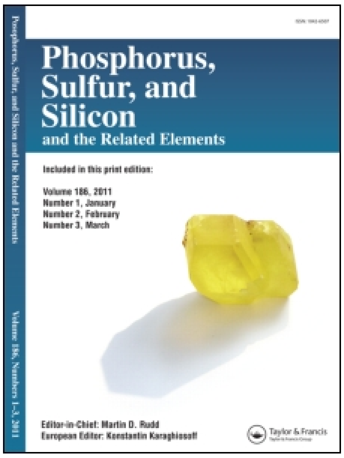

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INFLUENCE OF THE TEMPERATURE ON THE SOLVENT EXTRACTION OF SOME LANTHANIDE PICRATES BY A POSPHORYLATED CALIX[4]ARENE

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The extraction of four lanthanide (La, Pr, Nd and Eu) picrates from water into 1,2-dichloroethane using 5,11,17,23 -tetra-*tert*-butyl-25,26,27,28-tetrakis(diphenylphosphinoylmethoxy)calix[4]arene as extracting agent has been studied. The extraction process takes place via formation of a species having a 1:1:3 metal/ligand/picrate ratio. The investigation of the extraction as a function of temperature between 10–25°C reveals that the distribution ratio of metal ions decreases with increasing temperature. Thermodynamic parameters such as the free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes were evaluated from the distribution measurements. The extraction process in all cases is exothermic with positive entropy changes.

Keywords: calix[4]arene; phosphoryl; rare earths; solvent extraction; thermodynamics

INTRODUCTION

Calixarenes[1] are cyclic oligomers made up of phenol units. They have been used as useful basic skeletons for the preparation of ionophoric receptors[2–4]. Recent studies demonstrate that multiphosphorylated calixarene ligands provide interesting possibilities for the extraction and transport of lanthanides and actinides[5–12].

In our previous work we examined the extractive properties of some calix[4]arenes containing phosphoryl moieties towards rare-earth metal ions in the presence of nitrate [8–9] and picrate[11] ions. Among the calixarenes studied, 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(diphenyl-

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phosphinoylmethoxy)calix[4]arene (**1**) (Fig. 1) has shown the best extraction abilities in terms of extractability and selectivity.

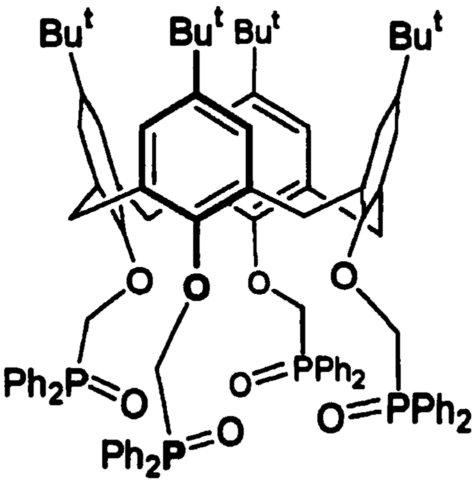

FIGURE 1 5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(diphenylphosphinoylmethoxy)-calix[4]arene (**1**)

In the present study we have looked at the influence of the temperature in the range 10–25°C on the extraction of La(Pic)$_3$, Pr(Pic)$_3$, Nd(Pic)$_3$ and Eu(Pic)$_3$ (Pic = picrate ion) from water into 1,2-dichloroethane solution of **1**. Using the distribution data the free energy, enthalpy and entropy changes associated with the extraction process are calculated.

