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Collaborative Virtual Reality Environments for Computational Science and Design

Michael E. Papka, Rick Stevens, and Matthew Szymanski
Futures Laboratory
Mathematics and Computer Science Division
Argonne National Laboratory
Argonne, IL 60439 USA

Abstract

We are developing a networked, multi-user, virtual-reality-based collaborative environment coupled to one or more petaFLOPs computers, enabling the interactive simulation of 10^9 *atom systems. The purpose of this work is to explore the requirements for this coupling. Through the design, development, and testing of such systems, we hope to gain knowledge that will allow computational scientists to discover and analyze their results more quickly and in a more intuitive manner.*

1. Introduction

As the complexity of material modeling simulations increases due to the availability of larger and faster computers, so does the size of the output. For this reason, new methods will be needed that enable the computational to examine, navigate, and explore results in a rapid and intuitive manner.

To facilitate the analysis of simulation data, a variety of experts may be needed. Hence, future visualization environments need to support *collaborative* interactions. Through the coupling of simulation and visual analysis, scientists will have unprecedented access to the capabilities of the next generation of computing systems.

The capabilities mentioned will need to be integrated with scheduling and resource management, discovery, and allocation systems. This integration will require the combination of many diverse and often separate computer science disciplines. In this paper we outline the key technologies needed, their current state, and our proposed approach for integrating them. We also discuss our experimental prototype system and the issues and problems we anticipate as we move forward.

DISCLAIMER

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SYNERGISTIC EFFECTS IN THE EXTRACTION OF METAL IONS BY MIXTURES OF DIALKYLPHOSPHORIC ACIDS AND SUBSTITUTED CROWN ETHERS

R.Chiarizia[1], M.L.Dietz[1], A.H.Bond[1], V.J.Huber[1], A.W.Herlinger[2] and B.P.Hay[3]

1. Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, USA
2. Department of Chemistry, Loyola University Chicago, Chicago, IL 60626, USA
3. Pacific Northwest National Laboratory, Richland, WA 99352, USA

ABSTRACT

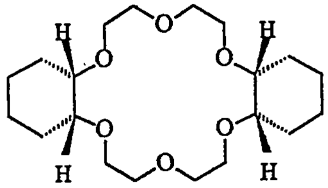
The extraction of alkaline earth cations from weakly acidic solutions by three dialkylphosphoric acids and various isomers of dicyclohexano-18-crown-6, both alone and in combination in toluene solutions, has been examined to determine the effect of both the crown ether stereochemistry and the structure of the organophilic anion on the magnitude of the synergistic effects. The synergistic effects have been found to differ considerably among the crown ether isomers and to vary with the extent of alkyl chain branching in the dialkylphosphoric acid. Attempts to correlate the synergistic effects with ligand strain energies from molecular mechanics calculations are described.

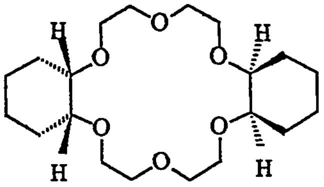
(Keywords: synergism, crown ether stereoisomers, dialkylphosphoric acids)

INTRODUCTION

In an effort to develop guidelines for the rational design of synergistic extraction systems for metal ions using macrocyclic polyethers, we have examined the extraction of Ca^{+2}, Sr^{+2} and Ba^{+2} into toluene by various organophosphorus acids and crown ether isomers, both alone and in combination. Although synergistic effects involving mixtures of crown ethers and organophosphorus acid anions are well known (1-7), few of the previously described studies have taken a systematic approach to the elucidation of the factors responsible for the observed synergism. By contrast, the present work employs structurally well-defined macrocycles and organophilic anions, thereby providing a means of determining the influence of the crown ether stereochemistry and anion structure on the observed synergistic effects.

The series of dicyclohexano-18-crown-6 (DCH18C6) isomers shown in Figure 1 and the dialkylphosphoric acids of increasing steric bulk shown in Figure 2 were used. The extraction data were then used to determine if a correlation exists between macrocyclic ligand strain energies (calculated by molecular mechanics) and the synergistic effects.


cis-syn-cis-dicyclohexano-18-crown-6 (A)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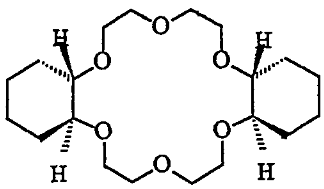
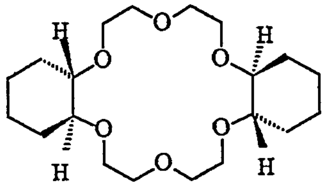

trans-syn-trans-dicyclohexano-18-crown-6 (C)


trans-anti-trans-dicyclohexano-18-crown-6 (D)

