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STUDY OF THE COMPLEXING OF LANTHANIDE IONS WITH 1-PHENYL-3-METHYL-4-HEPTAFLUROBUTYRYL PYRAZOLONE-5 AND TRIPHENYLPHOSPHINE OXIDE BY THE TWO-PHASE TITRATION METHOD

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The reaction of rare earth ions with 1-phenyl-3-methyl-4-heptafluorobutylpyrazolone-5 (PMHFP) and triphenylphosphine oxide (TPPO) in water-chloroform was studied by two-phase titrations. The compositions and stabilities of the complexes obtained are discussed. Stability constants of the complexes (β_{302}), dissociation constants (pK_a), two-phase dissociation constants (pK_{ac}) and two-phase distribution coefficients (pK_d) of the chelating agent PMHFP were also determined.

Keywords: Rare earths, dithizones, triphenylphosphine oxide, complexes, stability constants

INTRODUCTION

In homogeneous aqueous solution, the dissociation constant of a weak acid and the stability constant of a metal ion complex are easily measured by pH titration. However, it is difficult to measure in a heterogeneous system such as with two phases. In 1956 Dyrssen suggested that in a two-phase system the dissociation constant of a weak acid in water (K_a) and a two-phase distribution coefficient (K_d) can be measured by means of pH titration.^{1,2} Then (in 1959) Jensen investigated metal chelate equilibria in extraction systems by two-phase titration.^{3,4} This method, after being simplified and improved by Li,^{5,6} is a simple and practical way to study the synergic effect of a neutral ligand in an extraction system and its mode of action. A study of extraction by this method omits analysis of metal ion concentrations in the two phases (aqueous and organic), and simplifies the experimental procedure. It has been used to study some extraction systems and has given satisfactory results.⁶⁻⁸ In this paper, the complexing action of the new fluoro- β -diketone chelating agent, PMHFP,⁹ and TPPO with rare earth ions in a chloroform-water system is explored by means of two-phase titration. The two-phase distribution coefficients (pK_{ac}) of PMHFP and stability constants (β_{njk}) and compositions of complexes have been determined. In addition, we have prepared the solid complexes and studied their compositions and properties.

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EXPERIMENTAL

Reagents

PMHFP (m.p. 72°C) was prepared by using a modified previously reported procedure.⁹ Chloroform (analytical quality) was washed 4 or 5 times with doubly distilled water to remove alcohol and other impurities before use. Other reagents were of analysis grade. In order to avoid any change of solution volume after mixing the two phases, all solvents were saturated and equilibrated before use with 0.1 mol dm⁻³ aqueous NaNO₃ solution. The aqueous and organic phases were then separated for use respectively as the aqueous and organic solvents in later experiments.

All the aqueous solutions were prepared with doubly distilled water (pH > 6.2) from which CO₂ was removed by bubbling with argon gas. The solution of sodium hydroxide was prepared by the concentrated base method¹⁰ in which the content of CO₂ is less than 0.4%.

pH Measurements

The pH of the water phase at equilibrium was determined by a PHS-3 precision pH meter (China, precision 0.01 pH) that was standardized with two buffer solutions before and after use.

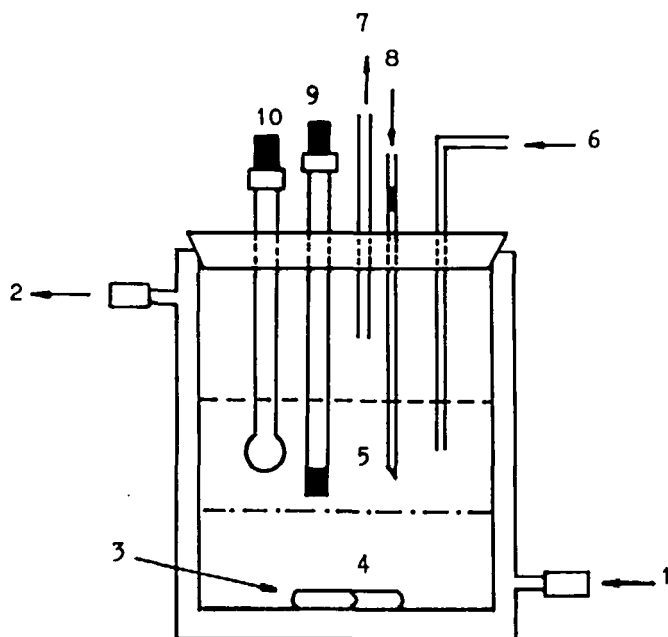


FIGURE 1 Titration vessel used. 1,2: constant temperature water ($25 \pm 0.1^\circ\text{C}$); 3: stirrer; 4: organic phase; 5: aqueous phase; 6,7: Ar gas; 8: injector; 9: calomel electrode; 10: glass electrode.

