Monatshefte für Chemie 118, 307—314 (1987)

Monatshefte für Chemie
Chemical Monthly

Influence of the Temperature on the Extraction of Some Lanthanides with 1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5

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(Received 19 August 1985. Accepted 17 September 1985)

The extraction of Pr, Gd and Yb with 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (H*PMBP*) diluted in $CHCl_3$, C_6H_6, and CCl_4 at 288 K, 298 K, 308 K, and 318 K has been investigated. A compound of the type *Me*(*PMBP*)$_3$H*PMBP* is formed in the organic phase. The values of the thermodynamic constants as well as of the parameters ΔH°, ΔS° and ΔG° have been determined.

(Keywords: Diluents; Lanthanides; Extraction; 1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5; Thermodynamical parameters)

Der Temperatureinfluß auf die Extraktion einiger Lanthaniden mit 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolon

Es wurde die Extraktion von Pr, Gd und Yb mit 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolon (H*PMBP*) in $CHCl_3$, C_6H_6 oder CCl_4 als verdünnendes Lösungsmittel bei 288 K, 298 K, 308 K und 318 K untersucht. Es wird eine Verbindung des Typs *Me*(*PMBP*)$_3$H*PMBP* in der organischen Phase gebildet. Die thermodynamischen Konstanten und auch die Parameter ΔH°, ΔS° und ΔG° wurden bestimmt.

Introduction

1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5 (H*PMBP*) is—in comparison with thenoyltrifluoroacetone—a relatively new chelating agent which is able to extract lanthanides and actinides from considerably more acidic solutions; this is due to the fact[1] that H*PMBP* is a stronger acid ($pK_a = 4.11$) than H*TTA* ($pK_a = 6.13$).

In spite of the comparatively numerous publications[1—13] on the use of H*PMBP* for the extraction of the trivalent lanthanides and actinides, the influence of the temperature on the established equilibria is not yet clarified.

The present study treats the influence of the temperature on the extraction of Pr, Gd and Yb with solutions of H*PMBP* in C_6H_6, $CHCl_3$ and CCl_4.

Experimental

All of the reagents used are of analytical grade (p. a.). The initial concentration of the metal cations was always $2.5 \cdot 10^{-4}$ *M*, of H*PMBP* 0.3 *M* and 0.5 *M*. The ionic strength was 0.1 *M*, maintained with (Na, H) Cl. The temperature constance was within the range of ± 1°.

Results and Discussion

The interaction between the metal ions Me^{3+}_{aq} of the water phase and the extrahent H*PMBP* diluted in the organic phase can be expressed by the equilibrium:

$$Me^{3+}_{aq} + (m+n)\mathrm{H}PMBP_{org} \rightleftharpoons Me(PMBP)_m \cdot n\mathrm{H}PMBP_{org} + m\mathrm{H}^+_{aq} \qquad (1)$$

The distribution coefficient *D*, the equilibrium concentrations of the components, the equilibrium constant *K*, and the factor *V* which comprises the influence of the activity coefficients and of the eventual by-processes of complexation, association and hydrolysis, are linked by the correlation[15]:

$$\log D = \log K - \log V + (m+n)\log[\mathrm{H}PMBP]_{org} + mpH_{aq} \qquad (2)$$

If in a definite interval of the experimental conditions the relations $\log D = f(\log[\mathrm{H}PMBP]_{org})$ and $\log D = f(pH_{aq})$ are linear, the value of $\log V$ is equal to zero[15].

The forming of the compound $Me(PMBP)_m \cdot n\mathrm{H}PMBP$ may be attributed to a process whose last stage proceeds in the organic phase:

$$Me(PMBP)_m + n\mathrm{H}PMBP \rightleftharpoons Me(PMBP)_m \cdot n\mathrm{H}PMBP \qquad (3)$$

Table 1. *Equilibrium constants for the extraction of Pr, Gd and Yb with* H*PMBP at different temperatures (estimated deviation for* log *K is equal to* ± *0.1)*

