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POLYMER-BASED SEPARATIONS:
SYNTHESIS AND APPLICATION OF POLYMERS
FOR IONIC AND MOLECULAR RECOGNITION

Annual Performance Report
August 1, 1989 - July 31, 1990

Spiro D. Alexandratos

University of Tennessee
Knoxville, Tennessee 37996

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Progress Report: August 1, 1989 - July 31, 1990

The current period has focused upon (1) the development of metal ion separations with the dual mechanism bifunctional polymers which we introduced, and (2) the initiation of studies into developing polymer-supported reagents for molecular separations. The former emphasis has resulted in the initial publication of a series of papers under the continuing title "Mechanism of Polymer-Based Separations"; the latter emphasis is evident by our initial publication on the topic.

Mechanism of Polymer-Based Metal Ion Separations.

Dual mechanism bifunctional polymers (DMBPs) is a new category of polymeric reagents designed for the selective complexation of target metal ions. The three classes of polymers within the DMBP category are (1) the ion exchange/redox resins, (2) the ion exchange/coordination resins, and (3) the ion exchange/precipitation resins. Each class operates through an access mechanism (ion exchange) which allows for the facile entry of metal ions into the polymer network, and a recognition mechanism (reduction, coordination, or precipitation) which leads to the observed specificity. Our research in this area has focused on gaining an understanding of the mechanisms of action displayed by these polymers under different solution conditions. This would then allow us to propose efficient utilization methodologies for the DMBPs and to design additional DMBPs with different specificities.

A comparative study between the phosphinic acid resin and the conventional sulfonic acid resin was our initial report on the mechanism of polymer-based separations.[1] The amount of Fe(III), Hg(II), and Mn(II) nitrate sorbed from aqueous acid solutions was determined for the two resins as a function of equilibrium solution pH. The initial solutions were 10^{-4}N in the metal nitrate and varying from 4N to 10^{-4}N in nitric acid. An additional series also contained enough sodium nitrate in each solution to provide a constant 4N nitrate background throughout the series. With respect to the strongly acidic sulfonic acid resin, the results allow us to conclude that it is non-selective in its sorption of hard and soft metal ions, and its ability to sorb transition metal ions drops precipitously in the presence of sodium ions. The phosphinic acid resin displays a far greater selectivity: it sorbs Fe and Hg quantitatively from each solution, the former through an entropy-driven coordination and the latter through an enthalpy-driven coordination (at least from solutions with pH values less than 1); ion exchange is the only sorption mechanism with hard divalent ions;and its affinity for transition metal ions is virtually unaffected by the presence of a large excess of sodium ions.

The phosphinic resin's ability to reduce certain metal ions was studied in acidic solutions (4N and 0.01N HNO_3).[2] It displays a selectivity series of Fe>Hg>Mn>Ag from 4N HNO_3 solutions with initial ratios of 1 milliequivalent (meq) of metal nitrate per meq of phosphorus ligands on the polymer.

Decreasing the solution acidity to 0.01N leads to a series of Hg>Ag>Mn>Fe. We thus conclude that: (1) the loading effect is a dominant influence on iron's position within a selectivity series; (2)mercury shows a dramatic increase in log D values upon going from 4N to 0.01N HNO_3 (0.30 to 3.88, respectively) with no loading effect evident from the latter (log D values of 3.41 and 3.80 from the two solutions having trace initial metal ion concentrations) which indicates that mercury reduction to the corresponding metal in the less acidic solution yields the high log D value and obviates a loading effect; (3) absorption of Ag(I) increases significantly upon going to the less acidic solution (1.41% vs. 88.08% absorbed) which can indicate intervention of the reduction reaction to yield silver metal.

The effect of the ligand acid strength on the selectivity series was determined through the affinity of the sulfonic, phosphinic, and carboxylic acid resins (ligand acidities of strong, moderate and weak, respectively) for eighteen metal ions.[3] The selectivity series were tabulated at each resin's optimum operating conditions which thus requires an increasing solution pH as the ligand acidity decreases (pH values of 1.00, 2.70, and 5.00 for the resins as listed above). The results may be summarized by the following limited series:

sulfonic: Fe(III)>Ba(II)>Mg(II)>Co(II)>Na(I)>Ni(II)
phosphinic: Mg >Ni >Ba >Co >Fe >Na
carboxylic: Co >Ni >Mg >Na >Ba (Fe hydrolyzes)

Mechanism of Polymer-Based Molecular Separations.

The development of polymer-supported reagents which can be used in efficient molecular separations is an area of increasing importance. Such polymers can be used in many applications including the recovery of biomolecules from recombinant DNA processes and of toxic organic compounds from water.

We have begun studies aimed at understanding the mechanisms by which polymers complex molecules (as opposed to metal ions). Our initial publication details our research with linear free energy relationships.[4] Polystyrene-based sulfonic, phosphinic, carboxylic, phosphonate monoester and phosphonate diester resins were contacted with a series of substituted phenols,anilines and benzoic acids. The sorption data was correlated with the electron density at the molecular functional group, as quantified by the Hammett sigma constant for the substituent on the phenyl ring. It is significant to note that the phosphorus acid resins showed the greatest level of molecular sorption specificity. The strongly acidic sulfonic resin completely sorbed each of the anilines while the weakly acidic carboxylic resin sorbed uniformly low levels; the moderately acidic phosphinic and phosphonate monoester resins were the only polymers to distinguish amongst the anilines, with increasing levels of sorption occurring as the $-NH_2$ basicity increased with electron-donating substituents.

Research Plan: August 1, 1990 - July 31, 1991

Development of Ionic Separations. Slope analysis of the logD/pH correlation is widely used to determine the mechanisms by which liquid extractants complex metal ions. The situation is far less straightforward with polymeric reagents because there is no well-defined organic phase concentration term. It will be an aim of this research in the current period to propose generalized categories of polymer - ion interactions based on logD/pH correlations through a systematic study involving the different DMBPs and a series of hard to soft metal ions in solutions of varying pH, ionic strength, and initial metal concentration. The sorption properties will be summarized by, what we are terming,a "Principle of Ionic Recognition by Polymer-Supported Reagents". This principle will derive from our observation that polymers with significant metal ion specificity can be prepared when synthesized with ligands allowing for an access mechanism and a recognition mechanism. Reactions controlling the recognition mechanism, and the possibility of superimposing steric effects for an additional level of specificity, will be fully explored.

Development of Molecular Separations. An experimental protocol for determining the molecular sorption properties of polymer-supported reagents will be defined. We will continue our linear free energy relationship studies, now expanded to include the role of solvent in the active site interaction between polymer and molecule.

PUBLICATIONS: AUGUST 1, 1989 to JULY 31, 1990

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5. S.D. Alexandratos, P.R. Danesi and E.P. Horwitz
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6. S.D. Alexandratos and J.D. Miller
   U.S. Patent 4,894,407 (issued Jan.16, 1990)