Experimental Procedure

All pH values were determined in a constant temperature titration vessel shown in Fig. 1. After the measuring system was set with two buffer solutions (pH = 4.003 and 6.864, at 25°C), 20 cm³ of a 0.01 mol dm⁻³ PMHF solution in chloroform and 20 cm³ of a water phase containing NaNO₃ (0.1 mol dm⁻³) and RE(NO₃)₃ (10⁻³ mol dm⁻³) were equilibrated in the titration flask after being stirred for 20 minutes. Then, a varying volume of chloroform solution containing TPPO (2.206 × 10⁻² mol dm⁻³) and PMHFP (0.01 mol dm⁻³) was titrated quantitatively into the flask. After being stirred at equilibrium (in most cases 10–15 minutes were sufficient), the pH of the water phase was measured in contact with the organic layer.

All measurements were performed at 25 ± 0.1°C and the system was protected by passing argon gas through it.

The principle of the two-phase titration has been discussed in detail in the literature.^{5,6} Here, simplified equations in relation to our experiments are introduced. The following symbols are used; HA: PMHFP; B: TPPO; M: trivalent rare earth ion (charge omitted); K_a: aqueous phase dissociation constant of PMHFP; K_{ae}: two-phase dissociation constant of PMHFP; K_d: two-phase distribution coefficient of PMHFP; C_{HA}: the concentration of PMHFP in the organic phase; C_M: the initial concentration of the rare earth ion in the water phase; V_o: volume of the organic phase; V: total volume of the aqueous phase; C_{NaOH}: concentration of standard NaOH solution; V_{NaOH}: volume of standard NaOH solution.

The dissociation constant, pK_a, of the chelating agent PMHFP in the aqueous phase can be expressed as in (1).

$$pK_a = \text{pH} - \log \frac{[(\text{Na}^+) + (\text{H}^+) - (\text{OH}^-)]}{[\text{C}_{\text{HA}} - (\text{Na}^+) - (\text{H}^+) + (\text{OH}^-)]} \quad (1)$$

The dissociation constant, pK_{ae}, of PMHFP in two phases is shown in (2),

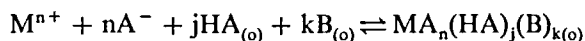
$$pK_{ae} = \text{pH} - \log \alpha - \log \frac{[\text{C}_A - \text{C}_H + (\text{H}^+)]}{[\text{C}_H - (\text{H}^+)]} \quad (2)$$

and the distribution coefficient, K_d, of the chelating agent in two phases is expressed as in (3),

$$pK_{ae} = pK_a + \log(1 + K_d) \quad (3)$$

where α, C_A and C_H are defined respectively as α = V_o/V; C_A = α C_{HA} and C_H = [V_oC_{HA} - C_{NaOH}V_{NaOH}]/V + OH⁻

The reaction for the formation of the synergic complex can be written as (“(o)” refers to the organic phase)



with the overall equilibrium constant (4),

$$\beta_{nj k} = \frac{[\text{MA}_n(\text{HA})_j(\text{B})_{k(o)}]}{[\text{M}^{n+}][\text{A}^-]^n[\text{HA}]_j[\text{B}]_k} \quad (4)$$

in which M^{n+} refers to the rare earth ion, A^- represents the anion of the acid chelating agent PMHFP and B refers to the neutral extractant TPPO. The complex formability Y can be expressed as in (5),

$$Y = \sum_{j=0}^J \sum_{k=0}^K \beta_{njk} [HA]_o^j [B]_o^k = \frac{\bar{n}'}{(\bar{n} - \bar{n}')\alpha(A)_n} \quad (5)$$

in which

$$\bar{n}' = \frac{[C_A - (C_M - [H^+])]}{C_M} \quad (6)$$

$$(A) = \frac{[C_A - \bar{n}'C_M]}{1 + ([H^+]/K_a)\{1 + aK_d(1 + K[B]_o)\}} \quad (7)$$

As no association of PMHFP and TPPO was seen to occur during preliminary experiments (that is $K = \frac{[HA \cdot B]_o}{[HA]_o[B]_o} \ll 1$) and $K_d = 1.78 \times 10^4 \gg 1$, (7) can be simplified to give (8).

$$(A) = \frac{K_{ac}(C_A - \bar{n}'C_M)}{[K_{ac} + \alpha[H^+]]} \quad (8)$$

From equations (6), (8) and (5) and the values of K_a , K_d and pH determined in the experiment, (A), \bar{n}' and Y are obtained. Then the stoichiometries of the complexes and the equilibrium constants can be obtained from the relationship of Y with $[HA]_o$ and $[B]_o$ by means of slope analysis or calculation.

