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AQUEOUS BIPHASE EXTRACTION FOR PROCESSING OF FINE COAL

Final Technical Report

October 1996 – July 2001

by

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EXECUTIVE SUMMARY

The objective of this research project is to develop an aqueous biphasic extraction process for the treatment of fine coals. Aqueous biphasic extraction is an advanced separation technology that relies on the ability of an aqueous system consisting of a water-soluble polymer and another component, e.g., another polymer, an inorganic salt, or a nonionic surfactant, to separate into two immiscible aqueous phases. The principle behind the partition of solid particles in aqueous biphasic systems is the physicochemical interaction between the solid surface and the surrounding liquid solution. In order to remove sulfur and mineral matter from fine coal with aqueous biphasic extraction, it is necessary to know the partitioning behavior of coal, as well as the inorganic mineral components. Therefore, in this research emphasis was placed on the partitioning behavior of fine coal particles as well as model fine inorganic particles in aqueous biphasic systems.

In the polyethylene glycol (PEG)/salt/H₂O system, it was found that pyrite partition was highly dependent upon pH conditions: at high pH the particles preferred the salt-rich (bottom) phase, while they moved to the polymer-rich (top) phase at low pH. This behavior is attributable to the different surface oxidation products associated with the pH variations: formation of FeOOH in alkaline solution, and a hydrophobic iron-deficient product (Fe_{1-x}S₂) in acidic environment. The partitioning behavior of oxide particles (e.g., Al₂O₃, Fe₂O₃, SiO₂, TiO₂) in the PEG/Na₂SO₄/H₂O system indicated that, in the absence of polymer-solid interaction, the surface hydrophilic/hydrophobic properties determined solid partition; otherwise, the specific polymer-solid interaction dominated the distribution of the solid particles.

Aside from the polymer/salt aqueous biphasic systems, the partitioning behavior of hematite and silica was also investigated in polymer/polymer (PEG/dextran) and polymer/nonionic surfactant (Triton X-100 (TX100)/dextran) systems. In these systems interaction between the phase components and the solid surface played an important role in determining the solids distribution. For both biphasic systems, hematite stayed in the bottom dextran-rich phase, which was attributable to the strong interaction between dextran and ferric oxide. However, the partitioning behavior of silica was found to be pH-dependent. At low pH the particles preferred the top phase; with increase in pH, the solids gradually moved to the interface, then to the bottom phase and they transferred back to the top phase again at very high pH. The results were attributed to the competition between dextran/SiO₂ and TX100/SiO₂ or dextran/SiO₂ and PEG/SiO₂ interactions.

Surfactant addition also offers an important way to change the surface chemistry of a solid. In the PEG/salt/H₂O system, it is found that only surfactants adsorbed chemically on the solid surfaces had a significant influence on solid distribution, e.g., xanthate/pyrite and oleate/hematite. In contrast, in the case where surfactant adsorption was predominantly electrostatic (physical), surfactant addition had no effect on partitioning behavior. In the other two types of aqueous biphasic systems, an interesting result was the finding that electrostatic forces generated through the addition of ionic surfactants could cause significant changes in the partition of solid particles. In the TX100/dextran system, dodecyl trimethyl ammonium bromide (DTAB) transferred hematite particles to the top phase or the interface at high pH. It was also noteworthy that, even though SDS and

DTAB had opposite charges, they could have the same effect on silica partition in the PEG/dextran system because the two surfactants preferred the conjugate phases. In contrast, in the TX100/dextran system, these surfactants had the opposite effects since they both concentrated in the top nonionic surfactant-rich phase.

After investigating the partitioning behavior of inorganic particles, this research also studied the partition of fine coal particles in the polymer/salt/water system. It was found that the coal particles preferred the top polymer-rich phase because of the naturally hydrophobic surface of this carbonaceous material. Additives (such as H_2O_2 and FeCl_3) and pH had no significant effects on the partitioning behavior. Also, the feasibility of processing fly ash of high carbon content by aqueous biphasic extraction was investigated. In order to improve the utility of fly ash, it is necessary to separate the carbon fraction from the fly ash to give a product with low carbon content and a carbon-rich product. According to the partitioning experiments of fly ash in the PEG/ Na_2SO_4 / H_2O system and the characterization of the beneficiated samples, it was concluded that the beneficiation of fly ash is possible. Based on the experimental results obtained, a flowsheet was proposed for the treatment of high-carbon fly ash with the aqueous biphasic extraction process.

TABLE OF CONTENTS

LIST OF TABLES	x
LIST OF FIGURES	xi
 Chapter 1. INTRODUCTION AND OBJECTIVES	 1
1.1 Problems in Fine Coal Processing	1
1.2 Aqueous Biphasic Systems and Aqueous Biphasic Extraction	3
1.3 Partition of Solid Particles in Aqueous Biphasic Systems	6
1.4 Research Objectives	10
1.5 References	11
 Chapter 2. PARTITIONING BEHAVIOR OF PYRITE IN POLYMER/SALT AQUEOUS BIPHASE SYSTEMS	 15
2.1 Introduction	15
2.2 Experimental Procedures	17
2.2.1 Materials	17
2.2.2 Phase Diagram Determination for the PEG/Na ₂ CO ₃ /H ₂ O System	18
2.2.3 Pyrite Partition Experiments	20
2.3 Results and Discussion	21
2.3.1 Phase Diagram for the PEG/Na ₂ CO ₃ /H ₂ O System	21
2.3.2 Pyrite Partition in the PEG/Na ₂ CO ₃ /H ₂ O System	27
2.3.3 Pyrite Partition in the PEG/Na ₂ SO ₄ /H ₂ O System	33
2.3.4 Effects of Additives on Pyrite Partition in the PEG/Na ₂ SO ₄ /H ₂ O System	40
2.3.5 Effects of Surfactants on Pyrite Partition in the PEG/Na ₂ SO ₄ /H ₂ O System	43
2.4 Conclusions	47
2.5 References	48

