Improvement of Separation in the Solvent Extraction of Alkaline Earths by the Use of 18-Crown-6 as a Masking Reagent

Shigeo Umetani,*[a] Masakazu Matsui[a] and Shigekazu Tsurubou[b]

[a] Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan
[b] Department of Chemistry, School of Liberal Arts, Asahi University, Hozumi-cho, Gifu 501-02, Japan

The improvement of separability among alkaline earths is shown to be achieved by employing 18-crown-6 as a masking reagent.

Generally, the extractability of metal ions with chelating reagents such as β-diketones is governed by the stability of the metal complexes formed. In the solvent extraction of alkali, alkaline earth and lanthanoid metal ions with a chelating reagent, the metal ions having the smaller ionic radii are extracted more easily. The stability of complex formation between crown ethers and the above-mentioned metal ions shows a different trend, however. Thus, solvent extraction of high selectivity may be possible by a combination of chelating reagents and crown ethers. In the present work, the separability in the synergistic extraction of alkaline earths with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (HPMBP) and tri-n-octylphosphine oxide (TOPO) is shown to be improved by adding 18-crown-6 (CE) into the aqueous phase as a masking reagent.

Figs. 1 and 2 show results for the extraction of alkaline earths with 0.05 mol dm^{-3} HPMBP and 0.01 mol dm^{-3} TOPO into cyclohexane in the absence (Fig. 1) and presence (Fig. 2) of 18-crown-6.† The concentrations of alkaline earths were at trace levels (1 $\times$ 10^{-5} to 1 $\times$ 10^{-4} mol dm^{-3}). It is clear that alkaline earths, especially strontium and barium, are extracted in the higher pH region in the presence of

† pH was adjusted with lithium hydroxide and acetic acid. Sodium perchlorate which is usually added in the aqueous phase to keep the ionic strength constant was not employed in the present work in order to avoid ion pair extraction. The number of TOPO units in the adduct(s) is two per metal for magnesium, calcium and strontium and three for barium.
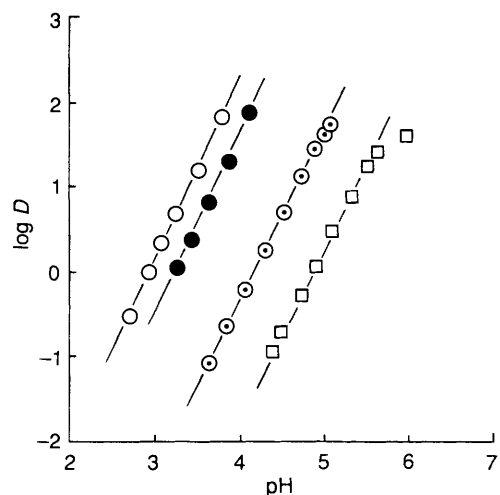
Fig. 1 Extraction of alkaline earths with HPMBP and TOPO. $[HPMBP]_o = 0.05$ mol dm^{-3}, $[TOPO]_o = 0.01$ mol dm^{-3}; O, Mg; ●, Ca; ⊙, Sr; □, Ba.
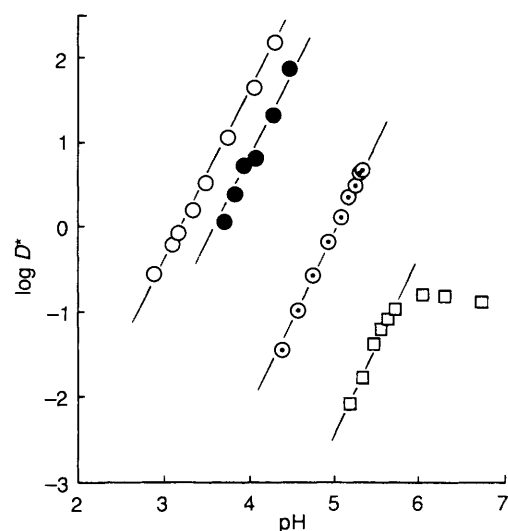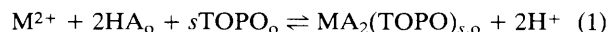

Fig. 2 Extraction of alkaline earths with HPMBP and TOPO in the presence of 18-crown-6. $[HPMBP]_o = 0.05$ mol dm^{-3}, $[TOPO]_o = 0.01$ mol dm^{-3}, $[CE] = 0.03$ mol dm^{-3}; symbols as in Fig. 1.

18-crown-6, while the separation for calcium–strontium and strontium–barium is much improved.

$$M^{2+} + 2HA_o + sTOPO_o \rightleftharpoons MA_2(TOPO)_{s,o} + 2H^+ \quad (1)$$

$$K_{ex,s} = [MA_2(TOPO)_s]_o[H^+]^2/[M^{2+}][HA]_o^2[TOPO]_o^s$$
$$= D[H^+]^2/[HA]_o^2[TOPO]_o^s \quad (2)$$