EXPERIMENTAL

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(diphenylphosphinoylmethoxy)calix[4]-arene (**1**) has been synthesized according to the procedure reported previously by Matt *et al.*[13]. Lanthanide picrates were prepared based on the methods described by Harrowfield *et al.*[14]. All other reagents used were experimental products. Solvents were washed three times with distilled water in order to remove their stabilizers before used in the extraction experiments. The solvent extraction experiments were carried out in stoppered glass tubes immersed in a thermostated

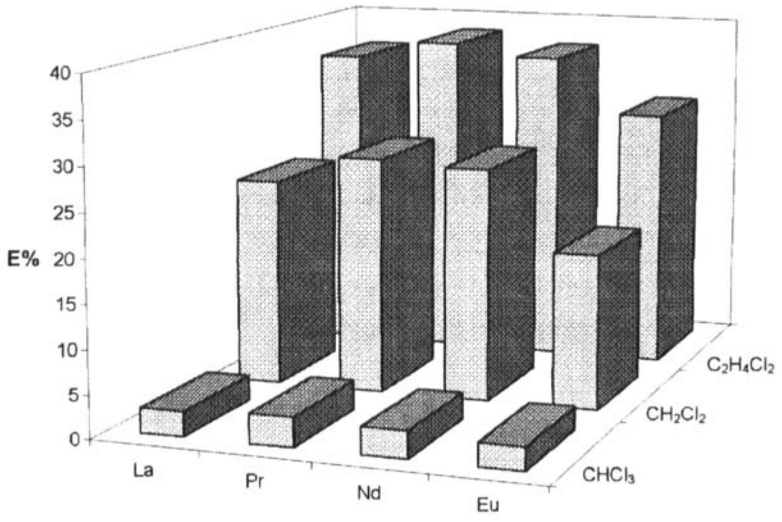

FIGURE 2 Extraction percentage of aqueous solutions of lanthanide picrates (2.5×10^{-5} M) by **1** (2.5×10^{-5} M) in various diluents at 25°C

water bath (± 0.1°C) using equal volumes (10 mL) of the aqueous and the organic phase. The extraction equilibrium was reached after 20 minutes magnetic stirring. This period of shaking was taken as long enough to establish the equilibrium, since shaking periods of 15, 20 and 25 minutes gave essentially identical results. The mixture was subsequently allowed to stand for 10 minutes to complete the separation. The concentration of the extracted metal was determined indirectly by measuring the picrate ion concentration in the aqueous phase spectrophotometrically (355 nm, $\varepsilon = 14416$ L mol^{-1} cm^{-1}[15]) before and after the extraction experiments. There was no significant extraction of metal picrates in the absence of the ligand in the organic phase.

RESULTS AND DISCUSSION

The abilitiy of calixarene **1** to extract lanthanide picrates has been tested by measuring the extraction efficiency (E%) from aqueous solutions of lanthanum, praseodymium, neodymium and europium picrates (2.5×10^{-5} M) by the ligand (2.5×10^{-5} M) in 1,2-dichloroethane. The ligand shows a better extraction efficiency (Fig. 2) towards lanthanide ions (≈40%) which is more efficient than the tetraphosphate-calix[4]arene (≈20%)[15].

It is well known that the diluent polarity could affect the extraction efficiency of a ligand in the extraction processes[16]. Figure 2 also shows the extraction percentages of the metal picrates by **1** in chloroform, dichloromethane and 1,2-dichloroethane. The polarity of the diluents is 4.9, 8.9 and 10.4 for the diluents, respectively[16]. It is seen that the extraction percentages are increased with the polarity of the diluents.

The extraction equilibrium for trivalent lanthanides (M^{3+}) with a neutral ligand (L) in the presence of picrate ions (Pic^-) can be described by:

$$M^{3+}_{aq} + 3Pic^{-}_{aq} + nL_{org} \rightleftharpoons ML_n(Pic)_3\,_{org} \tag{1}$$

The corresponding extraction constant can be written as:

$$K_{ex} = \frac{[ML_n(Pic)_3]_{org}}{[M^{3+}]_{aq}[Pic^-]^3_{aq}[L]^n_{org}} \tag{2}$$

By introducing the distribution ratio,

$$D = \frac{[M]_{org}}{[M]_{aq}} = \frac{[ML_n(pic)_3]_{org}}{[M^{3+}]_{aq}} \tag{3}$$

the logarithmic form of equation 2 becomes:

$$\log\frac{D}{[Pic^-]^3_{aq}} = \log K_{ex} + n\log[L]_{org} \tag{4}$$

Thus a plot of $\log\frac{D}{[Pic^-]^3_{aq}}$ as a function of $\log[L]_{org}$ gives a straight line of unit slope and the extraction equilibrium constant K_{ex} is calculated from the intercept.