Chapter 3. PARTITIONING BEHAVIOR OF OXIDE PARTICLES IN THE PEG/Na ₂ SO ₄ /H ₂ O SYSTEM	52
3.1 Introduction	52
3.2 Experimental Procedures	54
3.2.1 Materials	54
3.2.2 Partition Experiments	55
3.3 Results and Discussion	56
3.3.1 Partitioning Behavior of Oxide Particles in the PEG/Na ₂ SO ₄ /H ₂ O System	56
3.3.2 Effects of Surfactants on Hematite Partition in the PEG/Na ₂ SO ₄ /H ₂ O System	58
3.4 Conclusions	62
3.5 References	63
Chapter 4. PARTITIONING BEHAVIOR OF HEMATITE IN POLYMER/ POLYMER AND POLYMER/SURFACTANT SYSTEMS	67
4.1 Introduction	67
4.2 Experimental Procedures	69
4.2.1 Materials	69
4.2.2 Partition Experiments	70
4.3 Results and Discussion	74
4.3.1 Effect of pH on Hematite Partition in the Triton X-100/Dextran/H ₂ O System	74
4.3.2 Effects of Surfactants on Hematite Partition in the Triton X-100/Dextran/H ₂ O System	76
4.3.3 Effect of pH on Hematite Partition of in the PEG/Dextran/H ₂ O System	79
4.3.4 Effects of Surfactants on Hematite Partition in the PEG/Dextran/H ₂ O System	79
4.4 Conclusions	82
4.5 References	83

Chapter 5. PARTITIONING BEHAVIOR OF SILICA IN POLYMER/ POLYMER AND POLYMER/SURFACTANT SYSTEMS	86
5.1 Introduction	86
5.2 Experimental Procedures	89
5.2.1 Materials	89
5.2.2 Partition Experiments	90
5.3 Results and Discussion	92
5.3.1 Effects of pH on Silica Partition in the Triton X-100/Dextran/H ₂ O System	92
5.3.2 Effects of Surfactants on Silica Partition in the Triton X-100/Dextran/H ₂ O System	95
5.3.3 Effects of pH on Silica Partition in the PEG/Dextran/H ₂ O System	101
5.3.4 Effects of Surfactants on Silica Partition in the PEG/Dextran/H ₂ O System	104
5.4 Conclusions	107
5.5 References	109
Chapter 6. PARTITION OF FINE COAL AND FLY ASH IN AQUEOUS BIPHASE SYSTEMS	114
6.1 Introduction	114
6.2 Experimental Procedures	116
6.2.1 Materials	116
6.2.2 Partition Experiments	116
6.2.3 Characterization of Fly Ash	117
6.3 Results and Discussion	119
6.3.1 Coal Partition in the PEG/Salt/Water System	119
6.3.2 Fly Ash Partition in the PEG/Na ₂ SO ₄ /H ₂ O System	121
6.3.3 Characterization of the Fly Ash Fractions after Partitioning Experiments	123
6.3.4 Preliminary Flowsheet	131
6.4 Conclusions	133
6.5 References	135

Chapter 7. SUMMARY	138
LIST OF PUBLICATIONS	145

LIST OF TABLES

TABLE 2.1.	Effect of conditioning time (pyrite oxidation) on pyrite partition in the PEG-2000/ Na_2CO_3 / H_2O system (pH=11.9)	30
TABLE 2.2.	Effect of buffer solid on pyrite partition in the PEG-2000/ Na_2SO_4 / H_2O system; conditioning time = 2 hours	38
TABLE 2.3.	Effect of FeCl_3 on pyrite partition in the PEG-2000/ Na_2SO_4 / H_2O system	42
TABLE 2.4.	Effect of xanthate on pyrite partition to the polymer-rich phase of the PEG-2000/ Na_2SO_4 / H_2O system; conditioning time = 2 hours	46
TABLE 4.1.	Effect of ionic surfactants on hematite partition in the Triton X-100/dextran system	75
TABLE 4.2.	Effect of ionic surfatants on hematite partition in the PEG/dextran system	81
TABLE 5.1.	Effect of SDS concentration on silica partition in the Triton X-100/dextran/ H_2O system	97
TABLE 5.2.	Effect of DTAB concentration on silica partition in the Triton X-100/dextran/ H_2O system	100
TABLE 6.1.	The elemental compositions of standard samples in ICP-AES measurement	118
TABLE 6.2.	Effect of additives on coal partition in the PEG-2000/salt/ H_2O system	120
TABLE 6.3.	Effect of pH on fly ash partition in the PEG-2000/ Na_2SO_4 / H_2O system (solids content: 2 wt%)	124
TABLE 6.4.	Elemental composition of ash in the parent fly ash and several beneficiated samples (solid content of 2 wt%)	132

LIST OF FIGURES

FIGURE 1.1.	Schematic phase diagram illustrating the effects of polymer and salt concentrations on the one-phase and two-phase domains in polymer/salt/water systems	4
FIGURE 2.1.	Refractive index calibration curves for Na_2CO_3 and PEG	19
FIGURE 2.2.	Phase diagram of the PEG-2000/ Na_2CO_3 / H_2O system	22
FIGURE 2.3.	Phase diagram of the PEG-3400/ Na_2CO_3 / H_2O system	23
FIGURE 2.4.	Phase diagram of the PEG-4600/ Na_2CO_3 / H_2O system	24
FIGURE 2.5.	Phase diagram of the PEG-8000/ Na_2CO_3 / H_2O system	25
FIGURE 2.6.	Effect of PEG molecular weight on phase diagrams of the PEG/ Na_2CO_3 / H_2O system	26
FIGURE 2.7.	Mechanism of particle partitioning in aqueous biphasic systems	28
FIGURE 2.8.	Effect of pH on pyrite partition in the PEG-2000/ Na_2CO_3 / H_2O system: conditioning time = 2 hours	32
FIGURE 2.9.	Effect of pH on pyrite partition in the PEG-2000/ Na_2SO_4 / H_2O system; conditioning time = 2 hours	34
FIGURE 2.10.	The equilibrium Eh-pH diagram for the Fe-S- H_2O system at 25°C	35
FIGURE 2.11.	Effect of PEG molecular weight on pyrite partition to the polymer-rich phase of the PEG/ Na_2SO_4 / H_2O system; conditioning time: 2 hours	39
FIGURE 2.12.	Effect of pH on pyrite partition in the PEG-2000/ Na_2SO_4 / H_2O system in the presence of $0.1\text{M H}_2\text{O}_2$; no conditioning	41
FIGURE 2.13.	Effects of pH, oleate, SDS, and xanthate on pyrite partition to the polymer-rich phase of the PEG-2000/ Na_2SO_4 / H_2O system; conditioning time = 2 hours	44
FIGURE 3.1.	Effect of pH on partition of alumina, hematite, silica, and titania to the top phase of the PEG/ Na_2SO_4 / H_2O system	57
FIGURE 3.2.	Effect of pH on hematite partition to the top phase of the PEG-4600/ Na_2SO_4 / H_2O system in the presence of surfactants	61