According to the previous work,[1] the overall equilibrium in the synergistic extraction of alkaline earths (M^{2+}) with HPMBP (HA) and TOPO and the extraction constant, $K_{ex,s}$, can be expressed as in eqns. (1) and (2), where subscript o stands for the species in the organic phase and D is the distribution ratio defined as $[MA_2(TOPO)_s]_o/[M^{2+}]$. The log $K_{ex,s}$ values were obtained from Fig. 1 using eqn. (2) on the basis of known s values and are summarized in Table 1. The values are similar to those obtained in the previous work. On the other hand, the distribution ratio (D^*) in the presence of 18-crown-6 can be expressed as in eqn. (3), where β, the complex formation constant between alkaline earths and 18-crown-6 in the aqueous phase, is defined as $[M(CE)^{2+}]/[M^{2+}][CE]$. 18-Crown-6 can be considered to exist quantitatively in the aqueous phase, for the distribution of 18-crown-6
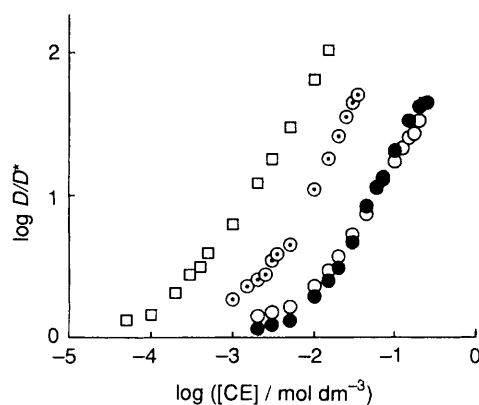
Fig. 3 Plots of log (D/D^*) vs. log [CE]. Symbols as in Fig. 1. pH = 3.8 (Mg), 3.9 (Ca), 4.9 (Sr) and 5.4 (Ba).

Table 1 Extraction parameters for alkaline earths

	log $K_{ex,s}$	s^a	log β	SF^b	SF^{*b}
Mg^{2+}	0.80	2	2.25	0.64	0.69
Ca^{2+}	0.16	2	2.30		
Sr^{2+}	−1.74	2	3.06	1.90	2.66
Ba^{2+}	−1.16	3	3.82	1.42	2.18

[a] Taken from ref. 1. [b] Separation factors for strontium and barium depend on $[TOPO]_o$ [see eqns. (5) and (7)]. They were obtained for the condition $[TOPO]_o = 0.01$ mol dm^{-3}.

into the cyclohexane phase is negligible.[2] Adduct formation with MA_2 or $MA_2(TOPO)_s$ and 18-crown-6 in the cyclohexane phase is also negligible. Dividing D by D^* gives eqn. (4).

$$D^* = [MA_2(TOPO)_s]_o/\{[M^{2+}] + [M(CE)^{2+}]\}$$
$$= K_{ex,s}[HA]_o^2[TOPO]_o^s/\{[H^+]^2(1 + β[CE])\} \quad (3)$$

$$D/D^* = 1 + β[CE] \quad (4)$$

Fig. 3 illustrates the plots of log D/D^* vs. log [CE] for $[HPMBP]_o = 0.05$ mol dm^{-3}, $[TOPO]_o = 0.01$ mol dm^{-3} and at appropriate pH. The slopes of the plots increase as [CE] increases and are unity in the higher [CE] range. The values of log β were obtained from the straight portion of the plots in Fig. 3 and are summarized in Table 1. The log β values increase in the order Mg, Ca < Sr < Ba, the opposite order to that of chelating reagents. Consequently, the pH region in which a metal ion with a larger ionic radius is extracted shifts to a higher pH region resulting in an improvement of separation. The log β values are reported to be 0.5–1.3 for calcium, 2.7–3.0 for strontium and 3.5–4.5 for barium.[3] As listed in Table 1, the log β values in the present work are in good agreement for strontium and barium.

The separation factor, SF, between two metal ions, M1 and M2, is defined as the difference of the logarithmic value of the respective distribution ratio [eqn. (5)]. Thus, SF in the absence of 18-crown-6 is derived from eqn. (2) as in eqn. (6), and is simplified when $s1$ equals $s2$ as in eqn. (7). SF^* in the presence of 18-crown-6 is derived from eqn. (3) as in eqn. (8), or eqn. (9) when $s1$ and $s2$ are the same and [CE] is high enough. Eqns. (6) and (8) mean that the separation factor can be improved as much as $β_{M2}/β_{M1}$.

$$SF = \log (D_{M1}/D_{M2}) \quad (5)$$

$$SF = \log (K_{ex,s,M1}/K_{ex,s,M2})[TOPO]_o^{s1-s2} \quad (6)$$

$$SF = \log (K_{ex,s, M1}/K_{ex,s,M2}) \quad (7)$$

$$SF^* = \log (D^*_{M1}/D^*_{M2})$$
$$= \log (K_{ex,s,M1}/K_{ex,s,M2})(1 + \beta_{M2}[CE])/$$
$$(1 + \beta_{M1}[CE])[TOPO]_o^{s1-s2} \tag{8}$$

$$SF^* = \log (K_{ex,s,M1}/K_{ex,s,M2})(\beta_{M2}/\beta_{M1}) \tag{9}$$

Separation factors in the presence and absence of 18-crown-6 are summarized in Table 1. The addition of crown ether disturbs the extraction through complexation in the aqueous phase, but improves the separability owing to the reverse complexation tendency.

The combination of chelating reagents and crown ethers having an opposite complexation tendency may be further applicable to the extraction of such metal ions as alkali or lanthanoids. In addition, the present extraction system should be extendable to other organic solvents, into which the distribution of crown ethers is not ignored. These extraction systems are now under examination. Finally, the present work could be the basis for a satisfactory and simple method for determining the complexation ability of water-soluble ligands.

References

1 S. Umetani, K. Sasayama and M. Matsui, *Anal. Chim. Acta*, 1982, **134**, 372.
2 Y. Meguro, H. Muto and Z. Yoshida, *Anal. Sci.*, 1991, **7** Supplement, 51.
3 R. M. Izatt, K. Pawlak and J. S. Bradshaw, *Chem. Rev.*, 1991, **91**, 1721.