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CONCENTRATION AND REMOVAL OF NITROGEN AND SULFUR CONTAINING COMPOUNDS FROM ORGANIC LIQUID PHASES USING ELECTROCHEMICALLY REVERSED CHEMICAL COMPLEXATION

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ABSTRACT

A process is being developed to concentrate and remove sulfur- and nitrogen- containing compounds from organic liquid phases. These phases could include coal liquids, oil from oil shale or tar sands, as well as conventional crude oil. This process uses reversible complexation and electrolysis. A cyclical contacting scheme is proposed: the compounds are first extracted from a polluted hydrocarbon phase using an aqueous phase containing a complexing agent; the aqueous phase is then contacted with a waste hydrocarbon phase and the complexing agent is oxidized, releasing any complexed pollutants into the waste hydrocarbon phase. This cycle is repeated to extract more pollutants, i.e. sulfur and nitrogen compounds, from the contaminated phase and concentrate them in the waste phase. A description of the process and preliminary results for one system are presented.

BACKGROUND

Synthetic fuels derived from coal liquids, tar sands or oil shale contain a wide variety of nonvolatile chemical compounds containing nitrogen and sulfur. Many of these compounds display mutagenic or carcinogenic activity. Therefore, these classes of compounds are undesirable pollutants which must be removed from synthetic fuels and other related hydrocarbon products.

In 1983 the DOE's Technical Information Center released the proceedings from a sponsored conference on the "Chemical Characterization of Hazardous Substances in Synfuels".(1) In this report, Wilson *et al.* (2) reported that " Work over the past few years has led to the recognition that a wide variety of heteroatomic polyaromatic hydrocarbons associated with fossil fuels or products of their use may act as genotoxins. The list of mutagens and potential carcinogens in direct coal liquefaction materials alone can be quite impressive...." The authors proceed to identify classes of sulfur containing compounds, including thiols, thioethers and heterocyclic sulfur compounds present in coal liquids. They also note that coal liquids contain a higher content of nitrogen compounds than other petroleum products. The authors note that "mutagenic activity has been reported for at least one heteroatomic polyaromatic hydrocarbon species...formed from incorporation of one nitrogen, one sulfur or one oxygen atom into the aromatic ring system." Clearly, organic liquids derived from coal will invariably contain a variety of nonvolatile organosulfur and organonitrogen compounds. Some of these compounds have known mutagenic and carcinogenic activity. Combustion of petroleum products containing these compounds will produce volatile oxides of nitrogen and sulfur which are constiuents of acid rain.

In addition to coal liquids, a need for selective removal of heterocyclic organic molecules from liquid hydrocarbon matricies can be identified in other areas. Synthetic fuels derived from tar sands can contain large fractions of these heterocyclic compounds. For example Wang and Noble (3) measured weight fractions of nitrogen and sulfur compounds exceeding 50% in oil derived from oil shale. Many hazardous waste sites contain contaminated hydrocarbon solvents which require extraction of heterocyclic organic compounds and other toxic materials.

The National Research Council (4) recently released a report which targeted high priority research needs and opportunities in chemical separations. They began their report with a discussion of the importance of separations to the US. They identified five areas where separation process efficiency is critical to future US competitiveness: biotechnology, critical and strategic metals, environment, ultrapurification, energy and feedstocks. This research addresses the

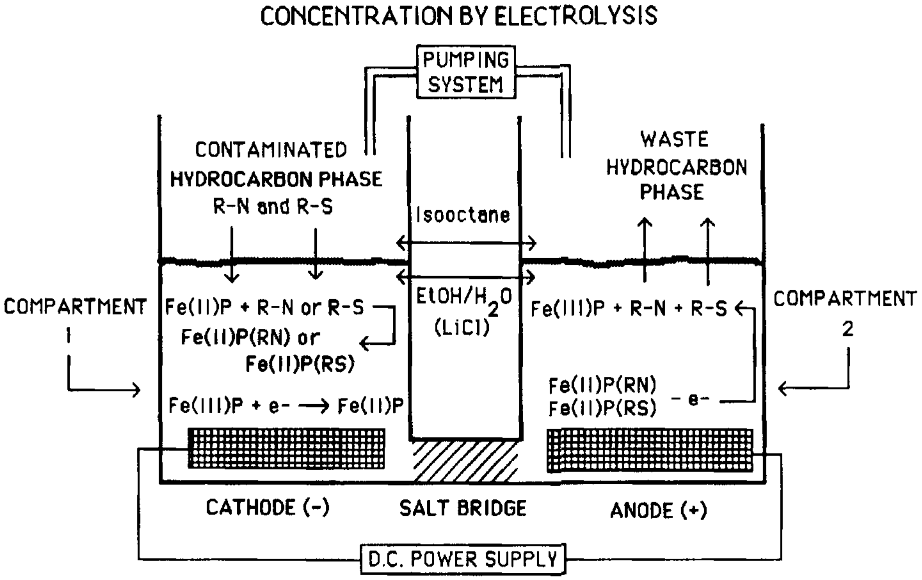


Figure 1. Cross section of electrolytic process for removal of pollutants and subsequent concentration in a waste phase.

needs in the areas of environment, energy and feedstocks. The report then points out six research areas which can have a major impact. The areas which are pertinent to this process include generating improved selectivity amoung solutes in separations, concentrating solutes from dilute solutions, increasing the rate and capacity of separations, developing improved process configurations for separation equipment, and improving energy efficiency in separation systems.