FIGURE 4.1.	Chemical structures of polymers and surfactants	71
FIGURE 4.2.	Phase diagram for the Triton X-100/dextran T500/water system at 4 °C	72
FIGURE 4.3.	Phase diagram for the PEG-8000/dextran-40/water system at 22 °C ...	73
FIGURE 4.4.	Effect of pH on hematite partition to the top phase of the Triton X- 100/dextran/H ₂ O system in the presence of DTAB	78
FIGURE 5.1.	Chemical structures of polymers and surfactants	91
FIGURE 5.2.	Effect of pH on silica partition in the Triton X-100/dextran/H ₂ O system	93
FIGURE 5.3.	Effect of pH on silica partition to the top phase of Triton X- 100/Dextran/H ₂ O system in the presence of SDS and DTAB	98
FIGURE 5.4.	Effect of pH on silica partition in the PEG/dextran/H ₂ O system	102
FIGURE 5.5.	Effect of pH on silica partition to the top phase of the PEG/dextran/H ₂ O system in the presence of SDS and DTAB	106
FIGURE 6.1.	Effect of pH on fly ash partition in the PEG-2000/Na ₂ SO ₄ /H ₂ O system (solids content: 1 wt%)	122
FIGURE 6.2.	The carbon contents in each liquid fraction (solids content: 1 wt%) ...	125
FIGURE 6.3.	XRD result of the parent sample (-400 mesh)	127
FIGURE 6.4.	XRD result of the sample in the upper zone of the polymer-rich phase at pH 12 (solids content: 1 wt%)	128
FIGURE 6.5.	XRD result of the sample in the lower zone of the polymer-rich phase at pH 12 (solids content: 1 wt%)	129
FIGURE 6.6.	XRD result of the sample in the salt-rich phase at pH 12 (solids content: 1 wt%)	130
FIGURE 6.7.	Proposed flowsheet for aqueous biphasic extraction of high-carbon fly ash	134

Chapter 1

INTRODUCTION AND OBJECTIVES

1.1 Problems in Fine Coal Processing

Coal represents the largest source of fossil energy in the U.S. This resource also represents the most readily accessible and socially acceptable substitute for oil and natural gas. In response to the stipulations of the Clean Air Act (1), advanced coal cleaning technologies are needed in order to more efficiently eliminate unacceptable levels of ash and sulfur from the run-of-mine coal prior to combustion. The ability to achieve mineral matter liberation from coal is fundamental to all separation techniques that seek to produce super-clean coal. It has been concluded from the microscopic examination of a wide variety of U.S. coals that, in many cases, grinding to 10 μm or below may be necessary in order to achieve the necessary liberation (2). It is clear, therefore, that future advanced coal cleaning technologies must be capable of accommodating micron size particles.

Large quantities of fine coals already exist in the rejects discharged into waste ponds. These fine coals are a result of the current highly mechanized production practices of continuous and longwall mining. As a result of the nonselectivity of cutting machines and the exploitation of higher ash/sulfur seams, these coal fines are characterized by high

contents of mineral matter. These coal fines must therefore be cleaned in order to produce a saleable product. Unfortunately, conventional coal cleaning techniques are not effective in treating such fine coals. The result is that large amounts of fine coals are discharged into refuse ponds, even though this material represents a potential source of energy. The proliferation of such waste ponds is no longer environmentally acceptable.

Among the potential fine coal cleaning processes commonly cited in the literature are the following (3-10): (a) heavy media cyclone separations, (b) froth flotation, (c) selective flocculation, and (d) oil agglomeration. Froth flotation is the most well established of these techniques. This method is, however, not very effective as particle size falls below 100 mesh ($< 149 \mu\text{m}$) (10). The low efficiency is associated with the following reasons: (a) small particle size reduces the collision efficiency between solid particles and air bubbles; (b) fine particles possess high specific surface areas and this leads to high flotation reagent consumption; (c) fine particles tend to undergo agglomeration or heterocoagulation with larger particles and this hinders the flotation selectivity; and (d) the large specific surface area of fines increases the probability of nonselective adsorption of collectors, which in turn causes flotation of undesired minerals (11-13).

There has also been some interest in selective oil agglomeration since, when applied to finely divided coals, this technology appears to surpass the efficiency attainable with froth flotation (8-10). The oil agglomeration process has, however, been criticized because of the need for heating (90-120 °C, with heavy oils), the potential fire hazards (especially when the relatively volatile light oils are used), relatively high cost of oil, and the need for very high energy input (mixing) in order to effect phase separation (10).

Finally, it has not yet been demonstrated that selective oil agglomeration can yield acceptable pyrite-coal separations (10). Thus, the search for efficient cleaning technologies for fine coals cannot be said to be over.

This research seeks to investigate the feasibility of adapting for fine coal cleaning, a novel separation technique uniquely suited to micron size particles, i.e., aqueous biphasic extraction (ABE). This separation technique, initially developed in the mid 50s for microbial cell separations (14-18), has recently attracted considerable attention and is being investigated for a broad range of applications such as protein separations (14-20), metal ion separations (21-24), and separation of ultrafine inorganic particles (25-31). This technique relies on the formation of a two-phase system in a mixture of a water-soluble polymer and another polymer, an inorganic salt, or a surfactant. In the following section, we briefly introduce the physicochemical phenomena underlying aqueous biphasic formation and the factors that determine the partitioning behavior of colloidal particles. The research objectives are then presented.

1.2 Aqueous Biphasic Systems and Aqueous Biphasic Extraction

If two water-soluble polymers are present in a solution, two phases may form when the concentrations of the polymers exceed certain limits; examples are polyethylene glycol (PEG)/dextran, PEG/poly(N-vinylpyrrolidone) (PVP) (14-18). Also, two-phase systems can be formed in the water-soluble polymer/non-ionic surfactant or polymer/inorganic salt systems, e.g., PEG/Tween-80, PEG/Na₂SO₄, and PEG/Na₃PO₄ (14

FIGURE 1.1. Schematic phase diagram illustrating the effects of polymer and salt concentrations on the one-phase and two-phase domains in polymer/salt/water systems.

