Developing New Chemical Tools for Solvent Extraction

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Introduction

Prospects for innovation and for greater technological impact in the field of solvent extraction (SX) seem as bright as ever, despite the maturation of SX as an economically significant separation method and as an important technique in the laboratory. New industrial, environmental, and analytical problems provide compelling motivation for diversifying the application of SX, developing new solvent systems, and seeking improved properties. Toward this end, basic research must be dedicated to enhancing the "tools" of SX: physical tools for probing the basis of extraction and molecular tools for developing new SX chemistries. In this paper, we describe our progress in developing and applying the general tools of equilibrium analysis and of ion recognition in SX.

Results and Discussion

Our FORTRAN least-squares modeling program (SXLSQA) now represents one of the most advanced tools available for the treatment of SX equilibria. From the earliest attempts to unravel the complexities of SX distribution behavior, a major barrier to progress has been the difficulty in correcting for effects of nonideality and in unambiguously identifying organic-phase species. SXLSQA challenges this barrier by solving the simultaneous mass-action equations with inclusion of aqueous ionic activity coefficients according to the Pitzer treatment and organic-phase activity coefficients according to the Hildebrand-Scott treatment (Baes et al. 1990). Equilibrium models that may be tested by use of SXLSQA consist of sets of aqueous- and organic-phase species that can be formed from a metal cation M^{i+}, an acidic extractant HA, a neutral extractant B, an extractable aqueous anion X^-, and water. Given a postulated model, SXLSQA uses adjustable parameters including equilibrium constants, ionic-interaction parameters, and solubility parameters to calculate phase compositions. The calculated phase compositions can then be used to calculate a variety of equilibrium properties such as distribution coefficients, spectral absorbance and titration heats.

SXLSQA has been instrumental in elucidating the complex equilibria associated with the representative SX system di-2-ethylhexylsulfoxide (DEHSO), n-dodecane, uranyl nitrate, nitric acid, sodium nitrate, water. We have been interested in this particular system as a model for U(VI) extraction by related neutral oxygen-donor extractants such as TBP. Moreover, because its radiolytic breakdown products are expected to cause minimal process difficulties and because its branched structure confers improved solubility in organic diluents, DEHSO may have application in nuclear separations. As shown in Figure 1, DEHSO behaves much like TBP in the extraction of U(VI) and Pu(IV) nitrates, providing for the extraction and stripping of these metals by appropriate adjustment of the aqueous nitric acid concentration. By use of classical slope analysis (Moyer et al., in press), the extraction of U(VI) by low concentrations of DEHSO in dodecane at 25°C may be clearly described in terms of the disolvate complex $UO_2(NO_3)_2(DEHSO)_2(H_2O)_w$ (w not determined). However, much greater complexity in this system can be discerned by the use of SXLSQA in modeling more extensive water, nitric acid, and U(VI) extraction data. For example, the downturn in the U(VI) distribution coefficient as the aqueous nitric acid concentration exceeds ca. 4 M (Figure 1) may be definitely linked to the competitive effect of nitric acid extraction. In addition, the DEHSO-concentration dependence of the extraction behavior indicates a stepwise solvation of extracted components of DEHSO.