In the chosen experimental conditions, various concentrations of the chelating agent PMHFP (0.01 mol dm^{-3} and 0.02 mol dm^{-3}) were used in the titration and the same results were obtained. This shows that the chelating agent binds rare earth ions in the form of A but not in the form of HA . A plot of $\log Y$ against $\log[B]_o$ gives a straight line whose slope is equal to 2, which indicates that the synergic complex REA_3B_2 is formed in the organic phase.

Preparation of Solid Complexes

A 20 cm^3 solution of $RE(NO_3)_3$ (0.05 mol dm^{-3}) whose pH was adjusted to 5 with ammonia was mixed with 40 cm^3 of a chloroform solution containing HA (0.1 mol dm^{-3}) and TPPO (0.1 mol dm^{-3}) in a separating funnel and shaken for 30 minutes. The aqueous and organic phases were separated by centrifugation. Petroleum ether was slowly added to the organic phase to precipitate the solid complex which was recrystallized from chloroform-petrol and dried to constant weight.

RESULTS AND DISCUSSION

Study of Liquid Phase Synergic Complexes

Table I gives the dissociation constant pK_a , two-phase dissociation constant pK_{ac}

and two-phase distribution coefficient K_d of PMHFP determined in the experiments.

Titration data and results for the complex $\text{Sm}(\text{PMHFP})_3(\text{TPPO})_2$ as an example are listed in Table II. The relationship $\log Y - \log[B]_0$ for some of the rare earth ions is shown in Fig. 2.

TABLE I
 $\text{p}K_a$, $\text{p}K_{ac}$ and K_d for PMHFP ($25.0 \pm 0.1^\circ\text{C}$; $\mu = 0.1 \text{ mol dm}^{-3}$).

found	$\text{p}K_a$	lit. ⁹	$\text{p}K_{ac}$	K_d
3.10		3.10	7.35	1.78×10^4

TABLE II
 Titration data and results for the complex $\text{Sm}(\text{PMHFP})_3(\text{TPPO})_2$.*

V_{TPPO}^* (cm^3)	pH	$[\text{H}^+] \times 10^3$ (mol dm^{-3})	$C_{\text{II}} \times 10^2$ (mol dm^{-3})	\bar{n}'	$[\text{A}^-] \times 10$ (mol dm^{-3})	$\log Y$	$\log[\text{TPPO}]_0$
0.10	3.13	0.933	1.005	0.541	4.342	18.43	-3.96
0.20	3.06	1.096	1.010	0.636	3.627	18.75	-3.66
0.30	2.99	1.288	1.015	0.747	3.027	19.07	-3.49
0.40	2.91	1.549	1.020	0.899	2.446	19.46	-3.36
0.60	2.82	1.905	1.030	1.106	1.911	19.91	-3.19
0.80	2.75	2.387	1.040	1.299	1.566	20.28	-3.07
1.20	2.69	2.570	1.060	1.491	1.316	20.61	-2.90
1.80	2.62	3.020	1.090	1.752	1.070	21.02	-2.74

* $[\text{Sm}^{3+}] = 1.724 \times 10^{-3} \text{ mol dm}^{-3}$; $\mu = 0.1(0.1 \text{ mol dm}^{-3} \text{ NaNO}_3)$; $C_{\text{IIA}} = 0.010 \text{ mol dm}^{-3}$; a TPPO ($0.02206 \text{ mol dm}^{-3}$)-PMHFP ($0.010 \text{ mol dm}^{-3}$)- CHCl_3 solution was titrant and V_{TPPO} is the volume of titrant used; $25.0 \pm 0.1^\circ\text{C}$.

The stoichiometries and stability constants for the complexes (except Pm^{3+} and Lu^{3+}) with PMHFP and TPPO determined by two-phase titration are listed in Table III.

