

Thermodynamic Parameters for the Extraction of Some Lanthanides with 1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5 and Trioctylamine

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The synergistic extraction of Pr, Gd and Yb with a mixture of 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 and trioctylamine diluted in C_6H_6 , $CHCl_3$ and CCl_4 at 288 K, 298 K, 308 K and 318 K has been investigated. The values of the equilibrium constants as well as of ΔH° , ΔS° and ΔG° have been calculated. The thermodynamic parameters indicate that the adduct formed becomes stable on the account of the enthalpy change which exceeds the antistabilizing effect of the entropy factor. A comparison is made to the extraction of the same elements with thenoyltrifluoroacetone.

(Keywords: Lanthanides; 1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5; Trioctylamine; Extraction; Thermodynamic parameter)

Die thermodynamischen Parameter für die Extraktion einiger Lanthaniden mit 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolon und Trioctylamin

Es wurde die synergistische Extraktion von Pr, Gd und Yb mit einer Mischung von 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolon mit Trioctylamin in C_6H_6 , $CHCl_3$ und CCl_4 bei 288 K, 298 K, 308 K und 318 K bestimmt. Die Gleichgewichtskonstanten und die Werte für ΔH° , ΔS° und ΔG° wurden berechnet. Die thermodynamischen Parameter legen den Schluß nahe, daß die Stabilität des gebildeten Addukts in Änderungen der Enthalpie begründet ist, wobei der destabilisierende entropische Effekt übertroffen wird. Die Ergebnisse werden mit der Extraktion mittels Thenoyltrifluoroaceton verglichen.

Introduction

The synergistic extraction of lanthanides and actinides with mixtures of 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (HPMBP) and neutral donors is investigated by many authors¹⁻⁶, but the combination between

HPMBP and amines and the influence of the temperature on such extraction systems have not been studied yet.

The aim of the present work is to obtain information about the influence of temperature on the synergistic extraction of Pr, Gd and Yb with solutions of mixtures from *HPMBP* and trioctylamine (*TOA*) in C_6H_6 , $CHCl_3$ and CCl_4 .

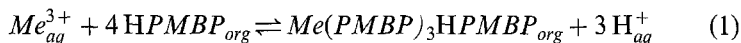
Experimental

HPMBP (Pharmachim-Sofia) and *TOA* (Fluka) were directly used. The solutions of metal cations were obtained from the oxides Pr_6O_{11} , Gd_2O_3 and Yb_2O_3 (Fluka, puriss.). Arsenazo III (Fluka) and all of other elements were of analytical grade "pure p. a."

The extraction was studied at 288 K, 298 K, 308 K, and 318 K (± 1 K). The ionic strength of 0.1 *M* was maintained by means of (Na, H)Cl and the *pH* values were measured with an accuracy of ± 0.01 . The experimental approach is identical with the described one in a foregoing publication⁷.

Results and Discussion

In a previous work⁸ the conclusion was drawn that lanthanides *Me* are extracted with *HPMBP* as a self-adduct:



In the presence of an acid the amine is transformed completely or partially into the corresponding salt. In the considered extraction system *TOA* is combined with HCl and *HPMBP*; the latter (in its enol form) acts as an acid and therefore *TOA*, *HPMBP*, $(TOA)_a(HCl)_b$ and $(TOA)_c(HPMBP)_d$ are expected in the organic phase. As far as no metal cations are introduced in the water phase, the total concentration (*tot*) of the amine and of the β -diketone is equal to a sum of the concentrations of the available compounds:

$$[TOA]_{tot} = [TOA] + [(TOA)_a(HCl)_b] + [(TOA)_c(HPMBP)_d]$$

$$[HPMBP]_{tot} = [HPMBP] + [(TOA)_c(HPMBP)_d]$$

The experimental conditions are chosen that the concentration of HCl does not exceed 1 *M* but is multifold higher than the concentration of the trioctylamine. The coefficients *a* and *b* are in that case⁹ equal to unity and $(TOA) = 0$, especially when high solvating agents (C_6H_6 , $CHCl_3$, CCl_4)¹⁰ are used as diluents. Since HCl is much stronger than the enol form of the β -diketone *HPMBP*⁶, one may assume that

$$[TOA \cdot HCl] \gg [(TOA)_c(HPMBP)_d] \approx 0.$$

In that case, $[TOA]_{tot} \approx [TOA \cdot HCl]$, and $[HPMBP]_{tot} \approx [HPMBP]$.

