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ACIDIC ORGANOPHOSPHORUS EXTRACTANTS–XIII

A SYNERGIC COMBINATION, *n*-OCTYL HYDROGEN *n*-OCTYLPHOSPHONATE–1-PHENYL-3-METHYL-4-BENZOYL-5-PYRAZOLONE, IN THE EXTRACTION OF LANTHANIDES(III)

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Abstract—A synergic enhancement of the extraction of Ce(III), Eu(III), Tb(III) and Tm(III) (generally Ln(III)) by *n*-octyl hydrogen *n*-octylphosphonate (HA) occurs in the presence of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HB). The suggested synergic mechanism is the conversion of the complexes $LnA_3 \cdot 2HA$ to $LnB_3 \cdot HA$. The conversion proceeds stepwise, the equilibrium being determined by the HB concentration. The tendency to form such complexes decreases with increasing atomic number of Ln(III); at the HB concentration 0·25M, conversion to $LnB_3 \cdot HA$ is complete only with Ce(III).

INTRODUCTION

Two BASIC synergic mechanisms can be expected to occur in the extraction of metal ions, M^{Z+}, with a solution of two acidic extractants, HA and HB, in an organic diluent. The two mechanisms are: (i) undissociated molecules of one of the extractants act as neutral electron donors and complexes of the type $MA_Z \cdot nHB$ are formed; (ii) anions of both extractants enter into the coordination sphere of M^{Z+} and the complexes of the type MA_nB_{Z-n} are formed. The former mechanism was observed, e.g. under certain conditions of extraction of Eu(III) with thenoyl-trifluoroacetone (TTA) and β-isopropyltropolone (IPT), with β-isopropyltropolone acting as the neutral ligand[1]. In the latter mechanism, the distribution of A^- and B^- between the individual sites of the coordination sphere is predominantly random in simple cases; this is true, e.g. in the extraction of Ln(III) and Eu(III) with the TTA–IPT pair, where the respective equilibrium constants can be predicted using simple statistical equations[1]. The coordination sphere of some cations is not occupied randomly by the same A^- and B^- and mixed complexes are formed, the stability of which is higher than predicted statistically; this was observed, e.g. in the extraction of Cu(II) and Zn(II) with the TTA–IPT pair[2]. In the extraction of one cation, namely UO_2^{2+}, with a series of extractants, the β-diketones, the formation of mixed complexes UO_2AB obeys the statistical equations, if two β-diketones with similar complex-forming ability are used[3].

The present paper describes the extraction of Ce(III), Eu(III), Tb(III) and Tm(III) with toluene solutions of two extractants forming chelates of different

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3. L. Newman and P. Klotz, *Proc. Int. Conf. Solvent Extraction Chemistry, Gothenburg, (August 27–September 1, 1966)*, p. 128. North Holland, Amsterdam (1967).

structure. *n*-Octyl hydrogen *n*-octylphosphonate (HO[OP]), or H*A*) forms complexes in toluene which are supposed to have two or three 8-membered chelate rings in their structure, formed by two HO[OP] molecules; probably this ring is typical for the complexes of monoacidic organophosphorus extractants [4]. The usual 5-membered ring is most probably present in the complexes of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP, generally H*B*).

EXPERIMENTAL

Informations on the procedures, the measurement of the hydrogen ion concentration as well as of the radioactivity, the preparation of extractants and the source of radioactive tracers were given previously[5–7]. PMBP was purified by recrystallization from ethanol. The ionic strength of the aqueous phase was adjusted always to 1·00 by sodium nitrate. The initial concentration of the extracted metals in the aqueous phase was always lower than 10^{-5}M. Toluene diluent, reagent grade, was used without purification.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the logarithm of the distribution ratio, $\log q_{\mathrm{Ln}}$, on the logarithm of the PMBP concentration at constant concentration of HO[OP]. A synergic enhancement of $\log q_{\mathrm{Ln}}$ can be observed, the extent of which decreases with increasing atomic number of the extracted lanthanide(III). The dependence of $\log q_{\mathrm{Ln}}$ on the logarithm of the hydrogen ion concentration has the expected slope -3 with Eu(III) and was not checked with the other lanthanides. Figure 2 shows the dependence of $\log q_{\mathrm{Ln}}$ on the logarithm of the HO[OP] concentration, that of PMBP being kept constant.