Metal	Diluent	288 K	298 K	308 K	318 K
Pr	CCl_4	—3.4	—3.2	—3.0	—2.8
	C_6H_6	—4.2	—4.0	—3.8	—3.6
	$CHCl_3$	—4.5	—4.3	—4.1	—
Gd	CCl_4	—2.5	—2.3	—2.1	—1.9
	C_6H_6	—3.1	—2.9	—2.7	—2.5
	$CHCl_3$	—3.4	—3.2	—3.0	—
Yb	CCl_4	—1.5	—1.3	—1.2	—1.0
	C_6H_6	—1.9	—1.7	—1.6	—1.4
	$CHCl_3$	—2.4	—2.2	—2.1	—

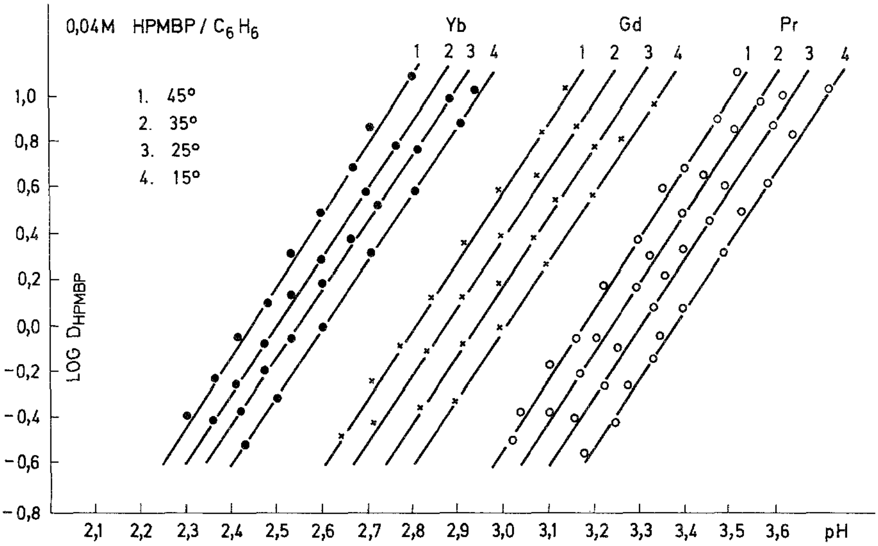

Fig. 1. Dependence of log *D* vs. *pH* for the extraction of Yb, Gd, and Pr

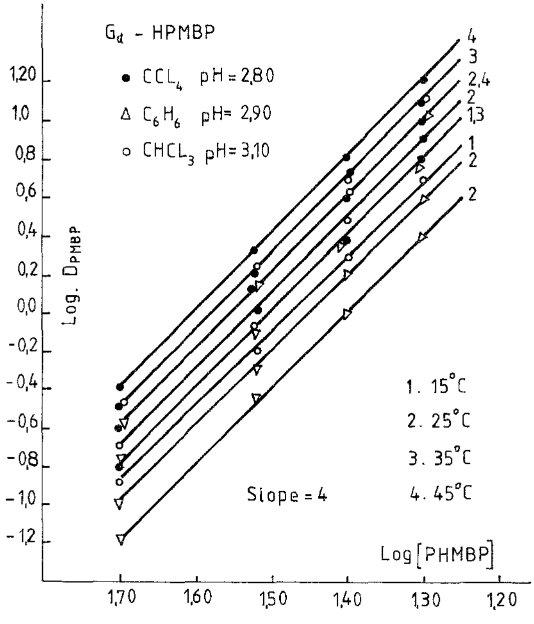

Fig. 2. Dependence of log *D* vs. log [H*PMBP*] for the extraction of Gd with H*PMBP* in different diluents

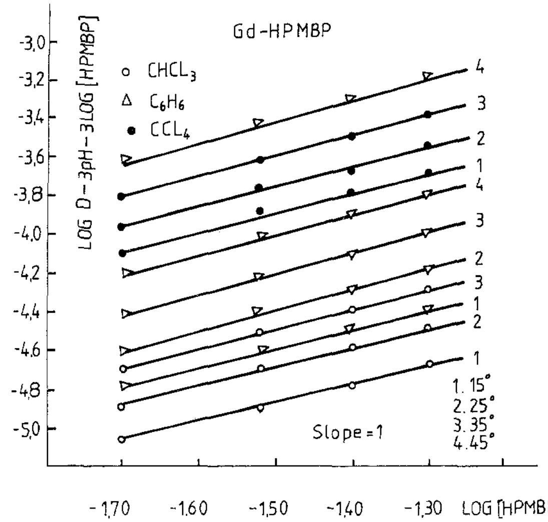

Fig. 3. Dependence of $\log D - 3pH - 3\log[\mathrm{H}PMBP]$ vs. $\log[\mathrm{H}PMBP]$ for the extraction of Gd