Ke and Li^{11,12} come to analogous conclusions at the experimental studies of the behaviour of mixtures of β -diketones and tertiary amines.

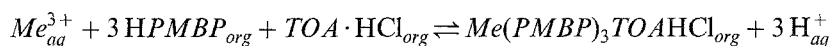
The drawn conclusions permit to establish the following equilibrium in the organic phase:



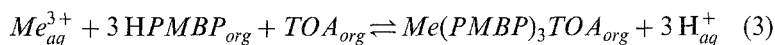
which may be formally substituted by the following equivalent equilibrium:



The total interaction proceeding between the components in the water and the organic phase is as follows:



This equilibrium may be replaced by the following one:



However, one has to keep in mind that the equilibrium constant for the interaction between *HPMBP* in toluene is only 13-fold less than the equilibrium constant for the interaction between *TOA* and *HCl*¹⁶. Therefore the neglect of the interaction *HPMBP*—*TOA* gives less accurate values of the variables.

It is obvious that between the equilibrium constants K_{PMBP} (of process 1), β (of process 2) and K_{syn} (of process 3) the following simple correlation exists:

$$\beta = \frac{K_{syn}}{K_{PMBP}} \quad (4)$$

After the distribution coefficient is introduced in the expression for K_{syn} , the following relation is obtained:

$$\log D_{syn} = \log K_{syn} + 3 \log [HPMBP] + 3 pH + \log [TOA] \quad (5)$$

The processing of the experimental results (Fig. 1 and 2) indicates that the slope of the linear relation $\log D_{syn} - 3 \log [HPMBP] - 3 pH = f(\log [TOA])$ is equal to unity and the slope of the straight line $\log D_{syn} =$

$f(\log [HPMBP])$ equals 3. This means that the assumptions for the extraction process expressed through the equilibria (2) and (3) are reliable and a complex compound of composition $Me(PMBP)_3 \cdot TOA \cdot HCl$ is extracted in the organic phase.

The thermodynamic¹³ constants K_{PMBP} , K_{syn} and β are calculated from the experimental results (Figs. 1 and 2) as well as from formula (4) and summarised in Table 1. Using the equation $\ln \beta = -\Delta H/(RT) + \Delta S/R$ for different temperatures the changes of enthalpy ΔH° and entropy ΔS° are determined from the β -value (Fig. 3); they are compared

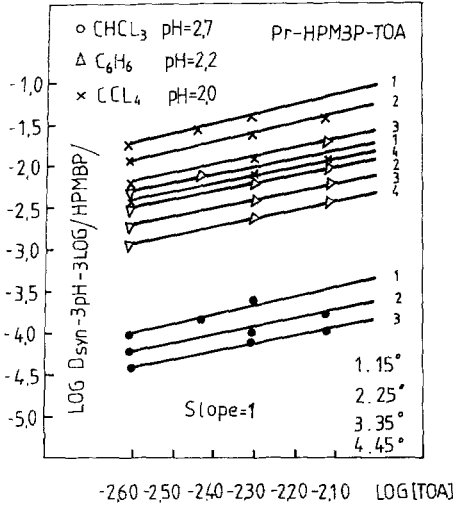


Fig. 1. Dependence of $\log D - 3pH - 3\log[\text{HPMBP}]$ vs. $\log \text{TOA}$ for the extraction of mixtures of HPMBP (0.04 M) and TOA at different temperatures

