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α,β-Substituent effect of dialkylphosphinic acids on lanthanide extraction†

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In this work, the effect of the substituent at the α or β position in dialkylphosphinic acids on the extraction of trivalent lanthanide ions was investigated using experimental and theoretical methods. Five dialkylphosphinic acids were synthesized. Their extractions of seven trivalent lanthanide ions, La/Pr, Nd/Dy, and Ho/Yb/Lu, which represent light, middle, and heavy rare-earth metals, were explored. A simplified coordination model was built to explore the bonding between the extractants and lanthanide ions. The results obtained using this model generally explained the experimental results. The model could therefore be used to study the effects of the α and β substituents of extractants on their extraction properties. The theoretical and experimental results indicate that the significance of a β substituent in the dialkylphosphinic acid on extraction was greater than that of an α substituent.

1. Introduction

Solvent extraction is important in rare-earth separation and purification. The effectiveness of the extraction depends mainly on the structure of the extractant. It is therefore necessary to explore structure–property relationships to improve or develop efficient extractants.[1]

Acidic phosphorus-based extractants such as P204, P507, and Cyanex272 are widely used in rare-earth separation and nuclear-waste processing.[2–4] The extraction performances of these compounds depend on the electronic properties of the reaction groups on the phosphorus, and are closely related to the structure of the alkyl substituent. The extraction behavior can therefore be adjusted through modification of the alkyl groups.[5,6] The effects of the α and β substituents adjacent to the phosphorus on the extraction performance are greater than those of substituents at the end position; for example, the lanthanum extraction equilibrium constant K_{ex} for *n*-octyl isopropylphosphonate is 8.94×10^{-2} compared with 1.67×10^{-3} for 1-methylheptyl isopropylphosphonate (α-methylated), 7.07×10^{-3} for 2-ethylhexyl isopropylphosphonate (β-ethylated), and 1.37×10^{-2} for *n*-dodecyl isopropylphosphonate (with an end *n*-butyl group).[7] Similarly, the normalized K_{ex} values for europium are 25 000 for 2-ethylhexyl *n*-octylphosphonate, 1650 for 2-ethylhexyl 2-ethylhexylphosphonate, and 800 for 2-ethylhexyl 1-methylheptylphosphonate. The extraction behaviors of these three extractants differ because of the presence of an end, α, or β alkyl group.[6] The α and β substituents, which are closer to the coordination centers of the extractants, not only affect the solubilities of the extractants and the corresponding extraction complexes, but also modify their respective coordination properties with metal ions. The α or β substituents are often adjusted to obtain the desired extraction performance.

Yuan *et al.* investigated the structure–property relationships of phosphorus-containing extractants; such relationships are useful in designing extractant structures.[1,6,8] They found that factors such as Hammett plots, logarithms of the acid dissociation constants, infrared spectra, and Taft parameters are directly related to the extraction ability of an extractant.[5,6] Their investigation of Hückel molecular orbitals showed that the bonding between coordinating atoms and metal ions is closely related to the electronic densities of the coordinating atoms.[9,10] Kolařík *et al.* showed experimentally that the extraction ability decreased greatly with increasing alkyl-chain branching, but was not affected by the chain length.[11] Many other similar results have also been reported, and are helpful in understanding extraction behavior. However, most of these studies were confined to summarizing the experimental results because of the limits of the experimental techniques. It is therefore difficult to deeply understand the effect of the extractant structure on ligand–metal interactions.

The thermodynamic energy of a coordination reaction can be used to quantify ligand–metal interactions, and can also be applied to extraction processes.[12] Nash *et al.* used isothermal titration microcalorimetry to measure the extraction enthalpies