- 18). A schematic phase diagram for these systems is presented in Figure 1.1. As shown in the diagram, the critical compositions which mark the transition from a one-phase system to a two-phase system lie on the binodal curve. In these aqueous biphasic systems, the top phase is usually enriched in one component, and another component is concentrated in the bottom phase. For example, combining equal volumes of a 20 wt% aqueous solution of sodium carbonate and a 30 wt% aqueous solution of PEG-2000 (polyethylene glycol, molecular weight = 2×10^3), a turbid mixture is produced which subsequently separates into two phases after a few minutes. In this system sodium carbonate is concentrated in the bottom phase and the top phase is PEG-enriched.

Aqueous biphasic systems can be exploited as extraction media, just like the oil/water two-phase systems used in traditional solvent extraction (14-18). Referring to Figure 1, the tie line shown in the two-phase region identifies the compositions of the top (A) and bottom (D) phases. The two-phase systems represented by points B and C have the same phase compositions. However, system B has a higher volume of the polymer-rich phase. Traveling along the tie line provides a convenient means of varying the phase volumes, as needed. The recovery, as well as the degree of purification, may be controlled by manipulating the phase ratios. The choice of tie line offers another means of controlling the separation. A tie line which is farther from the binodal curve will be characterized by conjugate phases which differ significantly in composition. Systems lying on such a tie line would be expected to give higher selectivity in the separation.

Compared with conventional solvent extraction and other fine particles processing techniques, aqueous biphasic extraction is especially attractive for waste treatment applications, because it avoids the use of an organic solvent which itself may be a

possible pollutant. In addition, the polymers used in aqueous biphasic systems are generally inexpensive, nontoxic, and biodegradable (26). Also the aqueous biphasic systems can be recycled, with the effective separation of dispersed particles and solution.

1.3 Partition of Solid Particles in Aqueous Biphasic Systems

The basic principle behind the partition of particles in aqueous biphasic systems is the physicochemical interaction between the solid surface and the surrounding liquid solution, rather than the bulk properties of the solid or solution such as density (14-18). Accordingly, differences in the surface chemistry of particles can be exploited to achieve selective separations. Also, approaches that change solid surface chemistry can be used to control the partitioning behavior of particles. Although a lot of research has been conducted on the application of aqueous biphasic extraction in biological science and technology, only a few results were found in the literature about the partition of inorganic particles in these systems. In the present context, the limited work with colloidal particles is especially relevant.

Ananthapadmanabhan and Goddard (25) were among the first to study the partitioning behavior of fine mineral particles in aqueous biphasic systems. The materials investigated included metal oxides (hematite, silica, titania), apatite, and metal sulfides (copper sulfide, lead sulfide, zinc sulfide, iron sulfide, nickel sulfide). The two-phase system was obtained by mixing 20 mL of 15 wt% solution of polyethylene glycol and the same volume of 7.5 wt% solution of sodium sulfate. It was found that almost all the

minerals went into the bottom salt-rich phase; the only exception was silica particles that concentrated in the top polymer-rich phase.

Chaiko et al. (26-28) investigated the possibility of applying ABE to separate radioactive Pu oxide from silicate. The experimental system typically consisted of 15% PEG-3400/7.5% Na₂SO₄. It was found that, irrespective of the pH, a diverse range of metal oxides, e.g., Al₂O₃, Fe₂O₃, TiO₂ partitioned into the lower salt-rich phase (26). However, it was found that all the SiO₂ consistently reported to the upper aqueous phase. Therefore, these authors demonstrated that it was possible to achieve a quantitative separation of silica from these metal oxides. Another interesting finding reported by these investigators (26) is the discovery that a clean separation between graphite and PuO₂ could be achieved, with the graphite reporting to the upper polymer-rich phase. Also, ABE was successfully used to reduce the uranium contamination in soil from 200,000 mg/kg to less than 50 mg/kg (29, 30). In the scale-up experiments, a Karr column was used as the extraction vessel, and the solid in each phase was recovered through a centrifugal filter. This process was found to be still effective even when the solid loading increased from 1 wt% to 20 wt% (29, 30).

The trends observed in the experiments of Chaiko et al. (26) were rationalized by referring to the interactions of the polymer and the inorganic solutes with the oxide/water interface. The polymer PEG is nonionic; it therefore interacts with the solid surface only via hydrogen bonding between the neutral surface silanol (Si-OH) groups and the O atoms in the PEG chain. The ability of the sulfate ion to adsorb on metal oxides such as Al₂O₃, Fe₂O₃, and TiO₂ is well documented (35, 36). It was proposed that at the relatively high sodium sulfate concentrations used for the ABE investigations, the sulfate ion

adsorbs on Al_2O_3 , Fe_2O_3 , and TiO_2 in preference to adsorption of PEG. As the oxide surface becomes more ionized (i.e., $\text{pH} \gg \text{pzc}$, $\text{pH} \ll \text{pzc}$), the surface concentration of neutral hydroxyl sites decreases and consequently polymer adsorption also decreases. Thus, manipulation of the pH can be used to control the partitioning of particles between the two liquid phases.

From the above discussion, it can be seen that the partitioning of colloidal particles in aqueous biphasic systems is a result of differences in surface chemical properties. Thus, many of the well established techniques of flotation technology can also be exploited here to modify particle separations. For example, selective adsorption of surfactants may be used to enhance the hydrophobicity of a given material and hence increase its partition into the polymer-rich phase. According to Chaiko et al (26), as a result of the prevailing high ionic strengths, surfactants which adsorb via physical interactions are not very effective as phase transfer agents. Addition of sodium dodecyl sulfate (known to adsorb via electrostatic interaction) had no effect on the partitioning of Al_2O_3 , Fe_2O_3 , and TiO_2 . However, when oleic acid, which chemisorbs via covalent bonding was used, the transfer of Fe_2O_3 and TiO_2 into the polymer-rich phase became feasible. Ananthapadmanabhan and Goddard (25) also reported that the partitioning behavior of mineral particles in aqueous biphasic systems can be modified with phase transfer agents. They found that addition of xanthate into the $\text{PEG}/\text{Na}_2\text{SO}_4$ system was able to transfer all the sulfide minerals from the bottom salt-rich phase to the top polymer-rich phase. The partitioning behaviors of oxide particles and apatite were also investigated in the presence of several surfactants (alkylbenzene sulfonate, oleic acid, and cetyl trimethyl ammonium bromide).