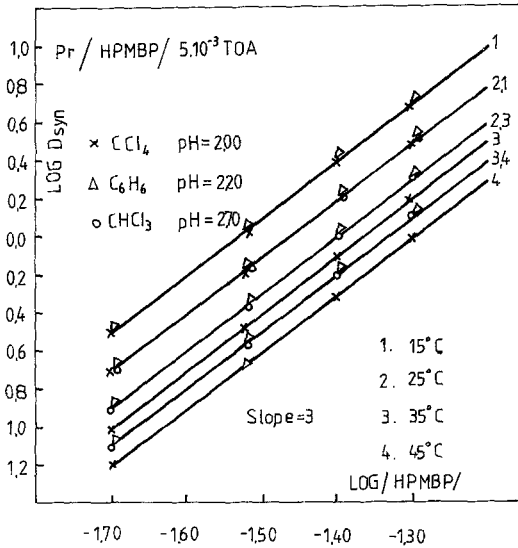


Fig. 2. Dependence of $\log D$ vs. $\log[\text{HPMBP}]$ for the extraction of Pr with mixtures of HPMBP and TOA (0.005 M) at different temperatures

Table 1. Values of the equilibrium constants (estimated deviation for $\log K$ is ± 0.1 and for $\log \beta$ ± 0.14)

Metal	Diluent	K	$\log K_{PMBP}$	$\log K_{syn}$	$\log \beta$
Pr	CCl ₄	288	-3.4	0.8	4.2
		298	-3.2	0.6	3.8
		308	-3.0	0.4	3.4
		318	-2.8	0.2	3.0
	C ₆ H ₆	288	-4.2	0.3	4.5
		298	-4.0	0.1	4.1
		308	-3.8	-0.1	3.7
		318	-3.6	-0.3	3.3
	CHCl ₃	288	-4.5	-1.4	3.1
		298	-4.3	-1.6	2.7
		308	-4.1	-1.8	2.3
		318	—	—	—
Gd	CCl ₄	288	-2.5	1.6	4.1
		298	-2.3	1.4	3.7
		308	-2.1	1.2	3.3
		318	-1.9	1.0	2.9
	C ₆ H ₆	288	-3.1	1.0	4.1
		298	-2.9	0.8	3.7
		308	-2.7	0.6	3.3
		318	-2.5	0.4	2.9
	CHCl ₃	288	-3.4	-0.4	3.0
		298	-3.2	-0.6	2.6
		308	-3.0	-0.8	2.2
		318	—	—	—
Yb	CCl ₄	288	-1.5	2.1	3.6
		298	-1.3	2.0	3.3
		308	-1.2	1.8	3.0
		318	-1.0	1.6	2.6
	C ₆ H ₆	288	-1.9	1.2	3.1
		298	-1.7	1.0	2.7
		308	-1.6	0.8	2.4
		318	-1.4	0.6	2.0
	CHCl ₃	288	-2.4	0.1	2.5
		298	-2.2	-0.1	2.1
		308	-2.1	-0.3	1.8
		318	—	—	—

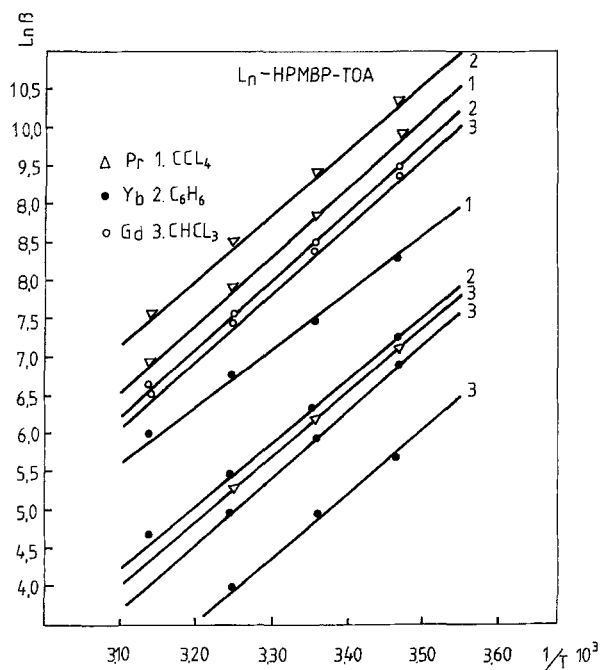


Fig. 3. Dependence of $\log \beta$ vs. $1/T$ for the extraction of Pr, Gd and Yb with mixtures of HPMBP and TOA in CCl₄, C₆H₆ and CHCl₃

