	98	Er(III)	0.97	106
Pr(III)	0.92	103	Tm(III)	0.97	106
Nd(III)	0.95	104	Yb(III)	0.92	101
Sm(III)	0.98	108	Lu(III)	0.90	99
Gd(III)	0.94	102			

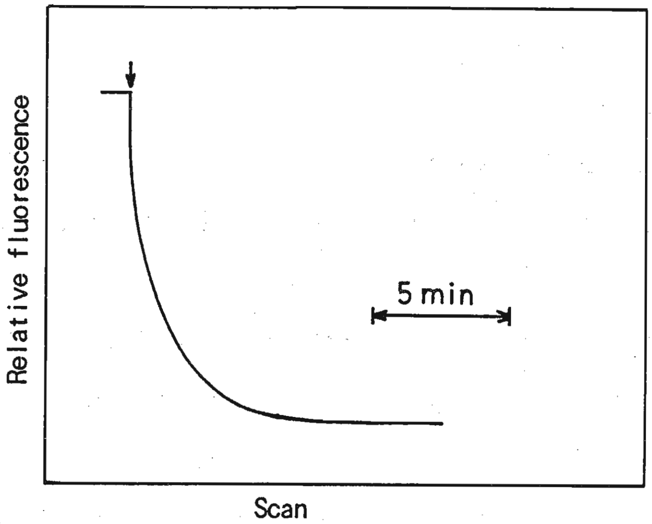

Fig.3 Stopped-flow signals obtained with the flow system in aqueous solution of BL-9EX. Eu(III)-BFA-TOPO-EDTA system. [Eu(III)] = 8 x 10^{-6} mol dm^{-3},[EDTA] = 8 x 10^{-5} mol dm^{-3}, pH = 3.5

The log(A_∞ - A) plots against time are shown for the systems of Eu(III)-BFA-TOPO-EDTA, Eu(III)-BFA-TOPO-DTPA and Eu(III)-BFA-TOPO-CyDTA in Fig. 4. The linearity of the plots for the each system showed first-order law with respect to the Eu(BFA)$_3$(TOPO)$_2$. The apparent first order rate constants, k sec^{-1}, were determined by using a Kezoly-Swinbourne plot.[19-20] The apparent rates of the exchange reactions for the systems were measured at pH 3.5. The apparent rate constants are given in Table 2.

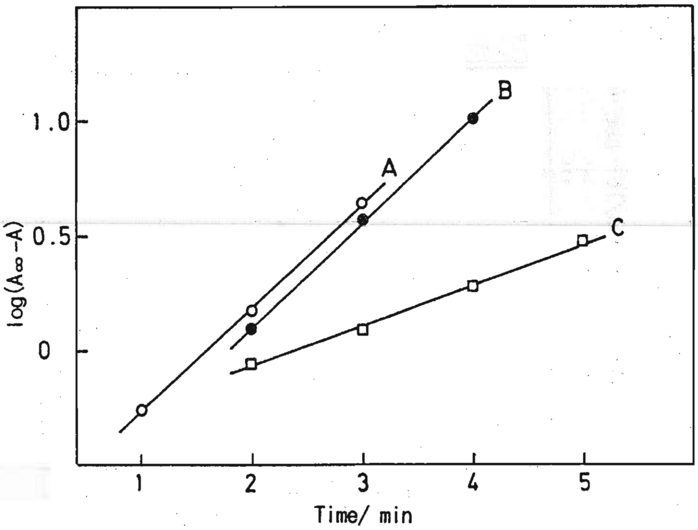

Fig. 4. First-order rate plots for the exchange reactions in aqueous solution of BL-9EX. [Eu(III)] = 8 x 10^{-6} mol dm^{-3} . A, [EDTA] = 8 x 10^{-5}; B, [DTPA] = 8 x 10^{-5}; [CyDTA] = 8 x 10^{-5} mol dm^{-3}

Table 2. Apparent rate constants for ligand exchange reactions of Eu(III)-BFA-TOPO complex by chelating agents in BL-9EX solution. [Eu(III)] = 8 X 10^{-6} mol dm^{-3} ; [Chelating agent] = 8 X 10^{-5} mol dm^{-3} at pH = 3.5.

Chelating agent	Apparent rate constant /10^3 sec^{-1}
EDTA	16.2
DTPA	15.2
CyDTA	6.5

The apparent exchange rates for the EDTA and DTPA systems are larger than that for the CyDTA system. For the CyDTA sytem, the rate of formation of product is assumed to be suppressed by the steric requirement of CyDTA.

Figure 5 shows the dependence of observed first order constant on the hydrogen ion concentration for the Eu(III)-BFA-TOPO-EDTA system. Many metal complexes are known to follow the same type of exchange mechanism by other metal ion with a first order hydrogen ion concentration and a first order metal complex dependence.[21,22]

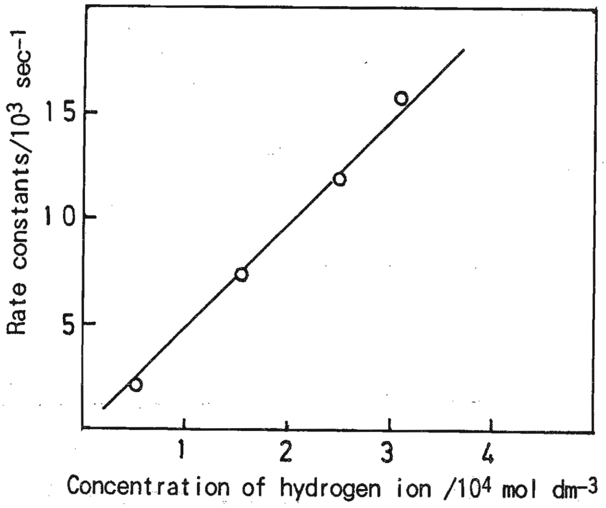

Fig. 5. Hydrogen ion dependence of the apparent first-order rate constant in aqueous solutions of BL-9EX. [Eu(III)] = 8 x 10^{-6}, [EDTA] = 8 x 10^{-5} mol dm^{-3}

The mechanism of the exchange reaction for europium(III)-BFA-TOPO complexes by EDTA is assumed to be as follows

$$Eu(BFA)_3(TOPO)_2 + 3H^+ = Eu^{3+} + 3HBFA + 2TOPO$$

$$Eu^{3+} + H_mL^{4-m} = Eu(H_mL)^{7-m}$$

where H_mL^{4-m} is EDTA anion.

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