As already noted above, aside from polymer/salt biphasic systems, other systems like polymer/polymer and polymer/surfactant can also be exploited as separation media for fine particle processing. However, prior to our own research, the only available result in the literature was that of Baxer et al. (31). They studied the partition of latices and TiO_2 in polymer/polymer two-phase systems (such as PEG/dextran, PEG/poly(N-vinylpyrrolidone) (PVP), and etc.). In the PEG/dextran system, the hydrophilic latices went into the bottom dextran-rich phase, while the hydrophobic latices stayed in the top PEG-rich phase. The partitioning behavior was also found to be greatly dependent upon the surface chemistry of the particles, i.e., the functional group on the particle surfaces. At pH 6.5, the latex particles with carboxyl groups on their surfaces preferred the PEG-rich phase of the PEG/dextran system; this result was attributed to the protonation of the surface COO^- groups. When pH was increased to 9.6, most of the carboxyl groups were deprotonated and the particles transferred to the dextran-rich phase. In the PEG/PVP system, the particles (both latices and TiO_2) with surface OH groups concentrated in the PVP-rich phase, while those with COOH groups dispersed in the PEG-rich phase. These results were attributed to the specific interaction between the functional groups on the solid surface and the molecular chain of polymers in the solution. Also, the qualitative separation of a mixture of latices with different surface groups was demonstrated for polymer/polymer biphasic systems (31).

1.4 Research Objectives

The overall objective of this research project is to develop an aqueous biphasic extraction process for the treatment of fine coals. The goal is to identify process conditions that optimize the separation of mineral matter from coal in the aqueous biphasic systems. The emphasis is on investigations into the partitioning behavior of model particles in different types of aqueous biphasic systems, with a view to identifying the controlling physico-chemical factors. An additional goal is to develop an improved coal-pyrite separation technique based on aqueous biphasic extraction.

In order to conduct a biphasic extraction, it is necessary to have a two-phase system. Thus, phase diagrams, if available, will provide a database that permits systematic selection of phase volumes and phase compositions. A number of phase diagrams are already reported in the literature (16, 37). However, for specific aqueous biphasic systems for which the relevant phase diagrams are not available, it was necessary to conduct experiments to generate these diagrams. The efforts in this connection are presented in Chapter 2.

According to the Clean Air Act (1), advanced coal cleaning technologies are required to reduce the content of ash and sulfur in the run-of-mine coal to acceptable levels prior to combustion. Therefore, before applying aqueous biphasic extraction to fine coal processing, it is necessary to conduct partition experiments involving various model particulate materials, with emphasis on the factors that influence the solid partition. In Chapter 2, the partitioning behavior of pyrite in polymer/salt/water systems is reported, including the influence of factors such as: pH, presence of oxidant, molecular weight of

polymer, and addition of collectors. Chapter 3 focuses on the distribution of several particulate oxide materials in polymer/salt/water systems, and the effect of surfactants on the behavior of hematite. The partitioning behavior of hematite and silica in polymer/polymer/water and polymer/nonionic surfactant/water systems are presented in Chapters 4 and 5, respectively. In these two chapters, the influence of ionic surfactants is also investigated. Chapter 6 reports the results of a first investigation into the partitioning behavior of fine coal and fly ash in polymer/salt/water systems. Finally, Chapter 7 presents the overall summary and conclusions of this research project.

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Chapter 2

PARTITIONING BEHAVIOR OF PYRITE IN POLYMER/SALT AQUEOUS BIPHASE SYSTEMS

2.1 Introduction

High-sulfur coal is a contributor to acid rain. Therefore, as mentioned in Chapter 1, in response to the Clean Air Act (1), it is necessary to remove most sulfur and ash from run-of-mine coal prior to combustion. Additional advantages of low-ash coal include reduced transportation costs, improved utilization capacity, and reduced boiler erosion, boiler slagging and fly ash disposal problems (2).

In this research, aqueous biphasic extraction (3-7) is under consideration as a technique for processing coal fines. In order to assess the applicability of this technology to fine coal processing, it is necessary to investigate the partitioning behavior of coal, pyrite, and other mineral materials in aqueous biphasic systems. From the partition experiments, it will be possible to identify conditions that favor the separation of coal from pyrite and mineral matter.

In order to effectively design aqueous biphasic extraction experiments, it is necessary to have a database of relevant phase composition and phase diagrams. The phase diagrams for several polyethylene glycol (PEG)/salt/water systems are available in the

literature, including the PEG/Na₂SO₄/H₂O (5, 17-23), PEG/Na₃PO₄/H₂O (5, 17, 24-26), and PEG/Na₂CO₃/H₂O (5, 17, 23) systems. However, the corresponding diagram for the PEG-2000/Na₂CO₃/H₂O system (where 2000 corresponds to the molecular weight of PEG) has not been found. Therefore, in this chapter, the phase diagrams of PEG/Na₂CO₃/H₂O systems are first determined. The effect of polymer molecular weight on the phase equilibria is also discussed.

Within the limited research (8-16) available on solid partition in aqueous biphasic systems, the only report on the partitioning behavior of sulfide minerals comes from the work of Ananthapadmanabhan and Goddard (8). They investigated the distribution of copper sulfide, lead sulfide, zinc sulfide, iron sulfide, and nickel sulfide in the PEG-3350/Na₂SO₄/H₂O system. It found that all the minerals stayed in the bottom sulfate-rich phase. In the presence of 0.01 wt% of potassium xanthate, all the sulfide particles transferred to the top polymer-rich phase. However, no systematic investigation has been conducted to investigate the partitioning behavior of pyrite in aqueous biphasic systems. Therefore, this chapter focuses on the partitioning behavior of this sulfide in polymer/salt/water two-phase systems. The polymer used was PEG and the salts selected were Na₂SO₄ and Na₂CO₃. Particle distribution experiments were conducted to investigate the influence of several factors, such as conditioning time, pH, polymer (PEG) molecular weight, and the presence of various additives.

In conventional flotation technology, surfactants are used to modify the surface hydrophobicity and an extensive literature exists on the flotation-related surface chemical effects (27, 28). In contrast, the effects of surfactants on solid partitioning in aqueous biphasic systems have been little explored (8, 9). As discussed above, xanthate showed the

ability to modify the partitioning of sulfide minerals in aqueous biphasic systems (8). Also, Chaiko et al (9) found that in the PEG/Na₂SO₄/H₂O system, oleic acid was able to transfer ferric oxide and titanium oxide particles from the bottom salt-rich phase to the top polymer-rich phase. These results show that phase transfer agents are able to modify the solid partition in aqueous biphasic systems. Accordingly, in this work, it was also decided to investigate the effects of flotation collectors on pyrite partition in aqueous biphasic extraction systems. Sodium dodecyl sulfate (SDS), potassium oleate, and potassium ethyl xanthate (xanthate) were chosen as model surfactants.