To know the composition of the PMBP complexes in the absence of HO[OP], $\log q_{\mathrm{Ln}}$ was measured as a function of the PMBP concentration in the organic phase (Fig. 1). The complexes $\mathrm{Ce}B_3{\cdot}\mathrm{H}B$, $\mathrm{Eu}B_3{\cdot}\mathrm{H}B$, $\mathrm{Tb}B_3$ and $\mathrm{Tm}B_3$ exist in the organic phase in the PMBP concentration range, in which synergism occurs in the presence of HO[OP]. Tb(III) exhibits an insignificant tendency to form the complex $\mathrm{Tb}B_3{\cdot}\mathrm{H}B$ at the PMBP concentrations > 0·2M. The extractability of Ce(III) is surprisingly high as compared with that of Eu(III), Tb(III) and Tm(III). The complexes of HO[OP] in the absence of PMBP have the composition $\mathrm{Ln}A_3{\cdot}2\mathrm{H}A$, Ln being a lanthanide(III)[5]. No significant interaction was assumed to occur between HO[OP] and PMBP, because of the existence of stable hydrogen bonded dimer of HO[OP] and an intramolecular hydrogen bond in the PMBP molecule.

To determine the composition of the synergic complexes, the $\log q_{\mathrm{Ln}}$ vs. $\log C_{\mathrm{PMBP}}$ curve obtained with Ce(III) is the most suitable for analysis, as it covers the largest $\log q_{\mathrm{Ln}}$ region. The ascending part of the curve tends to the limiting slope of 3 at a PMBP concentration > 0·1M. The dependence of the $\log q_{\mathrm{Ln}}$ on the concentration of HO[OP], measured at 0·25M PMBP, has a slope close to 0·5. As for the composition of the extracted complex, the formula $\mathrm{Ce}B_3{\cdot}\mathrm{H}A$ is much more plausible than $\mathrm{Ce}AB_2{\cdot}\mathrm{H}B$. Supposing that the tendency towards formation of a complex with a still higher content of PMBP is not very pronounced, so that the complex $\mathrm{Ce}B_3{\cdot}\mathrm{H}A$ exists over a sufficiently broad range of PMBP concentrations.

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5. Z. Kolařík, S. Dražanová and V. Chotívka, *J. inorg. nucl. Chem.* **33**, 1125 (1971).
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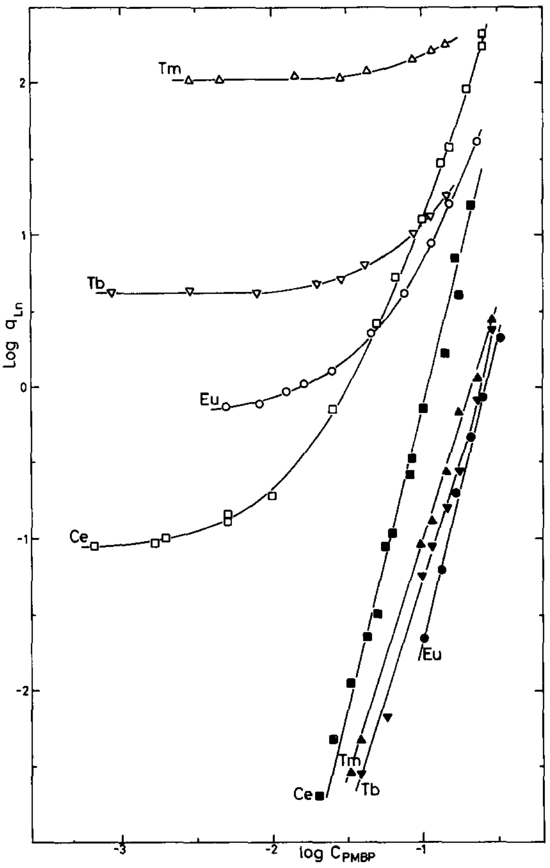

Fig. 1. Dependence of the distribution ratio, q_{Ln}, on the PMBP concentration, C_{PMBP}, in the absence of HO[OP] (●■▼▲) and in the presence of 0·025M HO[OP] (○□△▽). Aqueous phase 0·02M HNO_3 + 0·98M $NaNO_3$. Toluene diluent.