The stability constants $\log \beta_{302}$ increase and show a "double peak" effect (see Fig. 3) with increasing atomic number of the rare earths. This indicates that ionic bonding is important in these synergic complexes.

An inclined W plot is found from the graph of $\log \beta_{302}$ against the angular momentum quantum number, L , of the rare earth ions (see Fig. 4).

The value of the stability constant for the Y^{3+} ion is between that of the Ho^{3+} and Er^{3+} ions, and nearly equal that of the Er^{3+} ion. Under the experimental conditions, the synergic complexes in the organic phase can exist in two forms. One (for rare earth ions whose atomic numbers are less than or equal to Pr^{3+}) is RE_3B_2 when the concentration of TPPO is low. With increasing concentration of TPPO, the stoichiometries of the rare earth ion complexes change to RE_3B_3 . Sm^{3+} , Y^{3+} and those rare earth ions whose atomic numbers are greater than Sm^{3+} mainly form the synergic complexes RE_3B_2 . This is because the neutral ligand TPPO is a stronger complexing agent and the radii of light rare earth ions are larger than those of the heavy rare earth ions. Thus a third TPPO ligand can enter the light rare earth ion complexes RE_3B_2 to form RE_3B_3 , when TPPO concentrations increase.

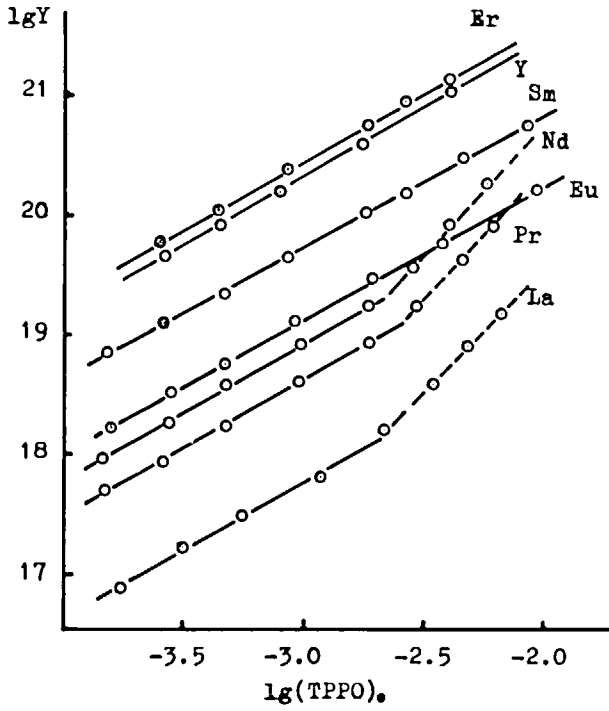


FIGURE 2 The relationship $\log Y - \log [B]_0$ for some of the RE^{3+} ions.

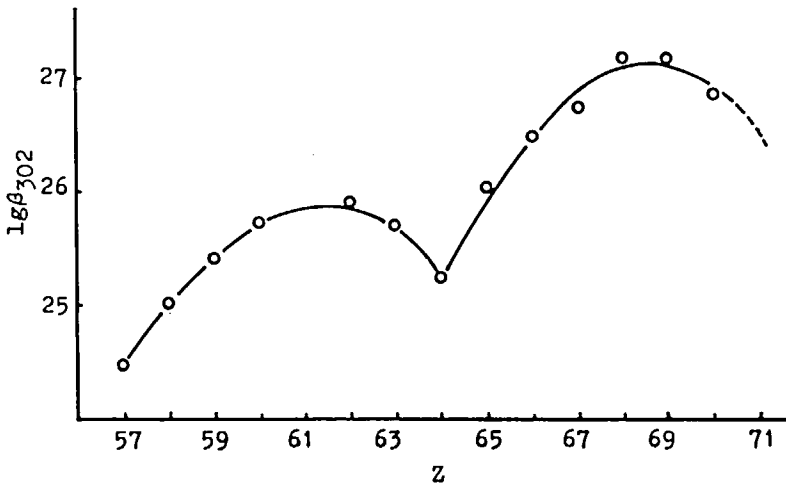


FIGURE 3 The "double-peak" effect found for the stability constants.

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TABLE III
The stoichiometries and stability constants of the complexes.