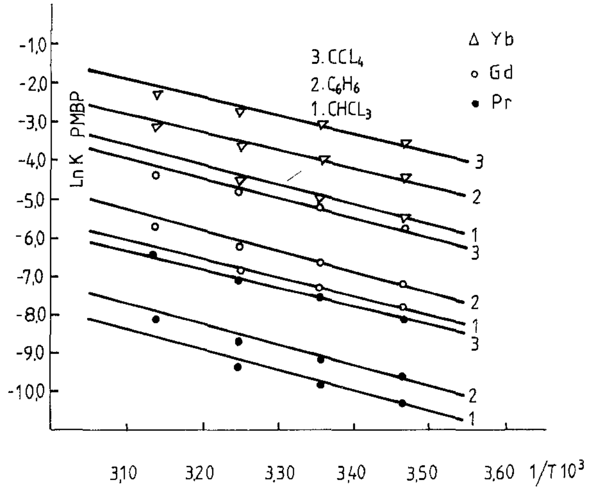

Fig. 4. Dependence of $\ln K_{PMBP}$ vs. $1/T$ for the extraction of Yb, Gd, and Pr

The relation $\log D = f(pH_{aq})$ has a slope equal to 3 (Fig. 1) and the slope of the straight lines $\log D = f([\mathrm{H}PMBP]_{org})$ is equal to 4 (Fig. 2). This means that the value of m in (1) and (2) is equal to 3 and of $m + n$ equals 4. The functional relation $\log D - 3pH - 3\log[\mathrm{H}PMBP] = f(\log[\mathrm{H}PMBP])$ has a slope equal to 1 and this indicates[14] that the number of the extra molecules in the self-adduct is one: *Me(PMBP)*$_3$H*PMBP*.

Table 1 shows the values of $\log K$ as a result of using the relation (2) and after processing the experimental results by means of a least squares method.

From these values, and using the equation $\ln K = —(\Delta H^\circ/R)(1/T) + \Delta S^\circ/R$, the changes of enthalpy ΔH° and entropy ΔS° for the extraction process have been calculated and then compared with the standard free energy changes $\Delta G^\circ_{298} = —RT \ln K_{298}$ calculated for 298.15 K (Fig. 4 and Table 2).

Table 2. *Thermodynamic parameters for the extraction of Pr, Gd and Yb with* H*PMBP (estimated deviation for* $\Delta H^\circ \leqslant 0.4$ *kJ/mol,* $\Delta S^\circ \leqslant 1.4$ *J/mol K,* $\Delta G \leqslant 1.1$ *kJ/mol)*

Metal	Diluent	H° (kJ/mol)	S° (J/mol K)	G° (kJ/mol)
Pr	CCl_4	34.8	55.6	18.2
	C_6H_6	34.8	40.3	22.8
	$CHCl_3$	34.8	34.6	24.5
Gd	CCl_4	28.2	51.7	12.9
	C_6H_6	34.8	61.3	16.5
	$CHCl_3$	34.8	55.6	12.9
Yb	CCl_4	29.1	72.0	7.7
	C_6H_6	27.8	60.5	9.7
	$CHCl_3$	28.3	52.6	12.8

It is evident that by using the same diluent, the extraction step increases in the order: Pr—Gd—Yb and this tendency may be ascribed to the "lanthan shrinkage" as well as to the polarizing effect of the respective ions[16].

When various diluents are used the equilibrium constants increase with decreasing solvent polarity. It seems that there is no proportionality between the values of the equilibrium constants when using various diluents as well as between the dielectric constants of $CHCl_3$, C_6H_6 and CCl_4 (which are 5.20, 2.30 and 2.24, respectively). There is no such correspondence in the comparison of the mutual solubility of the organic and the water phases (the solubility of C_6H_6 and CCl_4 in water are equal) as well as in the comparison between the standard entropies of the diluents alone.