Then the horizontal and ascending asymptotes intersect at a PMBP concentration, at which the concentrations of both limiting complexes, i.e. $CeA_3{\cdot}2HA$ and $CeB_3{\cdot}HA$, are equal. If stepwise addition of PMBP converts the former complex to the latter without formation of any intermediate complexes, the difference between the intersection point and the actual log q_{Ln} would be 0·3 logarithm unit. Actually, the difference is higher at 0·02M PMBP, where the asymptotes intersect, namely 0·7 logarithm units. Consequently, some amount of intermediate complexes are involved in the equilibrium in the organic phase, but the tendency towards their formation is not very pronounced. Their overall concentration is ~ 2·5 times higher than the concentration of each of the limiting complexes at $[CeA_3{\cdot}2HA] = [CeB_3{\cdot}HA]$. No more detailed analysis of the log q_{Ln} vs. log C_{PMBP} curve has been made. There is a theoretical possibility of the formation of four intermediate complexes even with the simplifying assumption that PMBP takes part in complex formation only as an anion and not as the undissociated molecule. These complexes can differ in the number of added HA molecules and, moreover, none of them probably prevails in any part of the PMBP concentration

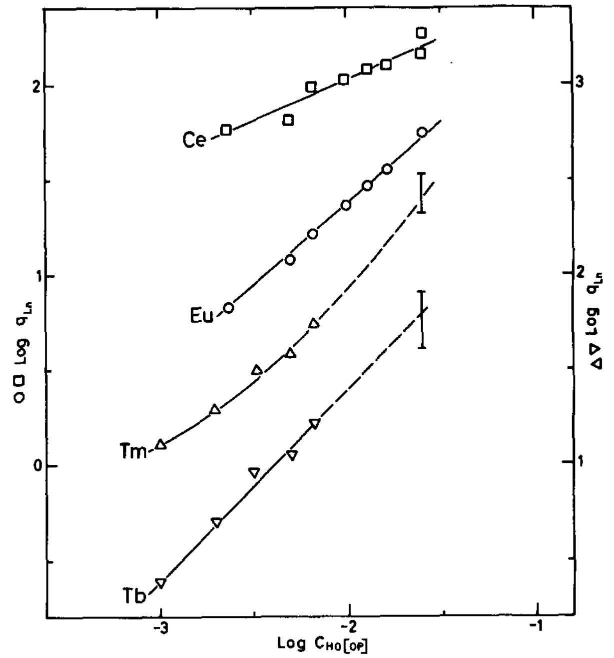

Fig. 2. Dependence of the distribution ratio, q_{Ln}, on the HO[OP] concentration in the presence of 0·25M PMBP. Aqueous phase 0·02M HNO_3+0·98M $NaNO_3$. Toluene diluent. The log q_{Ln} ranges for Tb(III) and Tm(III) at log $C_{HO[OP]} = -1{\cdot}60$ were obtained by the extrapolation of the respective curves in Fig. 1.

range, in which they are formed. Thus a large amount of precise data for various PMBP and HO[OP] concentrations would be needed for a computer analysis, which could give reliable results. Only the qualitative conclusion can be drawn that such intermediate complexes probably must be formed, in which HO[OP] and PMBP are present as anions A^- and B^- respectively. Thus, both synergic mechanisms described in the introduction apply to this system.

As for the other lanthanides(III) studied, a quite analogous reaction of $LnA_3{\cdot}2HA$ with HB probably takes place in the organic phase. This can be concluded because the idealized log q_{Ln} vs. log C_{PMBP} curve, which fits the Ce(III) data, fits also all the other data. As the tendency to convert $LnA_3{\cdot}2HA$ to $LnB_3{\cdot}HA$ decreases with increasing atomic number of Ln, the average content of HO[OP] in the complexes at the highest studied PMBP concentration should also decrease. This is true with Eu(III) and Tb(III), but an unexplained distortion of the sequence occurs with Tm(III) (Fig. 2). The relation between the atomic number and the extent of the synergism under these conditions can be easily understood, if it is taken into the account how differently the extractability of the lanthanides (III) varies with the atomic number of Ln(III) in the cases PMBP and HO[OP] separately (see Fig. 1).