PROCESS DESCRIPTION

A mechanism that utilizes reversible complexation and electrical energy for concentrating sulfur and nitrogen compounds is depicted in Figure 1. The system consists of an electrochemical cell containing a hydrophilic liquid phase. Initially, compartment 2 of the cell contains an Fe(II) complex ion [Fe(II)P] that has a high affinity for nitrogen and sulfur compounds (R-N and R-S). Compartment 1 of the cell contains the same complex ion in a higher oxidation state [Fe(III)P] that has only a slight affinity for R-N and R-S.

Prior to the situation depicted in Figure 1, compartment 2 containing Fe(II)P is contacted with a contaminated, immiscible hydrocarbon phase. Complexation with Fe(II)P causes R-N and R-S to partition into the hydrophilic phase. After equilibrium is established, a pumping system is used to transfer the contaminated hydrocarbon phase to compartment 1. At this time, a waste hydrocarbon phase is added to compartment 2. This is the situation depicted in Figure 1. A power supply is now used to reduce the Fe(III)P complex ions in compartment 1 and to oxidize the Fe(II)P complexes in compartment 2. In 1, additional nitrogen and sulfur compounds will be extracted from the contaminated hydrocarbon phase. In 2, nitrogen and sulfur compounds will be released into the waste hydrocarbon phase. The pumping system can then be used to switch the hydrocarbon phases between compartments 1 and 2, then electrolysis can be repeated in the opposite direction. Additional cycles will continue to remove R-S and R-N from the contaminated phase and to concentrate these species in the waste hydrocarbon phase.

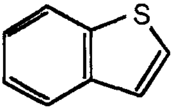
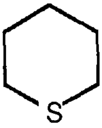
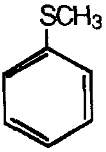
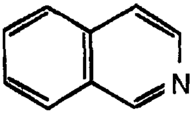
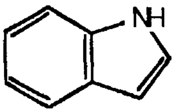
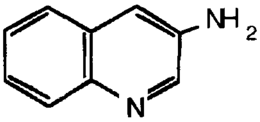
Selection of Representative Pollutants

Table 1 contains a listing of the classes of nitrogen and sulfur pollutants found in coal liquids. From the extremely large number of individual pollutants that could be studied, we have selected one compound from each class for our investigations. The structures of these compounds are also contained in Table 1. The compounds were selected based on availability and known complexation chemistry with Fe(II) complex ions. Compounds with known mutagenic or carcinogenic activity were avoided because their use would result in unacceptable safety conditions in the laboratory.

Selection of Solvent System and Carriers

Phase separation of iso-octane/ethanol/water/lithium chloride mixtures. Coal products are an extremely complex matrix for an initial study. Therefore, iso-octane (2,2,4-trimethyl-pentane) was chosen as a hydrocarbon phase because of its relatively low volatility, low solubility in water and its availability as a pure liquid. All of the sulfur and nitrogen compounds to be investigated are soluble in iso-octane. Water is an acceptable solvent for the electrolysis phase in that the proposed carriers are soluble while the permeates are relatively insoluble. In fact, many of the permeates would be sufficiently insoluble in pure water to preclude complexation. For this reason, it would be desirable to utilize a hydrophilic solvent in which the permeates have some solutility. Ethanol/water mixtures should be acceptable in this regard. While iso-octane and ethanol are miscible, ethanol/water mixtures containing up to 50% ethanol are immiscible with iso-octane. In the electrochemical experiments, a salt must be present for ionic conduction. Lithium chloride (LiCl) is soluble in ethanol/water mixtures and also decreases their solubility in iso-octane.

