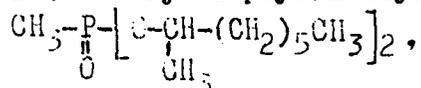


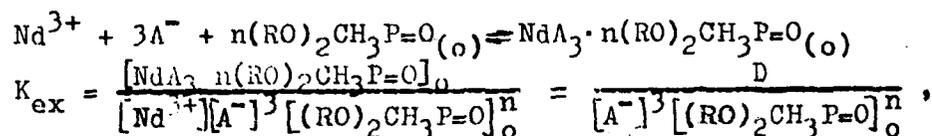
Chun-Hui Huang, Rong-Fang Xu, Hai Guo and Guang-Xian Xu, Research
 Centre of Rare Earth Chemistry, Peking University, China

Di(1-methyl-heptyl)methyl phosphonate



whose trade name is P-350, was developed in the sixties in China as an efficient neutral organophosphonate extractant. Although it finds wide application in industry for separation of light rare earths, investigation into extraction mechanism are nearly unknown [1]. Presented in this report is the determination of thermodynamic constants for the extraction of $\text{Nd}(\text{NCS})_3$, $\text{Nd}(\text{ClO}_4)_3$ and $\text{Nd}(\text{NO}_3)_3$ with P-350. A comparison is made between the structures of the extracted complexes and the corresponding solid complexes using triphenyl phosphine oxide as a model molecule of P-350, and the IR data of the saturated organic phases and the solid complexes have been discussed as well.

The thermodynamic research on extraction systems. The distribution ratios have been determined for the extraction of neodymium salts with P-350 for various P-350 concentrations using either kerosene or hexane as diluents, and using either NaNCS , NaClO_4 or NaNO_3 as salting out agents. The extraction reactions may be represented as follows:



where A^- designates NCS^- , ClO_4^- or NO_3^- . K_{ex} is the concentration equilibrium constant, and D is the distribution ratio. Then we have:

$$\log D = \log K_{\text{ex}} + n \log [(\text{RO})_2\text{CH}_3\text{P}=\text{O}]_0 + 3 \log [\text{A}^-]$$

The unknowns K_{ex} and n can be solved through slope analysis. Data show that the ratios of P-350 to Nd are equal to 3 for the extracted complexes, and the differences among the extraction equilibrium constants for the various systems for a given diluent are large. The value of K_{NCS^-} , $K_{\text{NO}_3^-}$ or $K_{\text{ClO}_4^-}$ is 50.56, 0.401 or 0.220 respectively.

According to the thermodynamic equation $\Delta G^\circ = RT \ln K$, the change or Gibbs free energy of extraction can be calculated. By using a direct static measurement with a Calvent calorimeter, the changes of enthalpy of all these extraction reactions have been obtained [2]. Consequently, the entropy changes can be calculated. The results are listed in Table 1. It can be seen that the extraction reaction of $\text{Nd}(\text{NCS})_3$ with P-350 is the only reaction which reacts spontaneously under standard state conditions, while the other two have positive free energy changes ΔG° . On the other hand, they are all exothermic reactions. Among them, the extraction reaction of $\text{Nd}(\text{ClO}_4)_3$ with P-350

is worthy of notice, since it has a remarkably large absolute value of ΔH° . All of the entropy changes are negative, that is, the disorders of the systems are relatively decreased after reaction.

Table 1. The thermodynamic parameters of the extraction reactions

System	ΔG° , KJ/mol	ΔH° , KJ/mol	ΔS° , J/mol K
P-350(hexane)-Nd(NCS) ₃	-9.719	-29.92	-67.78
P-350(hexane)-Nd(ClO ₄) ₃	3.752	-74.31	-261.9
P-350(hexane)-Nd(NO ₃) ₃	2.265	-22.69	-83.68

IR spectra. Hexane solutions of P-350 saturated with Nd(NCS)₃, Nd(ClO₄)₃ or Nd(NO₃)₃ and the respective solid complexes of triphenyl phosphine oxide (KBr window) were examined for infrared absorption in the range of 400-4000 cm⁻¹ by a Nicolet 7199B FTIR spectrometer. The characteristic absorption bands of the phosphoryl in these systems are listed in Table 2. The data show that these characteristic bands have been shifted towards lower wave number after coordination in either the saturated organic phases or in the solid complexes. It is very interesting that the perchlorate system have relatively large shifts in comparison with the other systems. This fact indicates that the structures of liquid saturated organic phase and the corresponding solid complexes are somewhat similar even though they are not exactly the same in composition. This phenomenon agrees well with the observation on the quaternary ammonium salt systems studied previously in our laboratory [6].

Table 2. Characteristic absorption bands of the P=O

Complex in hexane	Band of P=O, cm ⁻¹	$\nu_{P=O}$ shift	Complex in KBr	Band of P=O, cm ⁻¹	$\nu_{P=O}$ shift
P-350	1247.2		Ph ₃ P=O	1190.0	
A [⊖]	1183.9	63.3	D	1153.5	36.5
B	1177.3	69.9	E	1138.4	51.6
C	1184.5	62.7	F	1149.1	40.9

[⊖] A = Nd(NCS) ₃ .3(P-350)	B = Nd(ClO ₄) ₃ .3(P-350)
C = Nd(NO ₃) ₃ .3(P-350)	D = Nd(NCS) ₃ .4(Ph ₃ P=O)
E = Nd(ClO ₄) ₃ .4(Ph ₃ P=O)	F = Nd(NO ₃) ₃ .2(Ph ₃ P=O).C ₂ H ₅ OH

It is noted that the ratios of P-350 to Nd in hexane solution are lower than that for triphenyl phosphine oxide to Nd in solid complexes shown in Table 2. This may be caused by the replacement of P-350 by water while maintaining the same coordination number and the structure of the respective solid complexes. This is supported by the IR spectra of the saturated organic phases, in which strong broad bands appear in the region around 3300 cm^{-1} .

Discussions. In the cases of the extraction of $\text{Nd}(\text{NCS})_3$, $\text{Nd}(\text{ClO}_4)_3$ and $\text{Nd}(\text{NO}_3)_3$ with P-350, the reactions have the same Nd^{+3} cation, but have anions of differing size, of which ClO_4^- is the largest. Thus the reaction involving ClO_4^- has the largest hollow enthalpy and the smallest hydration enthalpy. Besides these two terms, the structure of the extracted complex in the perchlorate system has another peculiarity. It is known that the $\text{Ph}_3\text{P}=\text{O}$ is not bonded with a neutral molecule, but with a $\text{Nd}(\text{ClO}_4)_2^+$ cation in the solid state complex [4]. This cation has a relatively stronger attraction for the phosphoryl oxygen than either of the neutral molecules $\text{Nd}(\text{NCS})_3$ [3] or $\text{Nd}(\text{NO}_3)_3$ [5]. It has been observed experimentally that the $[\text{Nd}(\text{ClO}_4)_2 \cdot 4\text{Ph}_3\text{P}=\text{O}]^+$ cation, in comparison with the other two complexes, has the shortest $\text{Nd}-\text{O}_p$ bond length and the largest shift in IR spectra after coordination of the phosphoryl oxygen. This produces a more favorable condition in the exothermal reaction. This is why the largest exothermal heat has been observed in the extraction of $\text{Nd}(\text{ClO}_4)_3$ with P-350.

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