CHEMISTRY LETTERS, pp. 1181-1184, 1980. © The Chemical Society of Japan 1980

SEPARATION OF LANTHANOIDS WITH TETRAETHYLENE GLYCOL

Yoshiyuki HIRASHIMA, Yoshikazu MORIWAKI, and Jiro SHIOKAWA
Depratment of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamada-kami, Suita, Osaka 565

The yield of the solid complex of tetraethylene glycol(EO4) with a lanthanoid(Ln) nitrate decreases with increasing atomic number of Ln, and is greatly affected by H_2O present in the solution. The separation factors of EO4 are comparable to those of the separating reagents practically used.

The formation of the complexes of noncyclic poly(oxyethylene) derivatives with several metal salts has been reported.[1-4] Some noncyclic polyethers form crystalline complexes with lanthanoid nitrates, and the yields of the complexes vary with the atomic numbers of the lanthanoids.[5] This fact suggests a new lanthanoid separation method using the polyethers. This letter describes the separation of individual lanthanoids by fractional crystallization with tetraethylene glycol.

An ethyl acetate solution of a hydrated lanthanoid nitrate (or two different lanthanoid nitrates) was mixed with an equal volume of ethyl acetate solution of tetraethylene glycol. The concentration of water in the mixed solution was adjusted by dehydration or addition of water. The mixed solution was shaken at 25.0±0.1°C for two hours. The complex deposited was separated by filtration. The yield of the solid coplex(Y) was calculated by the equation, $Y = (\mathrm{Ln})_s/[(\mathrm{Ln})_s + (\mathrm{Ln})_l] \times 100$, and the separation factor(S), by the equation, $S_{\mathrm{Ln1,Ln2}} = (\mathrm{Ln1/Ln2})_s/(\mathrm{Ln1/Ln2})_l$, where the subscripts s and l denote the solid complex deposited and the solution, respectively, (Ln) and (Ln1/Ln2) being the amount of the lanthanoid and the molar ratio of the two lanthanoids in each phase, respectively.

The composition of the complex deposited is $\mathrm{Ln(NO_3)_3{\cdot}EO4}$ as was reported in our previous paper,[5] where EO4 denotes tetraethylene glycol, $\mathrm{HO(CH_2CH_2O)_4H}$.

Figure 1 indicates that the yield of the solid complex generally decreases as the atomic number of the lanthanoid increases, except in the anhydrous systems, where a minimum one is observed at Tb. The yields are higher than 90% for all the lanthanoids in the anhydrous systems. For La-Nd, the yields remain nearly constant(>95%) over the range of the concentration of water investigated(0-0.5M), however, for heavier lanthanoids, decrease with increasing H_2O concentration. The values obtained for some heavier lanthanoids(Tb-Lu) are decreased till to 0%, that is, no solid complexes of the lanthanoids are deposited within two hours, when H_2O concentration is increased to 0.25M or higher. These results indicate that water inhibits the formation of the solid complexes and that the effect of water is more serious for heavier lanthanoids. The yields are nearly equal for La, Ce, Pr, and Nd, whereas for heavier lanthanoids, those are significantly decreased with the atomic number when H_2O concentration is 0.25M (corresponding to that of a 0.05M solution of $Ln(NO_3)_3 \cdot 5H_2O$).

Figure 2 shows the variation of the yields with the ratio of EO4 to Ln. The values increase quasi-linearly with the increase of EO4 till the ratio, EO4/Ln, reaches unity, and then increase only little (for La-Sm) or even decrease (for Eu and Gd) with the increase of EO4 when the ratio is larger than unity. These results are consistent with the fact that only the 1:1 complexes can be formed.

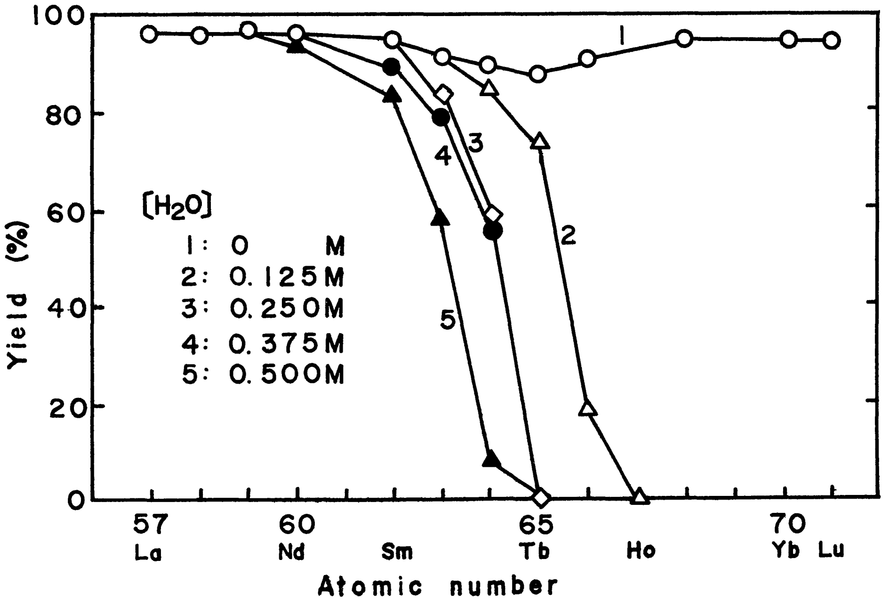

Fig. 1. The variation of the yield of the solid complex with the atomic number of the lanthanoid. Initial concentrations: $Ln(NO_3)_3$, 0.05M; EO4, 0.05M.