Table 1. Common Pollutants Found in Coal Liquids

Chemical Class	Biological Activity*	Example Compound
Volatile Sulfide	Toxic	Carbon Disulfide
Aromatic Sulfur Heterocycle	Weak Mutagen	 Thionaphthene
Cyclic Thioether	Irritant	 Pentamethylene Sulfide
Aromatic Thioether	Irritant	 Methylphenyl Sulfide
Tertiary Aromatic Nitrogen Heterocycle	Mutagen Carcinogen	 Isoquinoline
Secondary Aromatic Nitrogen Heterocycle	Mutagen Carcinogen	 Indole
Amino Aromatic Nitrogen Heterocycle	Probable Mutagen Carcinogen	 3-Aminoquinoline

*for certain compounds within class

Table 2. Extraction of Isoquinoline into Water/Ethanol/LiCl Solutions

Hydrophilic phase	Solubility	Distribution Coefficient
5.0 M LiCl	0.019 mM	26
2.5 M LiCl	0.039 mM	12
2.5 M LiCl 25% Ethanol	0.22 mM	1.3

As an example, the permeate isoquinoline (see Table 1) dissolved in iso-octane is only slightly extracted into an aqueous solution 2.5 M in LiCl. At a typical feed concentration of 0.5 mM isoquinoline only 0.039 mM of the permeate is detected in the aqueous phase. This was for an extraction in which the volumes of the aqueous and the organic phases were equal. Thus, the distribution coefficient (K_D) for this permeate would be about 12. This distribution coefficient can be adjusted in either direction by manipulating the composition of the aqueous phase. In Table 2 the solubility and the distribution coefficient are shown for the extraction of 0.5mM isoquinoline into an equal volume of three different aqueous phases. This data demonstrates that it is possible to adjust the solubility of the permeate in the aqueous phase without promoting the mixing of the two phases.

Water-soluble Fe(II) porphyrins. The carriers selected for these studies are water-soluble derivatives of Fe(III) metalloporphyrins. A porphyrin (P) is a tetradentate macrocyclic ligand; the structure of the porphyrin derivative to be used in this study is contained in Figure 2. Metalloporphyrins have numerous biological functions including the transport of oxygen. For this reason, the properties of metalloporphyrins have been studied extensively (5,6). These complex metal ions are often stable in several oxidation states and have well defined electrochemical properties. The Fe(II) form of the carrier depicted in Figure 2 can be readily prepared by chemical or electrochemical reduction of the +3 oxidation state which is available through commercial sources.

The metal ions in metalloporphyrins bind other molecules (ligands) in addition to the porphyrin itself. These bonds are perpendicular to the plane of the porphyrin (see Figure 2) so the bound molecules are referred to as axial ligands. Reversible reactions

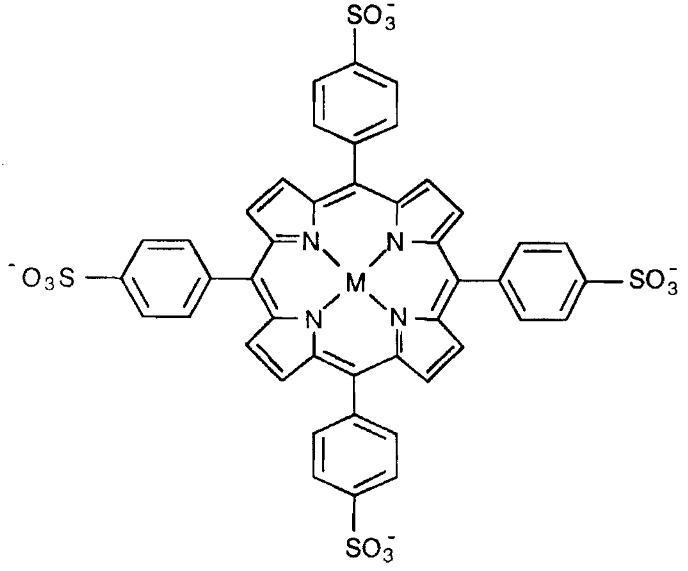


Figure 2. Complexing agent used in this study, tetra(4-sulfonatophenyl)porphyrin, Na^+ salt (TPPS).

between metalloporphyrins (carriers) and axial ligands (permeates) to form complexes are the basis for the separation procedures outlined in this paper. Many such reactions have been characterized for iron porphyrins (7-14). Iron metalloporphyrins may have one or two axial ligands depending on the oxidation state of the metal and the nature of the ligands that are available for binding. In the absence of other ligands, the axial positions in iron porphyrins are occupied by solvent molecules or anions. The pollutants depicted in Table 1 generally bind more strongly to Fe(III) and Fe(II), and would be expected to displace solvent molecules or anions.