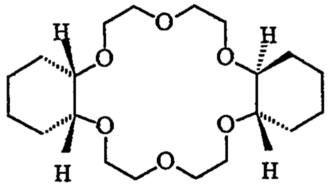
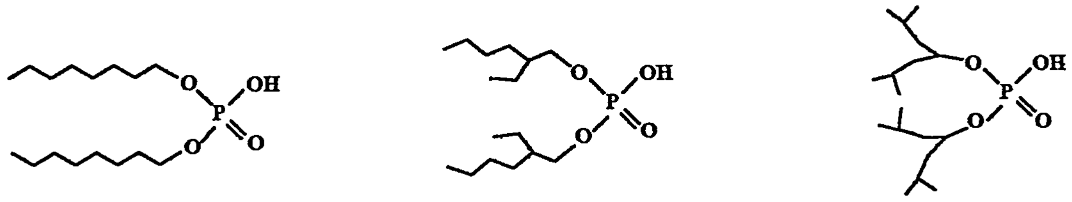

cis-trans-dicyclohexano-18-crown-6 (E)

Figure 1. DCH18C6 isomers used in this work


Di-*n*-octylphosphoric acid
HDOP

Di(2-ethylhexyl)phosphoric acid
HDEHP

Di(diisobutylmethyl)phosphoric acid
HD(DiBM)P

Figure 2. Dialkylphosphoric acids used in this work

EXPERIMENTAL

The preparation and purification of the materials used in this work can be found in reference 8. The distribution ratios, *D*, of ^{45}Ca, ^{85}Sr and ^{133}Ba were determined at 23±1 °C as reported in reference 9. For the pH dependencies of the metal distribution ratios, the procedure described in reference 2 was followed. The details of the calculations of the crown ether ligands reorganization energy, ΔU_{reorg}, are reported in reference 10.

RESULTS AND DISCUSSION

Figure 3 shows the results of a continuous variation study of the distribution ratios of Ca^{+2}, Sr^{+2} and Ba^{+2} as a function of the crown ether (CE) mole fraction in HDOP-CE mixtures at constant HNO_3 and metal ion concentrations. Similar results have been obtained for the other dialkylphosphoric acids used in this study.

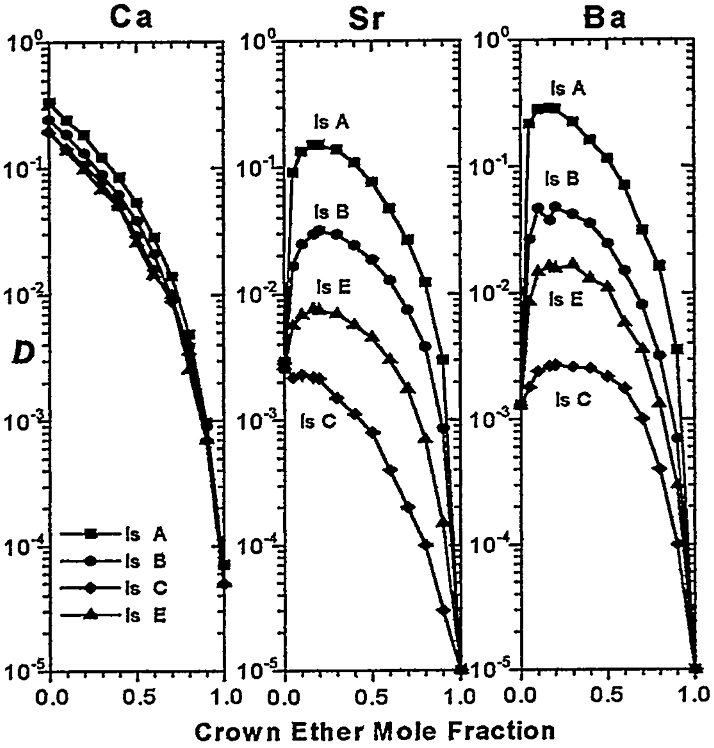


Figure 3. Continuous variation plots for the HDOP-CE system. [HDOP]+[CE] = 0.1 M in toluene; $[HNO_3]$ = 0.01 M; $[M(NO_3)_2]$ = 0.001 M

These data illustrate a number of features of the investigated systems. First, the extraction of the metal cations by the CE alone is negligible, which allows us to define a synergistic factor, SF, simply as the ratio of the *D* values in the presence and in the absence of crown ether under each set of experimental conditions. Next, no significant synergism is observed for Ca^{+2}, probably due to the poor ability of DCH18C6 to complex this cation (7,11). In contrast, a strong synergistic effect is observed with Sr^{+2} and Ba^{+2}, both of which are strongly complexed by 18-membered crown ethers (7,11). For these two cations, the various stereoisomers of DCH18C6 yield remarkably different SF values, in the order $A>B>E>C\geq D$ (*vide infra*). Finally, the maximum *D* values generally occur at a CE mole fraction of 0.2, indicating that the synergistic complexes of Sr^{+2} and Ba^{+2} contain four molecules of dialkylphosphorc acid for each CE molecule.

