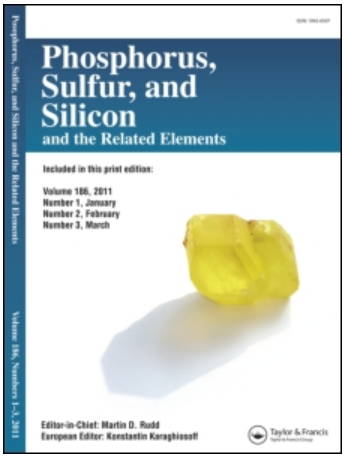

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Subtituent Parameters of Organophosphorus Compounds in Metal Extraction

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SUBTITUENT PARAMETERS OF ORGANOPHOSPHORUS COMPOUNDS IN METAL EXTRACTION

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Abstract The polar and steric effect of long chain alkyl and alkoxyl groups attached directly to the phosphorus atom were evaluated by experimental method and the method of molecular mechanics calculation.

INTRODUCTION

In quantitative structure-activity relationship (QSAR) studies of organophosphorus compounds in metal extraction, as in other chemical recations, it is important to establish suitable structure parameters for correlation analysis. The polar and steric effects of long chain alkyl and alkoxyl groups attached directly to the phosphorus atom were evaluated by experimental method and by the method of molecular mechanics calculation as described in this paper. Satisfactory to excellent correlation coefficients were resulted in QSAR studies of phosphorus-based ligand in metal extraction with the aid of these parameters. It is applicable both to the prediction of extraction behaviours and to the molecular design of extractants. This treatment achieved, however, considerable empirical success and led to a deeper understanding of the influence of chemical structure of phosphorus compounds upon reactivity in metal extraction It is also expected to extend the application of these parameters for the QSAR or liner free energy relationship (LEER) studies of organophosphorus compounds in general.

POLAR CONSTANTS AND GROUP CONNECTIVITY

The classical scale of Taft's σ^* constants for the polar effect of aliphatic substituents has met criticism from Shorter[1,2] and Charton[3]. Meanwhile, Kabachnik[4] suggested a set of polar constants for organophosphorus compounds by the pKa values of various phosphorus acids. Since the polar constants of long chain alkyl and alkoxyl groups are still insufficient in the literature, the QSAR studies of compounds bearing such groups was inhibited. We reported[5] eighteen σ^p constants, an extension of Kabachnik's scale, of long chain alkyl and alkoxyl groups based on the ionization constant determination of a series of mono-basic alkylphosphates and alkylphosphonates. It was observed that there is an excellent linear relationship between σ^p value and group connectivity, a term represented as $\sum[n_i/(4i^2-1)]$ was introduced by Hanson[6] as a parameter for the polarity of alkyl substituents. A preliminary study was performed on the influence of steric and self-coiling effect to the pKa value of mono-basic phosphates and phosphonates comprising long chain alkyl and alkoxyl groups. Based on our experimental date[7]. The extraction eqilibrium constants of rare earth (K_{ex}^{RE}) acidic phosphorus based ligands are therefore correlated linearly with the σ^p constants of the substitunts while the steric effect offers no significant influence on the extraction process. So we can predict extraction ability of ligands based on the substituents by these empirical equations.

SUBSTITUENT PARAMETERS FOR THE STERIC EFFECT

As demonstrated by us[8.9] the extraction behaviours of ligands are governed chiefly by three structural factors, namely polar, steric and solubility effects. The last factor can be neglected in case of approximately same numbers of carbon atoms in the substituents within the same series of extractants. Since the correlation analyses of equilibrium constants in nickel or cobalt extraction with σ^p and Charton's υ , a commonly used parameters for steric effects, gave only unsatisfied results, it is therefore necessary to establish a new parameter, reflecting steric effect of substituents of ligands in cobalt nickel separation by mono-basic alkylphosphonates and alkyl-phosphates. Based on the general quantitative expression between extraction constants with polar and steric effect of substituents of ligand, two series of parameters E_{PA}^{Co} and E_{PA}^{Ni} were evaluated besides E_{PA}^{RE} for lanthanide extraction. An excellent LFER existed, however, in correlating logKex to E_{PA}^{M} in addition to σ^p , indicating the applicability of these parameters for the steric effect of ligand substituents in metal extraction.

It is expected to use E_{PA}^{Co} or E_{PA}^{Ni} in extraction of those metals which possess identical configuration of coordination compounds in extraction process as cobalt or nickel. As shown by our systematic studies, E_{PA}^{RE} substitutent steric parameter of acidic phosphorus esters in lanthanide extraction works well in actinide extraction by neutral phosphorus esters.

The E_{PA}^{M} value is an empirical parameter consisting of residual factors besides steric effect. A theoretical calculation based on molecular mechanics (Allinger's MM2 program) was thus performed for this purpose. Dialkyl t-butyl phosphate or dialkyl t-butylphsophinate was chosen as model compound for the simulation of steric environment of the complexes in this preliminary study. The optimum geometry of the model structure and its parent acid were determined by the molecular mechanics program, the most stable structure were selected to compase with each other. It was found that the difference of the local steric energy of hydroxyl oxygen in both two compounds is closely correlated with the degree of the size of substituent and can thus be used as a measurement of the steric effect of the substituents(Es,ex). A series of Es,ex of alkyl and alkoxyl groups were evaluated.

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