2.2 Experimental Procedures

2.2.1 Materials

Pyrite (Zacatecas, Mexico) was purchased from Ward's Natural Science Establishment. It was ground, sieved through ASTM certified screens, and the -400 mesh fraction was collected and used in all the experiments. PEG-2000, -3400, -4600, -8000 (Aldrich), and universal buffer solid (Aldrich) were used as received. Sodium sulfate (Aldrich), sodium carbonate (Baker), sodium dodecyl sulfate (Aldrich), O-ethylxanthic acid potassium salt (Aldrich), oleate potassium salt (Aldrich), sodium hydroxide (Aldrich), and hydrochloric acid (Aldrich) were reagent grade. Distilled water was used to prepare all aqueous solutions. All experiments were conducted at room temperature (~23 °C).

2.2.2 Phase Diagram Determination for the PEG/Na₂CO₃/H₂O System

Sodium carbonate (20 wt%) and polymer (30 wt%) stock solutions were first prepared. The biphasic systems were then formulated by mixing appropriate volumes of polymer and salt stock solutions in 25 mL glass cylinders and were allowed to separate at room temperature (~20 °C) for 2 hours until neither phase showed visible turbidity. Samples (2-5 mL) of each phase were then collected with the aid of a pipette. To prevent contamination from the top phase when sampling the bottom phase, a tiny bubble of air was retained on the tip and expelled once in the bottom phase.

The concentration of sodium carbonate in the separated samples was determined by titration with 0.2 N hydrochloric acid, using methyl orange as the indicator. The total refractive index of each phase was measured at 20 °C (Lauda water bath) with a refractometer (Milton Roy Co.). The total refractive index (n) of each phase depends on the PEG and Na₂CO₃ concentrations, and is described by the following expression (18):

$$n = a_0 + a_1 w_s + a_2 w_p \quad [2.1]$$

where a_0 , a_1 , and a_2 are constants, and w_s and w_p represent the mass fractions of Na₂CO₃ and PEG, respectively. The value of a_0 is the refractive index of pure water at 20 °C, a_1 and a_2 were determined from the calibration plots of refractive index versus concentration for PEG-water and Na₂CO₃-water solutions, as shown in Figure 2.1. For each phase of the aqueous biphasic system, the concentration of PEG was calculated by rearranging Equation 1 as:

FIGURE 2.1. Refractive index calibration curves for Na₂CO₃ and PEG.

$$w_p = (n - a_0 - a_1 w_s) / a_2 \quad [2.2]$$

In Equation 2.2, w_s was known from the titration experiments.

2.2.3 Pyrite Partition Experiments

The aqueous biphasic systems used for the partition experiments were prepared by weighing fixed amounts of PEG and salt in a known volume of water. The composition of the total aqueous system was 15 wt% PEG, 10 wt% inorganic salt and 75 wt% water. The top phase was enriched with polymer, while salt was concentrated in the bottom phase. For most of the experiments based on Na_2SO_4 , universal buffer solid (typically at a level of 10 g/L) was used for pH control. Additionally, in some experiments, including all of the PEG/ Na_2CO_3 / H_2O systems and some of the PEG/ Na_2SO_4 / H_2O systems, the pH was adjusted by adding NaOH or HCl solution.

The extraction experiments were conducted in 200 mL glass containers; the total volume of aqueous biphasic solution was 100 mL and 0.5 g pyrite was added. After conditioning (with magnetic stirring) for 2 hours, the dispersion was transferred to a separatory funnel to allow liquid/liquid separation to occur. In many cases, there was some pyrite at the interface; this material was very difficult to separate accurately from the solids in either the top or bottom phases. At the same time, because the liquid-liquid interfacial area in the separatory funnel was too small to support all of the pyrite (0.5 g) at the interface, some pyrite settled down along the glass wall and went into the bottom phase. Therefore, for the mass balance calculations, the solids at the interface were generally combined with the solids in the bottom phase. The solids in each liquid phase

were collected by passing the liquid component through a Whatman membrane filter (0.2 μm). The recovered solids were rinsed with distilled water at least 6 times, dried in an oven at 100 °C, and weighed. The solids yield (Y) in each phase was calculated as:

$$Y = W/W_0 \quad [2.3]$$

where W and W_0 respectively represent the mass of solid in a given phase and the total mass of solids.

2.3 Results and Discussion

2.3.1 Phase Diagram for the PEG/Na₂CO₃/H₂O System

The phase diagrams of the PEG/Na₂CO₃/H₂O systems are presented in Figure 2.2-2.5. The key features of this type of phase diagram are the binodal curve and the tie lines (3-5). Above the binodal curve lies the two-phase zone; i.e., a system with a total composition in this zone will separate into two phases. On the other hand, a system with total composition below the binodal curve will only form one phase. For each of the tie lines indicated in Figures 2.2-2.5, the two data points on the binodal curve represent the compositions of the PEG-rich and the sodium carbonate-rich phases respectively; the central data point represents the total composition of the biphasic system. In aqueous biphasic extraction, the solute will partition into both phases equally if the total composition is close to the critical point (i.e., the point on the binodal curve where both

FIGURE 2.2. Phase diagram of the PEG-2000/Na₂CO₃/H₂O system.

FIGURE 2.3. Phase diagram of the PEG-3400/Na₂CO₃/H₂O system.

FIGURE 2.4. Phase diagram of the PEG-4600/Na₂CO₃/H₂O system.

FIGURE 2.5. Phase diagram of the PEG-8000/Na₂CO₃/H₂O system.

FIGURE 2.6 Effect of PEG molecular weight on phase diagrams of the PEG/
Na₂CO₃/H₂O system.

phases have the same composition). The farther the total composition is from the critical point, the more will the solute transfer into one phase. With the phase diagram in hand, it is easier to choose the phase composition that offers good partitioning results. Also, the tie lines are useful for estimating the compositions of the top and bottom phases if the total composition is known. The effect of PEG molecular weight on the phase equilibria is shown in Figure 2.6 for PEG(2000, 3400, 4600, and 8000)/Na₂CO₃/H₂O systems. It can be seen that, with increasing polymer molecular weight, the binodal curves shift in the direction of lower polymer and salt concentrations. This means that the higher the molecular weight of PEG, the lower the concentrations of PEG and Na₂CO₃ required for phase separation.