Figure 4 shows the pH dependencies of the metal distribution ratios at constant ionic strength and temperature measured with 0.1 M HDOP either alone or in the presence of 0.025 M CE (various isomers), that is, under conditions corresponding to the maxima in the continuous variation plots in Figure 3. Similar data, not shown here, were obtained for HDEHP and HD(DiBM)P. The data in Figure 4 confirm both the lack of synergism for

Ca^{+2} and the order of effectiveness of the various isomers of DCH18C6 in enhancing Sr^{+2} and Ba^{+2} extraction by HDOP (*vide supra*). The same order was verified with the other two dialkylphosphoric acids with one exception, the HD(DiBM)P- Sr^{+2} system, in which isomer B was slightly more effective than isomer A.

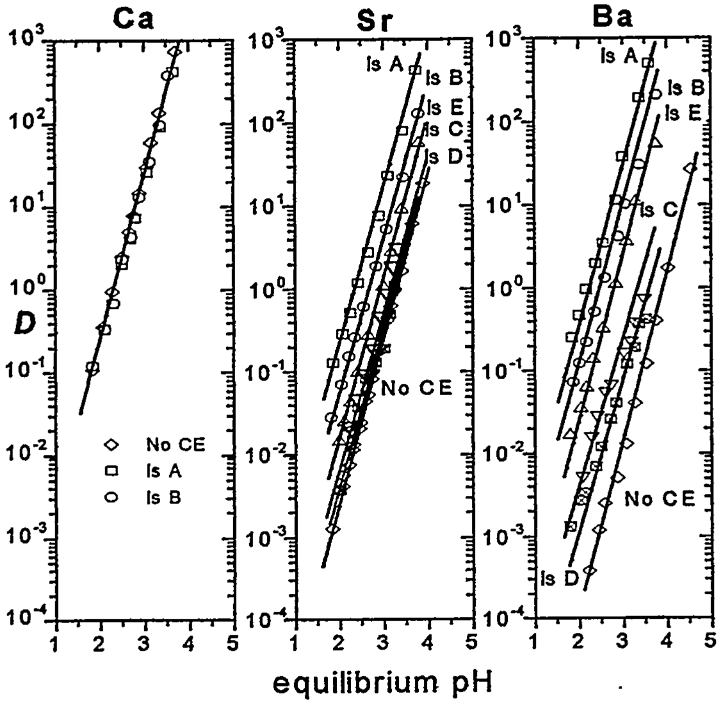


Figure 4. pH dependencies with 0.1 M HDOP alone or with 0.025 M DCH18C6 in toluene; $[M(NO_3)_2] = 0.001$ M

In all cases, the slope value of the pH dependencies is +2, indicating that when the cations are extracted by HDOP, HDEHP or HD[DiBM]P, either alone or in combination with the various isomers of DCH18C6, two H^+ ions are liberated during extraction.

The extractant dependencies of the *D* values were also measured and slope analysis of the logarithmic plots of *D* vs. extractant concentration obtained at a constant aqueous phase pH (between 2 to 3) and at very low organic phase loading was performed. With the dialkylphosphoric acids alone, slopes of the dependencies were 2.5 for Ca^{+2} and 3.0 for Sr^{+2} and Ba^{+2}, although some deviation from these values was observed with HD(DiBM)P. Overall, our results agree with previous literature information concerning extraction of alkaline earth cations by dialkylphosphoric acids (12).

Extractant dependencies were also determined for synergistic systems (not shown for the sake of brevity). In all cases, the slope of the logarithmic plots of *D* vs. the dialkylphosphoric acid concentration (at constant DCH18C6 concentration) was +2. When the DCH18C6 concentration was varied, keeping the dialkylphosphoric acid concentration constant, slope values of +1 were obtained. In several cases, however, slopes less than unity were observed at the highest CE concentrations, in agreement with previous studies (2). Using these results, together with the dimeric state of aggregation of organophosphorus acids in toluene (13) and the absence of interaction betwen the two extractants in the organic phase (confirmed by vapor pressure osmometry and infrared spectroscopy measurements (14)), the equilibria describing the extraction of alkaline earth cations by mixtures of dialkylphosphoric acids and DCH18C6 can be written as follows, where HA and B represent the two extractants in the organic phase:

$$M^{+2} + (2+n/2)(HA)_2 \Leftrightarrow M(HA_2)_2{\cdot}nHA + 2H^+ \qquad K_{ex}$$

in the absence of crown ether, with n = 1 for Ca^{+2} and n =2 for Sr^{+2} and Ba^{+2}. For Sr^{+2} and Ba^{+2} in the presence of DCH18C6, this becomes:

$$M^{+2} + 2(HA)_2 + B \Leftrightarrow MB(HA_2)_2 + 2H^+ \qquad K_{ex,s}$$

The synergistic constant K_s, defined as the $K_{ex,s}/K_{ex}$ ratio (13), corresponds to the organic phase reaction that leads to the formation of the final Sr^{+2} and Ba^{+2} complexes:

$$M(HA_2)_2{\cdot}2HA + B \Leftrightarrow MB(HA_2)_2 + 2HA \qquad K_s$$

The K_s values listed in Table 1 have been used to quantitatively describe the synergism in the investigated systems. Because of the low reagent concentrations in both phases, these values can be considered to be nearly thermodynamic constants.

Table 1: Values of the synergistic equilibrium constants, K_s

DCH18C6	**HDOP**		**HDEHP**		**HD(DiBM)P**	
isomer	**Sr**	**Ba**	**Sr**	**Ba**	**Sr**	**Ba**
A	(1.07±0.09) x10^2	(5.32±0.64) x10^3	(1.96±0.24) x10^3	(5.26±0.69) x10^3	(4.19±0.57) x10^2	(7.25±1.45) x10^3
B	(3.17±0.31) x10^1	(1.27±0.17) x10^3	(3.49±0.52) x10^2	(1.84±0.20) x10^3	(5.48±0.55) x10^2	(8.01±1.44) x10^2
E	(9.43±0.44) x10^0	(4.09±0.49) x10^2	(8.08±1.00) x10^1	(3.62±0.40) x10^2	(6.54±0.95) x10^1	(1.95±0.33) x10^2
C	(3.36±0.18) x10^0	(3.58±0.94) x10^1	(1.03±0.13) x10^1	–	(1.45±0.29) x10^1	–
D	(2.60±0.23) x10^0	(1.58±0.32) x10^1	–	–	–	–

Figure 5 shows the relationship between the log K_s (Table 1) and the ligand reorganization energy (ΔU_{reorg}) calculated through molecular mechanics for the metal complexes of the various stereoisomers of DCH18C6. These reorganization energies represent the degree to which complex formation between a crown ether and a given metal ion induces steric strain in the crown ether. Ligands highly organized for binding exhibit small ΔU_{reorg} values, down to the limiting value of $\Delta U_{reorg} = 0$ for ligands that are perfectly organized for binding. Extrapolation to $\Delta U_{reorg} = 0$ of the linear correlation between the logarithm of the binding constant and ΔU_{reorg} allows an estimation of the binding constant for ligands with an optimum configuration.

The results shown in Figure 5, which represent the first report of a correlation between synergistic constants and ligand strain energies, seem to indicate that the primary factor determining the magnitude of the observed synergistic effects is the reorganization energy of the various DCH18C6 isomers. It also appears that the steric hindrance due to the branching of the alkyl groups of the dialkylphosphoric acids also plays a role, although a more limited one.

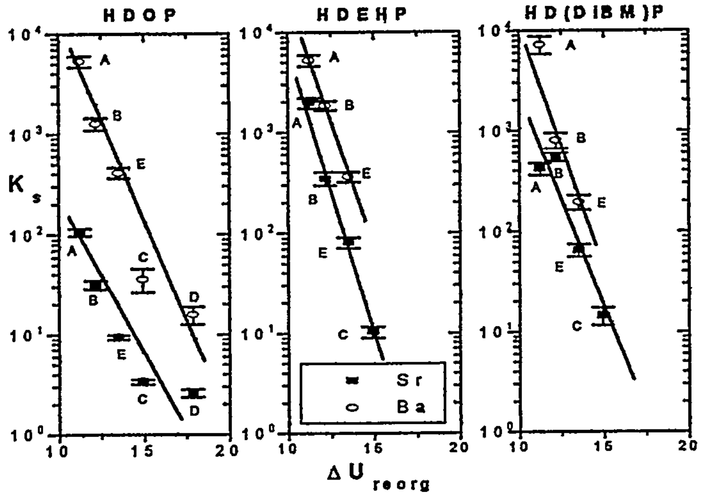


Figure 5. Relationship between log K_s values and DCH18C6 isomers reorganization energy

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