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† Electronic supplementary information (ESI) available: Table S1 collected the dimerization energies and structure parameters of monomers and dimers, while Table S2–S4 for the structure parameters of SM, DM, and DD model complexes, respectively. Fig. S1 shown the experimental extraction equilibrium constants, lg *K*, and the calculational first stability equilibrium constants of SM (lg K_1^{SM}), DM (lg K_1^{DM}), and DD (lg K_1^{DD}). Fig. S2–S6 shown the ball and bond type geometries of all structures, and the complete Gaussian 09 reference is given. The Synthesis and Characterization is also brief described. See DOI: 10.1039/c6ra10214j

of lanthanide ions with bis(2-ethylhexyl)phosphoric acid, and calculated the corresponding entropies and free energies based on previous reports.[13] They found that the interactions between extractants and metal ions were related to the thermodynamic energies of the extraction reactions. However, it is difficult to calculate these thermodynamic parameters directly and accurately. Extractants usually have long alkyl groups to achieve the required lipophilicity; therefore, extraction complexes often form large molecules with numerous conformations.[14,15] Moreover, a large number of coordination configurations can arise from the same experimental stoichiometry. It is impractical to compute and compare these microstructures one by one, therefore various simplified models have been reported for theoretical investigations of ligand–metal interactions; for example, only the first coordination shell of the central metal was considered,[16] the alkyl substituents were simplified,[17] and stepwise equilibrium constants were used.[18–20] These models provide significant guidance for theoretical studies of these interactions.

Since the successful application of dialkylphosphoric acids and alkyl alkylphosphonates such as P204 and P507 in rare-earth separation and purification, dialkylphosphinic acids have attracted much interest because of their lower stripping acidities and because they give more effective separations of heavy rare earths.[2,21,22] In this work, a simplified coordinated model was proposed to investigate the extraction and separation behavior of several dialkylphosphinic acids on trivalent lanthanide ions. Based on the experimental and theoretical results, the substitution effect was discussed.

2. Experiment and calculation sections

2.1. Experimental details

Synthesis. The five dialkylphosphinic acids were synthesized according to previous reports (Table 1), and the detail was added in section 5 of ESI.†[21]

Extraction equilibrium. The extractants were dissolved in *n*-dodecane to give a 0.2 mol L^{-1} solution. Dicyclohexylphosphinic acid is insoluble in *n*-dodecane, therefore toluene was used as a diluent to promote dissolution. Aqueous chloride solutions of rare earths (La, Pr, Nd, Dy, Ho, Yb, and Lu) were prepared by dissolving their oxides in concentrated hydrochloric acid, then diluted to 0.005 mol L^{-1} with deionized water. Equal volumes of the organic phase and aqueous phase were shaken for 30 min in a separating funnel at 25 °C.

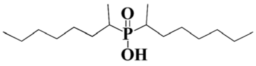
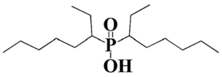
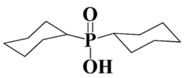
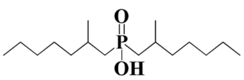
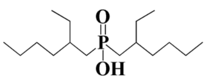
Analysis. The lanthanides were examined spectrophotometrically (using arsenazon(III)) or by using inductively coupled plasma atomic emission spectrometry, depending on their concentrations. When the extraction distribution ratio was low, the lanthanide concentrations in the organic phase were estimated by stripping with concentrated hydrochloric acid. The concentration equilibrium constants K were calculated as described in previous reports and used to evaluate extractability and selectivity.[21,22]

Automatic titration of pK_a. Ethanol (75%, 47.5 mL) was added to dialkylphosphinic acid (0.5 mmol), and the mixture was titrated with NaOH solution (0.1000 mol L^{-1}).[23] The pK_a values were automatically calculated using an automatic titrator (Table 1).

2.2. Computational details

All geometries were fully optimized at the B3PW91 theory level in a vacuum.[24] The vibrational frequency was computed for each structure to determine whether it was a minimum point (no imaginary frequency). The conformation with the lowest free energy was selected for molecules with more than one possible conformation. The 6-31+G* basis set was used for other carbon and hydrogen atoms on alkyl groups, and the 6-311++G** for others except lanthanoids.[25,26] The large-core relativistic effective core potential with 4f electrons in the core, developed by Dolg *et al.*, was used for the lanthanides.[27] Natural bond orbital analysis was performed to obtain more information on ligand–