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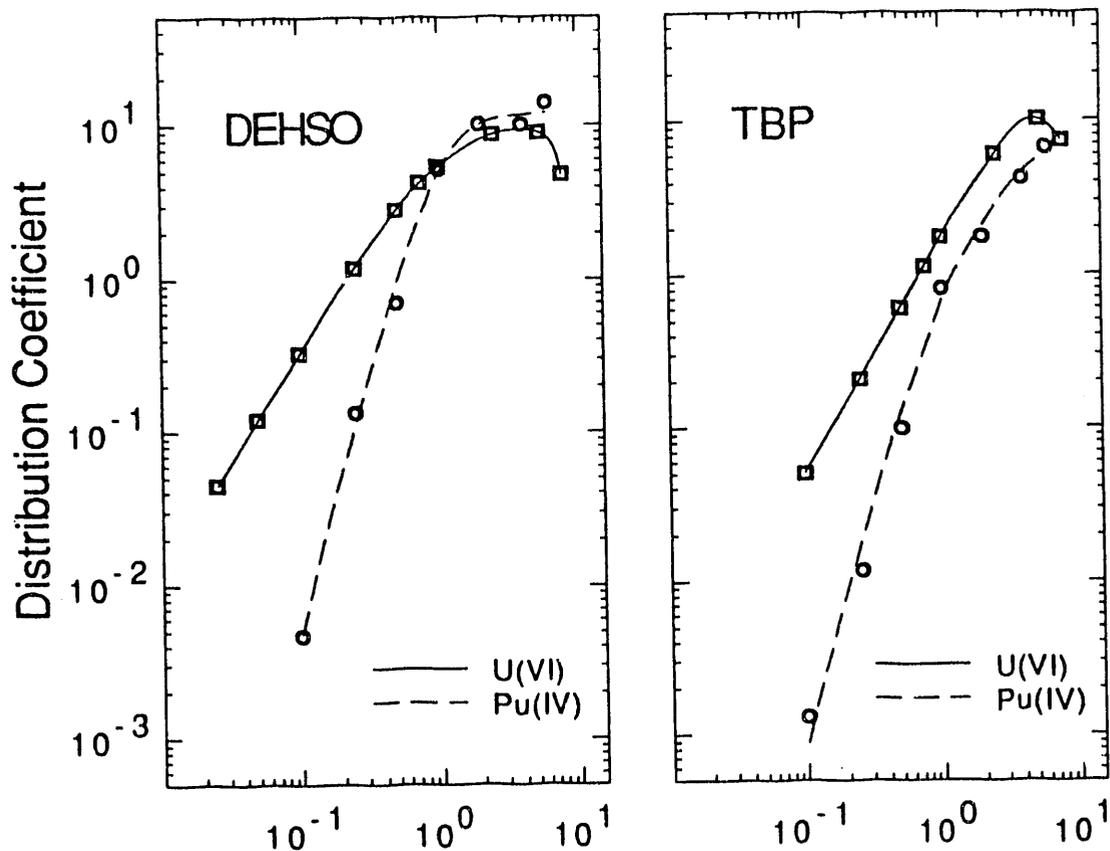(c) Etrac, Inc., Knoxville, Tennessee

Figure 1. Extraction of U(VI) and Pu(IV) from Aqueous Nitric Acid by 0.4 M Di-2-ethylhexylsulfoxide (left) and 0.4 M Tributylphosphate (right) in Dodecane. Conditions: ambient temperature (23 ± 2°C); 1:1 phase ratio; trace metal concentrations; 15-min contact by agitation in capped vials.
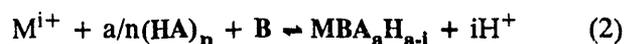
Whereas the history of SX has involved the coordination chemistry of "simple" monofunctional extractants such as TBP, much of the frontier may now lie in the direction of chemical "recognition" principles, entailing the idea that selectivity arises from an exclusive matching of bonding preferences of a receptor with those of a targeted ion or molecule. Recently, the molecular tools for enhancing recognition have leaped ahead through the study of polydentate ligands, including macrocycles, cages, and podands. In such ligands the variety of possible geometrical constraints and types of donor atoms greatly amplifies our control over metal binding. This control may be directed toward obtaining systems with selectivities not possible with conventional SX reagents (which usually possess strong preferences of their own). Some otherwise-difficult separations that we have found possible with crown ethers include alkali metals (e.g., Cs), alkaline earth metals (e.g., Sr,

Ra), and first-row transition metals (e.g., Mn, Cu, and Zn) (McDowell et al. 1986; McDowell 1988; Moyer et al. 1988; Lumetta and Moyer 1991).