In order to characterize the stoichiometry of the extracted species and to calculate the thermodynamic parameters the extraction experiments of aqueous lanthanum, praseodymium, neodymium and europium picrates by **1** in 1,2-dichloroethane as a function of ligand concentration at different temperatures were carried out (Fig. 3). For all the systems studied the slope is in agreement with a metal/ligand/picrate ratio of 1:1:3 (n=1). The present data confirm our previous results in the extraction of lanthanides with **1** in 1,2-dichloroethane in the presence of nitrate ions[8]. The analysis

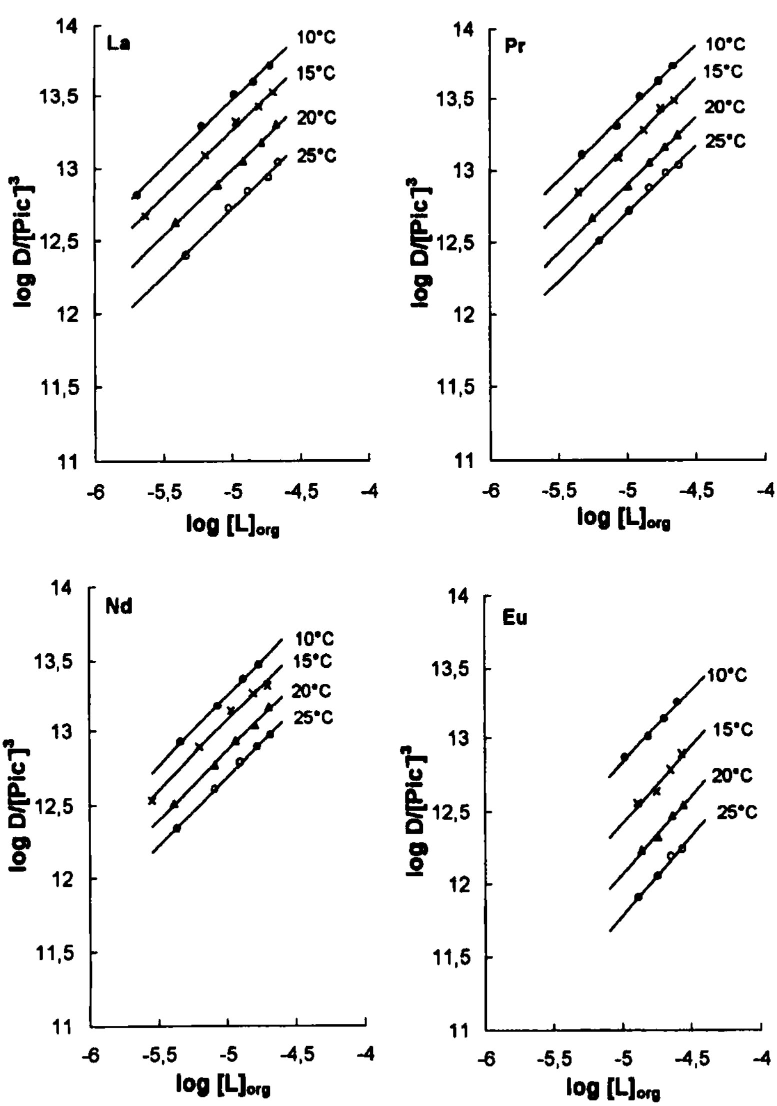

FIGURE 3 Extraction of aqueous La(Pic)$_3$, Pr(Pic)$_3$, Nd(Pic)$_3$ and Eu(Pic)$_3$with 1 in 1,2-dichloroethane at various ligand concentrations and at different temperatures

of the extraction data gives the log K_{ex} values at different temperatures. The calculated values are listed in Table I. It is seen that the extraction constants decrease with increasing temperature.