When E04/Ln was 4.0, the yields reached 89.8% and 75.6% for Eu and Gd, respectively, after three days, though no solid comlexes were deposited within two hours. This fact suggests that the presence of excess E04 rather slows down formation of the solid complexes than decreases the yields at equilibrium. The effect of excess E04 was not investigated in further detail.

The separation factors were determined for several bi-lanthanoid systems in order to evaluate the separation of lanthanoids with tetraethylene glycol. The values obtained here for the adjacent pairs (except for the Nd-Sm one) are given in Table 1 together with those reported for the systems with EDTA$^{6)}$ and D2EHPA$^{7)}$ (ethylenediaminetetraacetic acid and bis(2-ethylhexyl) hydrogenphosphate). The initial concentrations of the reactants are as follows: [Ln1] = [Ln2] = [E04] = 0.025M; [H_2O] = 0.25M. The reaction time is 2 hours.

The separation factors observed here were smaller for the La-Ce and Ce-Pr pairs and larger for the Nd-Sm, Sm-Eu, and Eu-Gd ones than those of the other two systems. This result corresponds to the variation of the yield of the solid complex with the atomic number described earlier. No reliable data were obtained for the Gd-Tb pair, for which a high separation factor had been expected, since the amount of the deposit was too little. The separation factors of E04 were, on the whole, comparable to those of D2EHPA and EDTA. This fact demonstrates that E04 is a promissing reagent for lanthanoid separation. Separation of

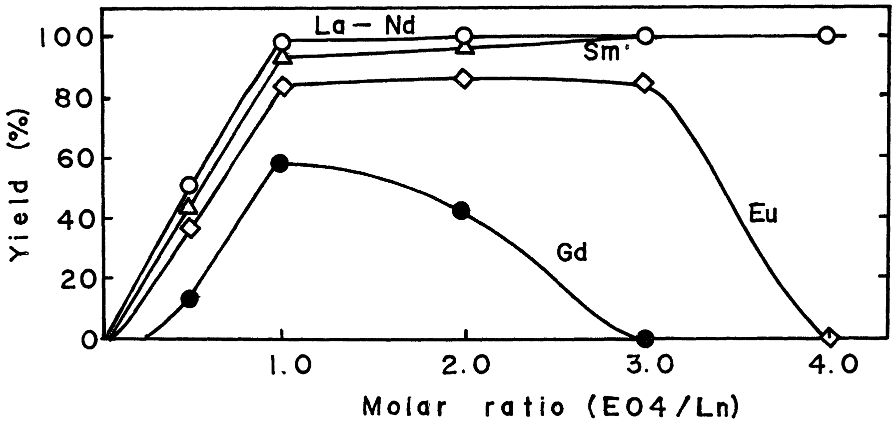

Fig. 2. The variation of the yields of the solid complexes with the ratio E04/Ln. Initial concn. of $Ln(NO_3)_3$: 0.05M, Concn. of H_2O : 0.25M.

Table 1. Separation factors for several bi-lanthanoid systems

Reagent	Separation factors for the pairs					
	La-Ce	Ce-Pr	Pr-Nd	Nd-Sm	Sm-Eu	Eu-Gd
E04[a)]	1.7	1.4	2.0	5.5	2.9	2.0
D2EHPA[b)]	2.4	2.8	1.7	5.0	2.2	1.6
EDTA[c)]	4.7	2.3	2.0	3.1	1.4	1.02

a) See text. b) Ref. 6). c) Ref. 7).

lanthanoids with E04 is considered to result from the difference of the stability and/or solubility of the lanthanoid-E04 complexes. The investigation on the stability and solubility is now in progress.

References

1) E.Weber and F.Vögtle, Tetrahedron Lett., 1975, 2415.
2) T.G.Mass, E.Weber, W.Wehhner, and F.Vögtle, J. Am. Chem. Soc., 99, 4683 (1977).
3) S.Yanagida, K.Takahashi, and M.Okahara, Bull. Chem. Soc. Jpn., 51, 1294, 3111 (1978).
4) H.Sieger and F.Vögtle, Tetrahedron Lett., 1978, 2709.
5) Y.Hirashima and J.Shiokawa, Chem. Lett., 1979, 463.
6) T.B.Pierce, P.F.Peck, and R.S.Hobbs, J. Chromatogr., 12, 81 (1963).
7) E.J.Wheelwright, F.H.Spedding, and G.Schwarzenbach, J. Am. Chem. Soc., 75, 4196 (1953).

(Received July 12, 1980)