2.3.2 Pyrite Partition in the PEG/Na₂CO₃/H₂O System

Interfacial Energy and Particle Partition. The mechanism of particle partitioning in an aqueous biphasic system can be understood in terms of the interfacial energy between the solid particle and the aqueous phase, as shown in Figure 2.7 (3). Let γ_{P-L1} , γ_{P-L2} , and γ_{L1-L2} represent the interfacial energy of the solid particle/polymer-rich phase, the particle/salt-rich phase and the polymer-rich phase/salt-rich phase, respectively. Then, the value of the parameter ζ , defined by Equation 2.4, will determine the partition of particles in the system.

$$\frac{\gamma_{P-L1} - \gamma_{P-L2}}{\gamma_{L1-L2}} = \zeta \quad [2.4]$$

FIGURE 2.7. Mechanism of particle partitioning in aqueous biphasic systems; γ_{P-L1} , γ_{P-L2} , and γ_{L1-L2} represent the interfacial energy of the solid particle/polymer-rich phase, the particle/salt-rich phase and the polymer-rich phase/salt-rich phase, respectively.

If $\zeta \leq -1$, the particle has a high affinity for the polymer-rich phase and it will partition preferentially into that phase. On the other hand, when $\zeta \geq 1$, the particle will prefer the salt-rich phase. If the particle possesses comparable hydrophilic and hydrophobic properties, the difference between γ_{P-L1} and γ_{P-L2} will be very small so that $|\zeta| < 1$. Under this condition, the particles will prefer the interface. In aqueous biphasic systems, the interfacial energy between the two liquid phases is generally about 0.01-1 mN/m. This value is much smaller than that for oil/water biphasic systems (33), which means that it is easier for particles to change their partition behavior in aqueous biphasic systems by small changes in their surface properties.

Effect of Conditioning Time. Aqueous biphasic extraction relies on the surface chemical properties of the particulate materials. The surface chemical properties are largely dependent on the interactions of the surface atoms with the aqueous environment, which at a minimum contains water molecules (H_2O), hydroxide ions (OH^-), and protons (H^+). In the case of pyrite, like other metal sulfides, the situation can be very complicated. This is because sulfide surfaces tend to be oxidized by air in aqueous solution, and the oxidation state of sulfur can vary over a very broad range, e.g., (-2) in S^{2-} , (-1) in S_2^{2-} , (0) in S^0 , (+2) in $S_2O_3^{2-}$, (+4) in SO_3^{2-} , and (+6) in SO_4^{2-} . Thus, for the surface chemistry of pyrite in aqueous solution, in addition to the usual acid–base reactions typical of metal oxide surfaces, redox reactions also need to be considered (29, 30).

Table 2.1 presents data showing the effect of conditioning time on pyrite distribution in the PEG-2000/ Na_2CO_3 / H_2O system at pH 11.9. It can be seen that initially, practically

TABLE 2.1. Effect of conditioning time (pyrite oxidation) on pyrite partition in the PEG-2000/Na₂CO₃/H₂O system (pH=11.9).

Time (hr)	Top Phase	Bottom Phase	Interface
0	Cloudy, no pyrite	Yellow, clear, little pyrite	Almost all pyrite, some coagulate to bottom
0.5	Clear, no pyrite	Yellow, cloudy, little pyrite	Almost all pyrite, some coagulate to bottom
2	Clear, no pyrite	Yellow, cloudy, some pyrite	Some pyrite
4	Clear, no pyrite	Brown, opaque, many pyrite	Some pyrite
17	Clear, no pyrite	Brown, opaque, almost all pyrite	Little pyrite

Total composition: 18 wt% PEG-2000, 8 wt% Na₂CO₃, 74 wt% H₂O

all the pyrite was located at the interface, and there was little distribution to the top and bottom phases. As the conditioning time increased, however, pyrite increasingly transferred to the salt-rich phase. For the duration of the experiment (17 hours), there was no pyrite partitioning to the polymer-rich phase.

At the beginning of the experiments, the pyrite surface was composed of hydrophilic sites associated with the Fe atoms and hydrophobic sites attributable to the S atoms. Apparently the hydrophilic/hydrophobic balance was such that pyrite stayed at the interface. In alkaline solutions, pyrite decomposition can be represented with an overall reaction such as (30, 31):

Therefore, in connection with the results in Table 2.1, it can be stated that, with the continued oxidation of the pyrite surface, FeOOH increasingly occupied the surface, rendering it more hydrophilic than the original FeS₂ surface. In polymer/salt aqueous biphasic systems, the top phase is enriched in the polymer and is more hydrophobic; in contrast, the bottom salt-rich layer is relatively more hydrophilic (3-5). When particles are dispersed in this kind of system, the hydrophilic particles would prefer the bottom phase, while the hydrophobic solids will choose the top phase (9). Therefore, the final result was the preferential transfer of pyrite to the bottom phase.

Effect of pH. Figure 2.8 shows the partitioning behavior of pyrite for the PEG-2000/Na₂CO₃/H₂O system. As can be seen, above pH 10.5, the distribution was indepen-

FIGURE 2.8. Effect of pH on pyrite partition in the PEG-2000/Na₂CO₃/H₂O system:
conditioning time = 2 hours.

dent of pH and practically all the pyrite particles transferred to the bottom phase; there was, however, always some pyrite at the interface. As discussed above, at such high pH values, the pyrite surface was oxidized by the surrounding aqueous solution, and a hydrophilic product, FeOOH, formed. With sufficient time (conditioning time = 2 hours), this oxidative reaction made the surface hydrophilic by covering it with a ferric oxide film. As a result, the sulfide mineral transferred from the interface to the bottom salt-rich phase. As the pH was lowered below 10.5, there was a hint of an increase in distribution to the top phase and a decrease in distribution to the bottom phase. The experiments could not be extended to lower pH because, below pH 10, the system only formed one phase. With decreasing pH, increasing amounts of CO_3^{2-} ions were protonated to HCO_3^- . Unlike the divalent carbonate, the monovalent bicarbonate does not support biphasic formation (32). Below pH 10, the concentration of divalent carbonate was apparently too small to permit the formation of two phases.