To exploit ion-recognition concepts in SX requires tailoring ligands to meet basic requirements of SX. A basic prerequisite for hydrometallurgical application entails the addition of sufficient hydrophobic bulk to a ligand to favor the partitioning of the ligand and its complexes to a water-immiscible organic phase. For example, the sodium salt of the ionizable lariat ether *sym*-dibenzo-14-crown-4-acetic acid partitions weakly to organic solvents. However, the bis(*t*-octyl) derivative, obtained through the alkylation of the benzo groups, partitions strongly to nonpolar diluents and thus may function effectively in transferring metals to the organic phase through many repetitive cycles without significant ligand loss. Ideally, the hydrophobic groups should also minimize unwanted effects such as

slow drop coalescence, emulsions, entrainment, and precipitation of third phases while maximizing extraction rates and ease of stripping. Other factors that must be considered in ligand design include stability to thermal and possibly radiation-induced degradation, ligand cost, and toxicity. Finally, since process economics ultimately determine the usefulness of an extractant, consumption of chemicals and waste production must both be minimized.

Equations 1-3 represent some possible equilibria in utilizing a macrocycle B in SX, where bold type denotes organic-phase species. Owing to the preferred use of nonpolar solvents, a special restriction of coordination chemistry in SX is the charge-neutrality of organic-phase species. Thus, anions play an important role in defining the equilibria and in determining the overall driving force.

$$M^{i+} + iX^- + B \rightarrow MBX_i \tag{1}$$

$$M^{i+} + a/n(HA)_n + B \rightarrow MBA_aH_{a-i} + iH^+ \tag{2}$$

$$M^{i+} + a/n(HC)_n \rightarrow MC_cH_{c-i} + iH^+ \tag{3}$$

A simple case involves coextraction of aqueous anions X^- to the organic solvent (eq. 1). Although some practical extraction systems have been devised based on such a scheme, the limitations associated with the dependence of the driving force on aqueous-anion dehydration has led us to consider the use of organophilic acids HA to provide charge balance through a coupled cation-exchange process (eq. 2). An example of such a system is the extraction of Cu(II) from sulfuric acid by a combination of thia macrocycles and didodecylnaphthalene sulfonic acid (HDDNS) as shown in Figure 2. This system gives good selectivities over other first-row transition metals, including ubiquitous Fe(III) (Moyer et al. 1988). Since the macrocycles negligibly extract Cu(II) from sulfuric acid owing to the poor driving force of anion transfer in eq. 1 and since HDDNS cation-exchanges metals relatively nonselectively, neither extractant is effective alone. Only the *combination* is effective. The cooperative effect resulting in enhanced extraction exceeding the summed effects of the two extractants (HA and B)
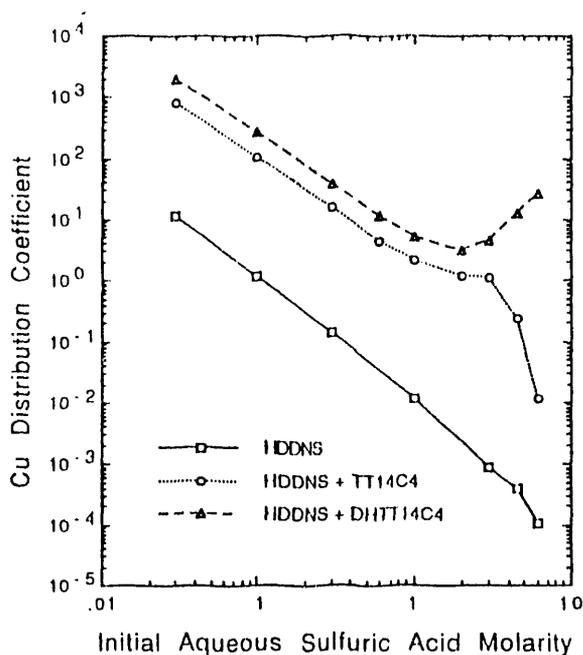

Figure 2. Synergistic Enhancement in the Extraction of Cu(II) from Aqueous Sulfuric Acid by Combination of 0.01 M Didodecylnaphthalene Sulfonic Acid (HDDNS) with 0.005 M Tetrathia-14-crown-4 (TT14C4) or 0.005 M 3,3-di-*n*-hexyl-tetrathia-14-crown-4 (DHTT14C4) in Toluene. Conditions: 25°C; 1:1 phase ratio; trace metal concentration; 16-117 h contact by gentle rocking in capped vials.

acting independently, as demonstrated in this example, is referred to as synergism.