Table 1 The five dialkylphosphinic acids

Label	Structure	Standard IUPAC name	pK_a^{a}
P118		Di(octan-2-yl)phosphinic acid	5.42
P127		Di(octan-3-yl)phosphinic acid	5.82
P1c6		Dicyclohexylphosphinic acid	5.36
P218		Bis(2-methylheptyl)phosphinic acid	5.41
P227		Bis(2-ethylhexyl)phosphinic acid	5.60

^{a} More than 99% purity was determined by potentiometric titration.

metal interactions, using a single-point calculation with the small-core relativistic effective core potential also developed by Dolg *et al.*, with 4f electrons treated as the valence shell.[28,29] All calculations were performed using the Gaussian 09 software package.[30]

3. Results and discussion

3.1. Model structures

In this work, five dialkylphosphinic acids, *i.e.*, P118, P127, P218, P227, and P1c6, were synthesized (Table 1), whose α- or β-position was substituted with methyl or ethyl. Their extraction abilities for seven lanthanides, *i.e.*, La, Pr, Nd, Dy, Ho, Yb, and Lu, were investigated. Various simplified coordination models of the extraction complexes were proposed. The corresponding reaction energies were computed using the density functional theory method. A combination of experimental results and the most suitable theoretical model was used to investigate the effects on rare-earth extractions of α and β substituents on the alkyl groups of dialkylphosphinic acids.

3.2. Model reactions and model extraction complexes

$[Ln(H_2O)_9]^{3+}$ (Ln = lanthanide) was used as the hydrated trivalent lanthanide ion. The hydrated proton was defined as $[H(H_2O)_4]^+$. The extractant was regarded as the dimer H_2L_2.[16,31–35] According to the report by Garcés, the stepwise equilibrium constants showed similar trends to those of the intrinsic equilibrium constants for particle adsorption.[19] The first stability equilibrium constants can similarly be derived from the thermodynamic energies of the reactions

$$1/2H_2L_2 + 3H_2O + [Ln(H_2O)_9]^{3+} \rightarrow [Ln(H_2O)_8L]^{2+} + [H(H_2O)_4]^+ \quad (1)$$

$$H_2L_2 + 3H_2O + [Ln(H_2O)_9]^{3+} \rightarrow [Ln(H_2O)_6(HL_2)]^{2+} + [H(H_2O)_4]^+ \quad (2)$$

where HL = P118, P127, P1c6, P218, and P227, were used for comparison with the experimental results. The corresponding intermediate extraction complexes $[Ln(H_2O)_8L]^{2+}$ or $[Ln(H_2O)_6(HL_2)]^{2+}$ were used to investigate ligand–metal interactions and the corresponding thermodynamic energies.[36] These thermodynamic energies might show similar trends to those of the extraction equilibrium constants.

Several models were tested to obtain a suitable coordination model for simulating the experimental results.[34] The stoichiometric complexes $[Ln(HL_2)_3]$, which are generally discussed in lectures, are nearest to the real extraction complexes. However, they contain more than 300 atoms and can adopt a large number of conformations, making theoretical calculations difficult.[37] In addition, simplification of the alkyl group on the extractant will remove the differences among the alkyl structures of different extractants. As mentioned above, the stepwise equilibrium constant largely reflects the trends in the overall equilibrium constant. Three models were developed to classify the extraction complexes: straight monomer residue (SM), distorted monomer residue (DM), and distorted dimer residue (DD) (Fig. 1). The SM model involves direct exchange of one water molecule of $[Ln(H_2O)_9]^{3+}$ with an extractant anion L^-. In practice, the extractant skeleton is distorted by coordination with the central metal, therefore the DM model, based on the roughly optimized $[Ln(HL_2)_3]$ structure, was developed, in which only one L^- was used and the other L^- and HL were replaced with water molecules. The DD model, in which one HL_2^- unit was used, was developed to take account of extractant dimerization.[33] Structure optimization began using a Dy complex with an extractant with a straight alkyl group. Substituents were then introduced at the α or β position of all the Dy complexes. The minimum energy conformation was calculated. After the optimized conformation was obtained, the central metal of the complex model, *i.e.*, Dy, was replaced by the other six rare-earth metals. The calculated thermodynamic energies for eqn (1) and (2) are listed in Table S1.† The calculation results indicate that the Gibbs free energies of the DM model are most consistent with the experimental observations; therefore, the DM model was chosen to explore the effects of the alkyl structures of extractants on their extraction performances.