TABLE I Logarithm of the extraction equilibrium constant at 10–25°C for solvent extraction of aqueous lanthanum, praseodymium, neodymium and europium picrates with **1** in 1,2-dichloroethane

Cation	*log K_{ex}*			
	10°C	*15°C*	*20°C*	*25°C*
La^{3+}	18.09	17.84	17.53	17.30
Pr^{3+}	18.16	17.91	17.62	17.40
Nd^{3+}	18.12	17.89	17.57	17.34
Eu^{3+}	17.90	17.68	17.40	17.20

The free-energy changes (ΔG°) for the extraction equilibrium (equation 1) are calculated using the equilibrium constant K_{ex} by equation 5,

$$\Delta G^\circ = -RT \ln K_{ex} \tag{5}$$

The free-energy changes are related to the enthalpic (ΔH°) and entropic changes (ΔS°) through the Gibbs-Helmholtz equation [17]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{6}$$

Combining equations 5 and 6, we obtain equation 7 which describes the temperature dependence of K_{ex},

$$\log K_{ex} = \left(\frac{1}{2.303}R\right)\left(\Delta S^\circ - \frac{\Delta H^\circ}{T}\right) \tag{7}$$

TABLE II Thermodynamic parameters at 25°C in kcal mol^{-1} for the solvent extraction of aqueous lanthanum, praseodymium, neodymium and europium picrates with **1** in 1,2-dichloroethane

Cation	*-ΔG°*	*-ΔH°*	*-TΔS°*
La^{3+}	23.60	20.67	−2.93
Pr^{3+}	23.73	20.00	−3.72
Nd^{3+}	23.66	20.42	−3.23
Eu^{3+}	23.45	18.41	−5.04

The thermodynamic parameters can be determined by plots of the log K_{ex} values as a function of 1/T (Fig. 4). The thermodynamic parameters obtained are listed in Table II. It can be seen from the data that the extraction of all lanthanide picrates studied is exothermic in nature. The extraction of all metal picrates is favored by high negative enthalpy and positive entropy changes.

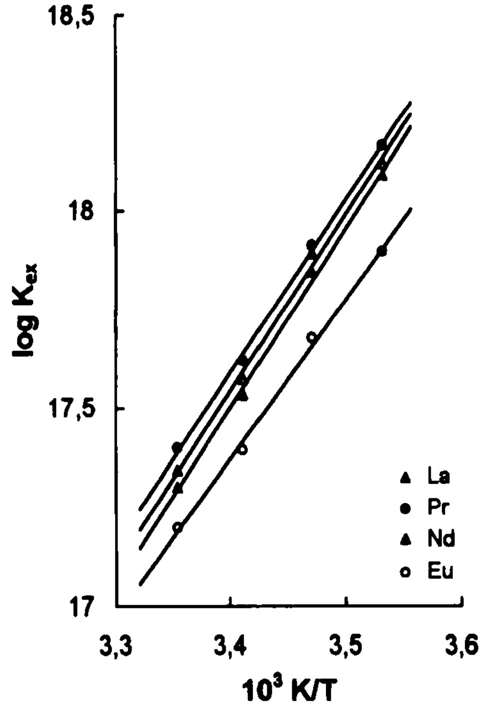

FIGURE 4 Plots of log K_{ex} vs. T^{-1} for the solvent extraction of $La(Pic)_3$, $Pr(Pic)_3$, $Nd(Pic)_3$ and $Eu(Pic)_3$ with 1 in 1,2-dichloroethane

In the solvent extraction processes the formation of extractable species is inherently unfavorable from the entropic aspects. This process is driven first by the enthalpic gain from the electrostatic interactions of the metal ion and the donor atoms of the ligand.