	$\log\beta_{302}$		
	calcd.	slope anal.	average value
La(PMHFP) ₃ (TPPO) ₂	24.45	24.48	24.47
Ce(PMHFP) ₃ (TPPO) ₂	25.03	25.00	25.02
Pr(PMHFP) ₃ (TPPO) ₂	25.40	25.42	25.41
Nd(PMHFP) ₃ (TPPO) ₂	25.75	25.70	25.73
Sm(PMHFP) ₃ (TPPO) ₂	25.94	25.90	25.92
Eu(PMHFP) ₃ (TPPO) ₂	25.72	25.73	25.72
Gd(PMHFP) ₃ (TPPO) ₂	25.27	25.25	25.26
Tb(PMHFP) ₃ (TPPO) ₂	26.03	26.05	26.04
Dy(PMHFP) ₃ (TPPO) ₂	26.47	26.49	26.48
Ho(PMHFP) ₃ (TPPO) ₂	26.71	26.74	26.73
Er(PMHFP) ₃ (TPPO) ₂	27.21	27.19	27.20
Tm(PMHFP) ₃ (TPPO) ₂	27.19	27.18	27.19
Yb(PMHFP) ₃ (TPPO) ₂	26.86	26.83	26.85
Y(PMHFP) ₃ (TPPO) ₂	27.15	27.17	27.16

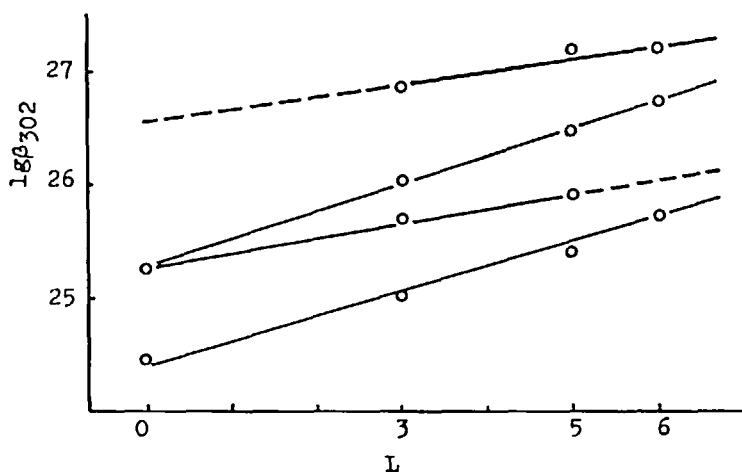


FIGURE 4 Inclined \bar{W} plot for the data.

Solid Complexes

In order to determine the compositions of the complexes in the organic phase, the solid complexes of Eu^{3+} and Yb^{3+} prepared from the two-phase system were studied. The elemental analysis data for the solid complexes are as follows. Calcd. for EuA_3B_2 : C, 51.6; H, 3.0; N, 4.6; Eu, 8.4%. Found: C, 51.4; H, 2.9; N, 4.8; Eu, 8.8%. Calcd. for YbA_3B_2 : C, 51.0; H, 2.9; N, 4.6; Yb, 9.4%. Found: C, 50.9; H, 2.9; N, 5.0; Yb, 9.5%. This is the same stoichiometry as obtained from the two-phase titration. The solid complexes are easily soluble in alcohol, methanol, acetone, chloroform and benzene, and slightly in petrol and water. The molar conductivities of the complexes

determined in alcohol solution are less than $10 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, which indicates that the complexes are non-electrolytes.

The important UV absorption bands of the ligands and their complexes in alcohol are listed in Table IV.

TABLE IV
UV spectra data(nm) for the ligands and selected complexes.*

PMHFP	TPPO	EuA ₃ B ₂	YbA ₃ B ₂
233	262	253	253
272	268	292	293
	276	267	266
		276	276
		286	285

* Values are maxima in the spectra.

It can be seen that all the important bands of the chelating agent PMHFP and ligand TPPO shift to longer wavelengths (in varying degrees) in the complexes.

The main changes found in the IR spectra are (i) the shift of the C=O stretch from 1671 cm^{-1} in PMHFP to 1630 cm^{-1} with chelation of PMHFP to rare earth ions, (ii) the characteristic $\nu_{\text{P=O}}$ band in the ligand TPPO, after coordinating with rare earth ion, shifts to 1165 cm^{-1} , and (iii) the disappearance of the OH absorption band centred at 2700 cm^{-1} is due to PMHFP chelates with the enol form. This indicates that no molecular HA exists in the complexes, as indicated by the two-phase titrations.

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