By the use of the nonselective cation exchanger HDDNS, the selectivity of synergistic SX systems can be manipulated almost exclusively by the neutral ligand added. In these systems, crown ethers have allowed size discrimination of alkali and alkaline-earth metals, including the fission products Cs and Sr (McDowell et al. 1986; Bryan et al. 1987). Selectivity for the pseudo alkaline-earth metals Mn(II) and Zn(II) can also be obtained by the use of cyclohexano-15-crown-5; water competes effectively for coordination of the transition metals Fe(II) - Cu(II), and little or no synergistic effects for them have been observed (Lumetta and Moyer 1991). Alternative cation exchangers have also been tested in these systems. Long-chain carboxylic acids, for example, permit alkaline-range extraction but exert more influence

on selectivity owing to their stronger coordination properties relative to the sulfonic acids (McDowell et al. 1986).

X-ray crystallography and vibrational spectroscopy have been particularly effective at elucidating the relative roles of the macrocycle and anion in the metal binding in synergistic extraction systems. Analogs of extraction complexes have been crystallized, structurally characterized, and spectroscopically compared to actual extraction complexes for several divalent metal systems. In the cases of Sr^{2+}, Ba^{2+}, Mn^{2+}, Zn^{2+}, and Cu^{2+} ions, encirclement of the metal cations occurs with appropriate oxa and thia crown ethers (Burns and Bryan 1988; Burns and Lumetta, in press; Glick et al. 1976). The case of Sr^{2+} extraction is typical. In the truncated extraction complex Sr(DC18C6-A)((CH_3)_3CCOO)_2·H_2O (where DC18C6-A is cis-syn-cis-dicyclohexano-18-crown-6), the macrocycle encircles the Sr^{2+} cation, and the axial sites are occupied by bidentate carboxylate anions (Burns and Bryan 1988). Water does not coordinate but rather bridges two such complexes in a centrosymmetric dimer through hydrogen bonds to carboxylate oxygen atoms. As shown in Figure 3, infrared-spectral correlations, especially coincidences of sensitive carboxylate and ether stretching bands, provide evidence that the coordination environment about the metal remains intact in the corresponding extraction system employing a long-chain carboxylic acid as cation exchanger. However, the water-mediated dimerization observed in the crystal does not appear to be significant in solution, since vapor-phase osmometry shows that the extraction complex is monomeric (Moyer et al. 1986). Karl Fischer titrations show that the extraction complex in CCl_4 binds water to the average extent of approximately one water molecule per complex at unit water activity. The bound water is associated with a hydrogen-bonded OH stretch at 3318 cm^{-1} (broad) and a nonbonded OH stretch at 3680 cm^{-1} (sharp) in the FTIR spectrum (Figure 3). The observed peak positions and widths suggest water attachment by a hydrogen bond (leaving one hydrogen free) rather than by coordination. Thus, from the available evidence, it is suggested that the predominant solution complex has a structure similar to that of the symmetrically cleaved dimer in the crystal.
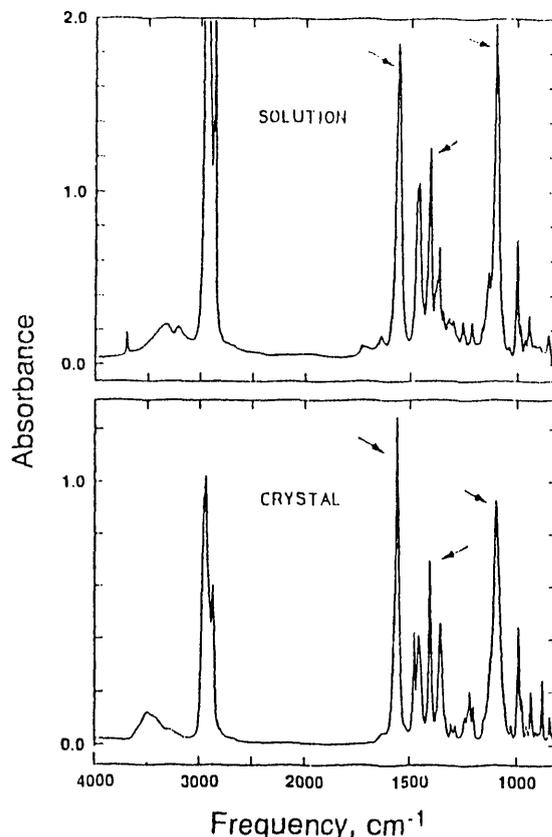