Another factor favoring the extraction is the positive entropy change in the step of dehydration of ions during the formation of the extracted species. The positive entropy changes for all cases in our experiments reveal that the dehydration of high degree hydrated lanthanide and picrate ions must be fairly extensive. The results show that a decrease in entropy changes caused by the formation of the extracted species is compensated effectively by the increasing entropy in the dehydration process. A positive entropy change has also been observed in the extraction of highly hydrated tetravalent plutonium ions in a nitric acid medium by diethyl sulfoxide[18].

Acknowledgements

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References

[1] C. D. Gutsche, Calixarenes, *Monographs in Supramolecular Chemistry*, J. F. Stoddart (Ed.), Royal Society of Chemistry, Cambridge (1989).

[2] J. Vicens and V. Böhmer, *Calixarenes: A Versatile Class of Macrocyclic Compounds*, Kluwer Academic Publishers, Amsterdam (1991).

[3] V. Böhmer, *Angew. Chem., Int. Ed. Engl.*, **34**, 713 (1995); *Angew. Chem.* **107**, 785(1995).

[4] C. Wieser, C. B. Dieleman and D. Matt, *Coord. Chem. Rev.*, **165**, 93 (1997).

[5] J. F. Malone, D. J. Marrs, M. A. McKervey, P. O'Hagan, N. Thompson, A. Walker, F. Arnaud-Neu, O. Mauprivez, M.-J. Schwing-Weill, J.-F. Dozol, H. Rouquette and N. Simon, *J. Chem. Soc., Chem. Commun.*, 2151(1995).

[6] F. Arnaud-Neu, V. Böhmer, J.-F. Dozol, C. Grüttner, R. A. Jakobi, D. Kraft, O. Mauprivez, H. Rouquette, M.-J. Schwing-Weill, N. Simon and W. Vogt, *J. Chem. Soc., Perkin Trans. II*, 1175 (1996).

[7] J. M. Harrowfield, M. Mocerino, B. J. Peachey, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1687 (1996).

[8] M. R. Yaftian, M. Burgard, D. Matt, C. B. Dieleman and F. Rastegar, *Solvent Extr. Ion Exch.*, **15**, 975 (1997).

[9] M. R. Yaftian, M. Burgard, C. Wieser, C. B. Dieleman and D. Matt, *Solvent Extr. Ion Exch.*, **16**, 1131 (1998).

[10] M. R. Yaftian, M. Burgard, D. Matt and C. B. Dieleman, *J. Membr. Sci.*, **144**, 57 (1998).

[11] C. B. Dieleman, D. Matt, I. Neda, R. Schmutzler, A. Harriman and M. R. Yaftian, *J. Chem. Soc., Chem. Commun.*, 1911 (1999).

[12] F. Arnaud-Neu, J. K. Browne, D. Byrne, D. J. Marrs, M. A. McKervey, P. O'Hagan, M.-J. Schwing-Weill and A. Walker, *Chem. Eur. J.*, **5**, 175 (1999).

[13] C. B. Dieleman, D. Matt, and P. G. Jones, *J. Organomet. Chem.*, **545–546**, 461 (1997).

[14] J. M. Harrowfield, W. Lu, B. W. Skelton and A.H. White, *Aust. J. Chem.*, **47**, 3212 (1994).

[15] F. Arnaud-Neu, S. Cremin, D. Cunningham, S.J. Harris, P. McArdle, M.A. McKervey, M. McManus, M.-J. Schwing-Weill and K. Ziat, *J. Incl. Phenom.*, **10**, 329 (1991).

[16] J. Rydberg, C. Musikas and G, R. Choppin, *Principles and Practice of Solvent Extraction*, Marcel Dekker, New York (1992).

[17] Y. Inoue, F. Amano, N. Okada, H. Inada, M. Ouchi, A. Tai and T. Hakushi, *J. Chem. Soc., Perkin Trans. II*, 1239 (1990).

[18] G. R. Mahajan, M. S. Murali, D. R. Prabhu, J. P. Shulka, G. M. Nair and P. R. Natarajan, *Thermochim. Acta*, **180**, 185 (1991).