Therefore the observed non-proportionality between the values of the equilibrium constants as well as of the main parameters of the diluents should be attributed to the change of the thermodynamic parameters during the extraction process.

Since the enthalpy change for various diluents (Table 2) is practically the same, the decisive factor determining the value of the extraction equilibrium constant is the entropy change. In the realization of the extraction process, the entropy in all investigated systems increases; this is due to the mutual solubility of the two phases, to the destruction of the hydrate shell around the metal cations in the water phase, to the bond breaking in the complexes (which are initially present in the both phases), to the appearance of new complex compounds in the organic phase, and so on.

The increase of entropy with $CHCl_3$ does not correlate with the polarities of the diluents indicating an additional effect. This might be due to the capability of chloroform[17] to form hydrates $CHCl_3 \cdot 18\,H_2O$.

For Gd the influence of the diluents on the entropy change are inversed ($CHCl_3 \lesssim CCl_4 < C_6H_6$), i.e. when CCl_4 or $CHCl_3$ are used, the order in the extraction system is higher than by using benzene. $CHCl_3$ and CCl_4 are included as solvates into the composition of the extracted complexes of Pr, Gd and Yb and decrease the entropy of the system. The particle sizes of the self-adducts correlate with the atoms and the ion radii of the extracted metals; small sized ions built up smaller complex units, but the stronger polarizing ability of the smaller ion can determine also an opposite effect. Hence, when $CHCl_3$ is used as a diluent, the self-adduct of Gd coordinates molecules $CHCl_3$ as well as $CHCl_3 \cdot 18\,H_2O$. The entropy of the formed solvated self-adducts (Table 2) is larger than the entropy of the solvated self-adducts of Pr and Yb because they coordinate either only $CHCl_3 \cdot 18\,H_2O$ or $CHCl_3$.

Since carbon tetrachloride gets not hydrated, the solvation of all self-adducts is characterised by only one type of particles. This decrease in entropy results is in a relative correspondence with the change of the atom (ionic) radii of Pr, Gd and Yb as well as of their self-adducts; however, some deviations are found for Gd. This deviation is probably due to the presence of a half filled (seven electrons) 4f—shell.

A comparison with the extraction of Pr, Gd, and Yb with thenoyltrifluoroacetone (H*TTA*)[21] shows the following differences:

The values of the free energy changes and the extraction constant changes indicate that H*PMBP* is a better extrahent for lanthanides than H*TTA*, which is probably due to the relatively hydrophobic character of H*PMBP* and to the autosynergism[22] of its molecules.

The thermodynamic parameters reflect that the H*TTA* system is more arranged (negative values of entropy) than the H*PMBP* system (positive values of entropy). It has been estimated that the change of the entropy factor $T\Delta S$—caused by the bonding of one hydrate water molecule—is equal to 15–17 kJ/mol. The relatively low values of entropy change (Table 2) indicate that rthe formation of the self-adduct metal chelate with H*PMBP* is accompanied by liberation of a maximum of one water molecule; the destruction of the hydratation layer around the complex causes a substantial increase in entropy. The weaker hydrophobity of H*TTA* permits the presence of water molecules in the structure of $Me(TTA)_3$; this hydration shell is stable because no self-adduct is formed (the system is characterized by a lower entropy).

The values of the entropy changes indicate that in contrast to H*PMBP* systems the H*TTA* extraction systems are most arranged when the least polar diluent CCl_4 is used. It should be expected for the H*TTA* systems that the disorder would be the greatest when $CHCl_3$ is used (because its dielectric constant is higher); however, the entropy change in the presence of $CHCl_3$ is almost the same as in CCl_4. This is due to the possibility of $CHCl_3$ to form hydrogen bonds and to the solvatation of the H*TTA* complex.

The established positive values of the enthalpy change correspond to the assumption that the bond energy of the hydrated metal cations in the water phase is higher than the bond energy of the metal chelates in the organic phase[19, 20]. In every of the extracted systems the disorder and entropy enhancement is not able to prevail over the positive enthalpy change and this determines the positive values of the free energy ΔG°. However, these positive values are relatively low and therefore the extraction process is proceeding spontaneously. However, the estimated equilibria are characterized by relatively low equilibrium constants.

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