In general, complexation reactions have greater equilibrium constants when the metals are in the +2 oxidation state. Furthermore, the number of axial ligands bound to the metal can also differ. For Fe(II)P, two axial ligands (L) are often bound in subsequent reaction (5,14):

$$\mathrm{Fe(II)P} + \mathrm{L} \longleftrightarrow \mathrm{Fe(II)P(L)}$$
$$\mathrm{Fe(II)P(L)} + \mathrm{L} \longleftrightarrow \mathrm{Fe(II)P(L)_2}$$

The tendency for one or two displacing ligands to be bound to Fe(II) depends on the magnitude of the equilibrium constants of the above reactions and the concentration of L. For most of the pollutants in Table 1, the equilibrium constants are sufficiently large that two molecules will be bound if the concentration of L is millimolar or greater. For Fe(III), binding of two axial ligands only occurs at very high concentrations of L, i.e. the predominant reaction is (5,14):

$$\mathrm{Fe(III)P + L \longleftrightarrow Fe(III)P(L).}$$

For molecules similar to those in Table 1, the equilibrium constant for binding a single L to Fe(III) will be smaller than the value for Fe(II). While a detailed picture of the bonding in these complexes is complicated, the difference in reactivity for Fe(III) and Fe(II) can be qualitatively explained by the fact that Fe(II) is a softer Lewis base and therefore has a greater affinity for soft Lewis acids such as organosulfur and heterocyclic nitrogen compounds. This difference in reactivity was confirmed for Fe(III)TPPS complex ion using isoquinoline as the incoming ligand (permeate). The binding of isoquinoline to Fe(III)TPPS at neutral pH's, could not be detected spectrophotometrically, but Fe(II)TPPS quickly reacted with an excess of isoquinoline changing the solution color from green to peach. The Fe(III)TPPS was easily reduced to Fe(II) by electrolysis under nitrogen at a mercury pool.

The ability to alter the affinity of a carrier for a permeate by changing its oxidation state is the basis for the separation processes diagrammed in Figure 1. In particular, the fact that Fe(III) porphyins have much lower tendencies to form complexes with molecules like those in Table 1 than does the Fe(II) form is exploited. As mentioned earlier, interconversion of the Fe(III) and Fe(II) states in metalloporphyrins is a kinetically facile process at metal electrodes. The reduction potentials for this process depend on the substituents on the porphyrin ring and to a lesser extent on the solvent and supporting electrolyte. The value for the iron porphyrin in Figure 2 is 0.2 V vs. SHE (15). By applying relatively mild potentials, it should be possible to achieve the cyclical process:

$$\begin{array}{ll}
\text{cathode:} & \mathrm{Fe(III)P + e^- \longrightarrow Fe(II)P} \\
 & \mathrm{Fe(II)P + R\text{-}N \text{ or } R\text{-}S \longrightarrow Fe(II)P(RN \text{ or } RS)_{1 \text{ or } 2}} \\
\text{anode:} & \mathrm{Fe(II)P(RN \text{ or } RS)_{1 \text{ or } 2} \longrightarrow Fe(III)P + e^- + R\text{-}N \text{ or } R\text{-}S.}
\end{array}$$

Relative to other coordination compounds, metalloporphyrins are very stable in a chemical sense (5,6). The porphyrin molecule itself is stable due to the conjugated double bonds around the periphery of the ring. The overall formation constants between porphyrins and Fe(II) or Fe(III) are extremely large because the porphyrin is a tetradentate ligand (forms four bonds to the metal). For these reasons, the selected

Table 3. Preliminary Extraction Results
1. Solutions Used for Extractions

Aqueous Phase	Contaminated Organic Phase	Waste Organic Phase
0.2 M LiCl 0.02 M Citric Acid pH=6	0.5 mM isoquinoline iso-octane	iso-octane

2. Final Solute Concentrations

Extraction Phase	Concentration (mM) Before	After
Contaminated	0.5	0.1
Waste	0.0	0.2
Aqueous	0.0	0.2

carriers will display a high degree of thermal stability. Thus, it should be possible to operate the proposed separation systems at temperatures up to the boiling point of the hydrophilic phase.

In addition to the pollutants in Table 1, the Fe(II) porphyrin carriers will react with certain gaseous molecules such as O_2, CO, SO_2 and NO (12,13). With the exception of carbon monoxide, these reactions are irreversible and the presence of these gases would be deleterious to the system. For laboratory experiments, dissolved gases are removed with Ar or N_2. For practical separations, dissolved gases could be removed from the hydrocarbon phases with CO_2.

PRELIMINARY RESULTS

The results of one cyclical process are shown in Table 3. The complexing agent used is FeTPPS shown is Fig. 2 where M=Fe. This initial study provides proof of concept for the process. Equilibrium was reached in about 3 to 4 cycles. About 80% of the isoquinoline initially present was removed from the contaminated organic phase. Of that 80% extracted, half is extracted into the waste iso-octane phase while the other half remains in the aqueous phase. The isoquinoline in the aqueous phase includes both free isoquinoline and isoquinoline bound to the carrier. It should be noted that this will remain constant even if there were more isoquinoline to be extracted from the contaminated isooctane phase.

Further work will focus on single and multi-component extractions. Modifications of the aqueous phase and complexing agent will result in an optimal extraction and recovery system.

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