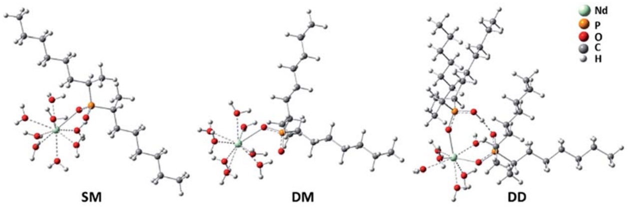


Fig. 1 The Ball and Stick structure of SM, DM, and DD model, exampled with Nd^{3+} and P218 case (see ESI† for detail).

3.3. Comparison between experimental lg *K*s and theoretical lg K_1s

The extractions of La, Pr, Nd, Dy, Ho, Yb, and Lu with P118, P127, P218, P227, and P1c6 were examined. The thermodynamic energies were calculated using the DM model. The corresponding extraction equilibrium constants are shown in Fig. 2. Precipitation occurred during the extractions of Yb and Lu with P218 and P1c6, therefore no data were obtained. Use of the logarithm of the first stability equilibrium constant (lg K_1) when the value was more than 100 was largely impractical,

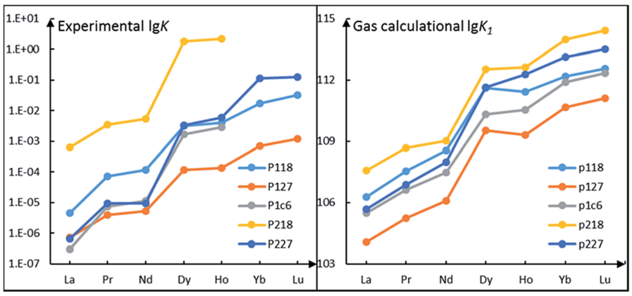


Fig. 2 The experimental lg *K*s and gas calculational lg K_1s.

Table 2 The bond length/WBIs of Ln–L bond in the DM model of the extraction complexes (Å)

Metal	p118	p127	p1c6	p218	p227
La	2.4630/0.3695	2.4590/0.3725	2.4523/0.3753	2.4397/0.3789	2.4508/0.3769
Pr	2.4254/0.3997	2.4214/0.3912	2.4137/0.4028	2.3981/0.4150	2.4136/0.4078
Nd	2.3991/0.4018	2.4040/0.3898	2.3982/0.3967	2.3812/0.4117	2.3991/0.3998
Dy	2.3387/0.3718	2.3231/0.3800	2.3319/0.3784	2.3057/0.3846	2.3224/0.3786
Ho	2.3085/0.3809	2.3169/0.3821	2.3149/0.3825	2.2952/0.3901	2.3136/0.3886
Yb	2.2796/0.3817	2.2821/0.3817	2.2867/0.3789	2.2624/0.3868	2.2817/0.3802
Lu	2.2728/0.3540	2.2742/0.3516	2.2797/0.3503	2.2551/0.3575	2.2748/0.3518

mainly because solvation effects were neglected, especially for trivalent lanthanides, for which the hydration energies are about 800 kcal mol^{-1}.[16,32] However, all of the experimental lg *K*s are lower than 10. The trends in the calculated lg K_1 agreed well with those of the experimental lg *K* (overall equilibrium constant). Their differences are therefore systematic, and also agree with Garcés' results.[19] Similar results were reported by Shi *et al.*, in which the energy differences between complexes of CMPO and PhCMPO extractants with europium and americium are similar, for 1 : 1, 2 : 1, and 3 : 1 ratios.[18] Consequently, it is reasonable to use the DM model to study and predict the ligand–metal interactions in extraction systems.