Figure 3. FTIR Spectra of Crystalline and Solution Complexes of Dicyclohexano-18-crown-6 (DC18C6) with Strontium Carboxylate Salts. Bottom: Sr(DC18C6-A) ((CH_3)_3CCOO)_2-H_2O as mineral-oil mull; mineral-oil bands are subtracted; DC18C6-A is the cis-syn-cis isomer of DC18C6. Top: extraction complex formed by extracting excess Sr(OH)_2 from 0.5 M Sr(NO_3)_2 at 25°C by a CCl_4 solution containing 0.05 M DC18C6 (mixed isomers) and 0.1 M Versatic acid (a long-chain carboxylic acid); spectrum of wet CCl_4 is subtracted. Arrows indicate, from left to right, bands due to stretches of the carboxylate (asym and sym) and ether (asym) groups. Spectra were recorded at nominal 2-cm^{-1} resolution with triangular apodization.

Whereas the macrocycles tested play a straightforward role in many of the synergistic extraction systems, the sulfonic acid and carboxylic acid cation exchangers display complicated structural and equilibrium behavior. Crystal structures reveal varied anion-metal interactions

where the same anion may coordinate in several ways. Equilibrium analysis using SXLSQA to model some representative systems shows that the distribution of metals can only be understood in terms of aggregated species, as indicated in eqs. 2 and 3. For example, HDDNS forms small, hydrated aggregates consisting of 5-8 monomers in CCl_4 at 25°C (Lumetta et al. 1991). In the presence of an added crown ether, the extraction behavior is further complicated by antagonistic bonding interactions between the crown ether and the cation exchanger; these interactions must be modeled by assuming the formation of species $(HA)_a B_b$ (Bryan et al. 1987). Undoubtedly, these interactions are mediated by hydrogen bonding, consistent with the ability of crown ethers to bind water (Bryan et al. 1990).

Equation 3 represents the logical progression from *inter*molecular synergism (eq. 2) to *intra*-molecular synergism wherein the cation-exchange functionality has been incorporated into an ionizable macrocycle HC. We have synthesized a series of ionizable lariat ethers built upon the rigid *sym*-dibenzo-14-crown-4 frame and having acetic, propanoic, oxyacetic, methylphenylphos-phinic, and (oxymethyl)phenylphosphinic acid sidearms (Burns and Sachleben 1990; Sachleben et al. 1988; Burns and Sachleben, in press; Sachleben and Burns 1991). These compounds represent an attempt to enhance selectivities through constraining the anionic functionality. Crystallographic data indicates that the anionic sidearms prefer to bind to the cations held by neighboring lariat ethers in the crystal, so that dimeric and polymeric structures are observed. Solution studies are currently being carried out to reveal more clearly the role of the sidearm in extraction.

Conclusions

Nearly half a century after the field of SX began in earnest, coordination chemistry continues to provide the impetus for important advance-ments in understanding SX systems and in con-trolling SX chemistry. In particular, the physical tools of equilibrium analysis, X-ray crystallog-raphy, and spectroscopy are elucidating the molecular basis of SX in unprecedented detail.

Moreover, the principles of ion recognition are providing the molecular tools with which to achieve new selectivities and new applications.

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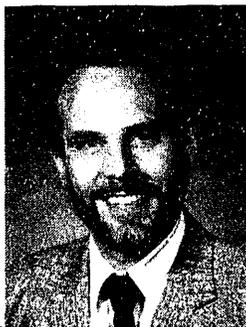
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