Table 2. Thermodynamic parameters for the synergistic extraction of Pr, Gd and Yb with mixtures of HPMBP and TOA (estimated deviations for $\Delta H^\circ \leq 0.4$ kJ/mol, $\Delta S^\circ \leq 1.4$ J/mol K, $\Delta G^\circ \leq 1.1$ kJ/mol)

Complex	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)	Diluent
Pr(PMBP) ₃ TOA · HCl	-27.9	-59.0	-110.3	CCl ₄
	-23.4	-69.6	-155.3	C ₆ H ₆
	-15.4	-69.6	-182.1	CHCl ₃
Gd(PMBP) ₃ TOA · HCl	-20.9	-67.5	-156.3	CCl ₄
	-21.1	-71.0	-167.5	C ₆ H ₆
	-14.8	-69.5	-183.9	CHCl ₃
Yb(PMBP) ₃ TOA · HCl	-18.5	-56.7	-128.0	CCl ₄
	-15.7	-60.2	-149.7	C ₆ H ₆
	-12.2	-63.1	-171.3	CHCl ₃

with the free energy changes $\Delta G_{298}^{\circ} = -RT \ln \beta$ calculated for 298 K (Table 2).

The values of the thermodynamical parameters show that the synergistic interaction in the organic phase is a result from the enthalpy decrease of the system which prevails over the destabilizing influence of the entropy factor (negative value of $T\Delta S$). There is a relation between the dielectric constant and the values of the free energy change for the synergistic reaction—the values of the free energy increase with increasing dielectric constant.

The value of the organic phase reaction constant β (Table 1) decrease in going from Pr to Gd to Yb. Such results are in agreement with the fact¹⁷ that the light rare earths form more stable adducts than the heavy rare earths.

The low value of β in CHCl_3 is probably explained⁸ assuming that the self-adduct $\text{Me}(\text{PMBP})_3\text{HPMBP}$ is best shielded with a solvat layer (especially in CHCl_3) and this layer hinders interaction (2) which proceeds in the organic phase.

The negative values of ΔS° concerning equation (2) are higher than those by using of a mixture of thenoyltrifluoroacetone (*HTTA*) and *TOA*¹⁴. This indicates that a factor acts in the systems *HTTA*—*TOA* which creates a bigger disorder than in the system *HPMBP*—*TOA*. It is possible that this factor is due to the fact that one C=O group in *HPMBP* is bound with the pyrazolone ring while the two C=O groups in *HTTA* are positioned in a noncyclic side chain. As a result, the keto-enol equilibrium in the *HPMBP* systems ought to be different from that in *HTTA* and in addition, *HPMBP* is a stronger hydrophobic compound than *HTTA*. (The correctness of the latter conclusion is supported by the fact that the equilibrium constants are higher for the extraction of the lanthanide with *HPMBP* than for the extraction with *HTTA*.)

The presence of an adduct (in the case of *TOA*·HCl) catalyzes the keto-enol equilibrium¹⁵ but probably in a different degree in the presence of *HTTA* compared to *HPMBP*. The weaker hydrophobic ability of *HTTA* allows the presence of water molecules in the structure of $\text{Me}(\text{TTA})_3$ which are replaced in course of the synergistic interaction with *TOA*. HCl, enhance the disorder and cause the lower negative entropy in these extraction systems. In addition, *HTTA* is a fluorinated β -diketone which forms more stable adducts in comparison with non-fluorinated β -diketones¹⁷. Therefore the hydrates $\text{HTTA} \cdot (\text{H}_2\text{O})_n$ may be included in the organic phase resulting in a further enhancement of the disorder. It is reasonable to assume that in the stronger hydrophobic systems *HPMBP*—*TOA*·HCl the hydrate forms $\text{HPMBP}(\text{H}_2\text{O})_n$ are almost not involved and the order is higher.

From the thermodynamic functions of neutralization of *TOA* by

HCl¹⁸ one may conclude that the low entropy values resulting in the metal adducts are rather due to the neutralization between *TOA* and HCl than to the replacement of *HPMBP* with *TOA*. This means that in the case of the *HTTA*—*TOA* system *TOA* acts as a synergist while in the case of *HPMBP*—*TOA* the synergist is *TOA*·HCl.

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