3.4. α,β substituents effect

Extractants with highly branched alkyl groups had lower extraction abilities (Fig. 2); this is in good agreement with previous reports.[11] Although P118 (methyl at the α position) and P218 (methyl at the β position) have similar pK_a values (see Table 1), their extraction abilities differed by two orders of magnitude, as shown in Fig. 2 (P118 light-blue line, P218 yellow line). The situation is similar for the ethyl-substituted extractants P127 (ethyl at the α position, orange line) and P227 (ethyl at the β position, blue line). This indicates that the steric hindrance of the substituent at the α position is greater than that of the β substituent. However, the extraction ability of P1c6, which has a more sterically hindered substituent at the α position, was higher than that of P127. This could be because the restricted cyclohexyl group in P1c6 limits free rotation, leading to lower steric hindrance than in P127. This is also reflected by the optimized geometries (see ESI†). For different rare-earth metals, different α- or β-substituted extractants have more obvious effects on the extractions of heavy rare-earth metals than of light ones. For instance, for La^{3+}, P127 and P227 gave similar extraction performances, but for extractions of Yb^{3+} and Lu^{3+}, lg *K* with P227 was 158.81 times higher than that with P127 (Yb^{3+}), and 104.06 times higher than that with P127 (Lu^{3+}). In addition, the extractability curves of P118 and P227 cross at Dy^{3+}, which suggests that P227 is more efficient for the separation of lanthanides than P118.

Both the experimental and theoretical data revealed that the differences between the extraction abilities of P218 and P118 for La^{3+} were almost the same as those for Lu^{3+}. However, the differences between the extraction capabilities of P227 and P127 for La^{3+} were obviously smaller than those for Lu^{3+}. This means that the differences between the lg K_1 or lg *K* of α- and β-methyl-substituted extractants are smaller than those between the lg K_1 or lg *K* of α- and β-ethyl-substituted extractants for different lanthanides.[38] The use of α- or β-ethyl-substituted extractants to adjust the extraction and separation ability is therefore more efficient than use of α- or β-methyl-substituted ones. This explains why the extraction performances of P204, P507, and P227 are better than those of the β-methyl-substituted congeners.[3,4,21]

3.5. Metal–ligand interactions

More information on the interactions between the extractants and metal ions was obtained by examining the Ln–L Wiberg bond indexes (WBIs) and bond lengths for the DM model (Table 2); the WBIs were 0.35–0.42 and the bond lengths were 2.25–2.47 Å for all the Ln–L bonds, indicating that the metal–ligand interactions are mainly ionic (electrostatic).[12,39,40] The changes in the WBIs and bond lengths showed similar trends, which is in accordance with the thermodynamic energies. For each extractant, the WBI and bond length both decreased from La^{3+} to Lu^{3+}, as a result of the lanthanide contraction.[39] The WBI order for each metal ion is roughly P218, P227 > P1c6 > P118, P127; the reverse order holds for the bond lengths. The difference between the Ln–P218 and Ln–P227 bond lengths is about 0.02 Å, and the WBI difference is small. The difference between the Ln–P118 and Ln–P127 bond lengths is only about 0.01 Å, and the WBI difference is also small. These results agree well with Kolařík's report that the extraction efficiency was lowered by branching of the alkyl group.[11] The WBIs and bond lengths also show that the differences among the extraction performances of α-substituted extractants for different metal ions were smaller than in the case of β-substituted extractants. The introduction of a substituent at the β position on the extractant will have a more significant effect on the extractability and selectivity than will a substituent at the α position. This can be partly explained by the geometries of the extraction complexes (see ESI†). For α-substituted extractants, the α substituent may be stuck in the main chain, and would make little contribution to the hydrophobic effect.

4. Conclusions

In summary, the effects of α and β substituents in an extractant on its extraction performance were investigated experimentally and theoretically. The calculated first extraction stability constant pK_1s showed a similar trend to that of the experimental overall extraction equilibrium constant pKs. A simplified coordination model, *i.e.*, the DM model, provides a useful tool for exploring the relationship between the structures of phosphorus-based extractants and their extraction abilities. This studies will help us to understand the effect of the alkyl structure on metal extraction and separation, and will provide a reliable theoretical foundation for the structural design of dialkylphosphinic acids. This will also promote applications of these new extractants.

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