2.3.3 Pyrite Partition of in the PEG/ Na_2SO_4 / H_2O System

Effect of pH. Figure 2.9 illustrates the effects of pH on the partition of pyrite in the PEG-2000/ Na_2SO_4 / H_2O system. Almost all the pyrite transferred into the salt-rich phase above pH 9. On the other hand, below pH 5, the pyrite particles moved into the polymer-rich phase and the salt-rich phase remained clear. Between pH 5 and 8, the sulfide mainly stayed at the interface and there was little solid material in the polymer-rich and salt-rich phases. For all pH conditions, there was always some pyrite at the interface. However, as mentioned above, for purposes of mass balance, the solids at the interface were combined with the pyrite in the salt-rich phase.

FIGURE 2.9. Effect of pH on pyrite partition in the PEG-2000/Na₂SO₄/H₂O system;
conditioning time = 2 hours.

FIGURE 2.10. The equilibrium Eh-pH diagram for the Fe-S-H₂O system at 25°C; [S] = 0.067 M, [Fe] = 0.033 M. The squares represent measured redox potentials.

From: D. Wei, K. Osseo-Asare, *Colloids Surf. A*, **1995**, 118: 51. (41)

It can be inferred from Figures 2.8 and 2.9 that, above pH 10, the partitioning behavior of pyrite in the PEG/Na₂SO₄/H₂O systems was similar to that in the PEG/Na₂CO₃/H₂O systems. At high pH, particles in these two systems were mainly in the bottom salt-rich phase (although there was some solid in the top phase of the PEG/Na₂CO₃/H₂O system at pH 10). It can be stated that the inorganic salts have little effect on the partitioning behavior of pyrite in these two systems under high pH conditions.

It is well known that the oxidation of pyrite in aqueous solution depends upon the oxidation condition and the pH of the solution (Figure 2.10). In alkaline solution, the oxidation of pyrite may be expressed as indicated by Equation 2.5 (31). The corresponding oxidation reaction in acidic media might be written as (30):

Because Fe_{1-x}S₂ is Fe-deficient (and therefore sulfur-rich), it is expected to be more hydrophobic than FeS₂; while FeOOH is more hydrophilic than FeS₂. After 2 hours conditioning in an alkaline medium, a surface coating of FeOOH developed and the particles became more hydrophilic. It is speculated that this led to an increase in $\gamma_{\text{P-L1}}$ and a decrease in $\gamma_{\text{P-L2}}$ simultaneously. When the surface was sufficiently hydrophilic so that the condition $\zeta \geq 1$ was satisfied, the particles transferred into the salt-rich phase (Figure 2.7). For pH below 5, the fraction of Fe_{1-x}S₂ sites on the pyrite surface became sufficiently high to make the particles hydrophobic. Under these conditions $\gamma_{\text{P-L1}}$ became less than $\gamma_{\text{P-L2}}$ and the condition $\zeta \leq -1$ was satisfied. Accordingly, pyrite transferred into

the polymer-rich phase. Between pH 5 and 9, pyrite behavior was transitional between the above two extremes so that the solids mainly concentrated at the interface.

Effect of Buffer Solid. In the PEG/Na₂SO₄/H₂O system, two different methods of pH adjustment were used, i.e., the introduction of universal buffer solid and addition of HCl or NaOH. Table 2.2 compares experimental data obtained with the two methods for pyrite partition in the PEG-2000/Na₂SO₄/H₂O system. The results show that there was no significant difference between these two methods. The implication is that the buffer solid had no serious effect on the partitioning behavior of pyrite particles in the aqueous biphasic systems.

Effect of PEG Molecular Weight. The partitioning results of pyrite in the PEG-2000, PEG-4600 and PEG-8000/Na₂SO₄/H₂O systems under different pH conditions are shown in Figure 2.11. In actuality, almost all the pyrite stayed at the interface for the pH 5-8 range; however, this material was combined with pyrite in the salt-rich phase, as noted previously above. Variation in pH resulted in similar partitioning trends in the different systems. However, in the pH range of 5-12, there was more pyrite transfer to the polymer-rich phase of the PEG-8000/Na₂SO₄/H₂O system, compared with the other two systems. Overall, it can be concluded that in the PEG/Na₂SO₄/H₂O systems, the polymer molecular weight had no significant effect on the partitioning behavior of pyrite.

TABLE 2.2. Effect of buffer solid on pyrite partition in the PEG-2000/Na₂SO₄/H₂O system; conditioning time = 2 hours.

Buffer Solid			HCl or NaOH		
pH	Y _t *	Y _b *	pH	Y _t *	Y _b *
3.4	81.2	0.9	3.2	81.9	3.7
5.6	9.5	84.1	5.6	26.0	61.7
11.4	1.3	91.1	11.5	2.6	89.2

* Y_t: yield of pyrite in top phase; Y_b: yield of pyrite in bottom phase

FIGURE 2.11. Effect of PEG molecular weight on pyrite partition to the polymer-rich phase of the PEG/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ system; conditioning time = 2 hours.

2.3.4 Effects of Additives on Pyrite Partition in the PEG/Na₂SO₄/H₂O system

Some additives, such as hydrogen peroxide, ferric chloride, and sodium sulfide, have been reported to be effective in suppressing the agglomeration of pyrite in oil agglomeration of fine-size coal (34). In order to effectively separate the mineral matter from fine coal with aqueous biphasic extraction, it is worthwhile to study the effects of these additives on the partitioning behavior of pyrite in aqueous biphasic systems. The partitioning behavior of pyrite in the PEG-2000/Na₂SO₄/H₂O system in the presence of H₂O₂ is shown in Figure 2.12; Table 2.3 gives results of pyrite partitioning in the PEG-2000/Na₂SO₄/H₂O system in the presence of FeCl₃ at pH 3 and 8.

As shown in Figure 2.12, the partitioning behavior of pyrite in the PEG-2000/Na₂SO₄/H₂O system in the presence of H₂O₂ was similar to that in the absence of H₂O₂. The main difference was that when pyrite went into the polymer-rich phase or the salt-rich phase, there was no pyrite at the interface. Another difference was that, with H₂O₂, the partitioning process did not need a long conditioning time; the solids went directly into the top phase or bottom phase after mixing. In the presence of FeCl₃ (Table 2.3), all the particulate materials went into the polymer-rich phase at both pH 3 and 8. Also, the partition did not need the conditioning step. From the above results, it appears that both H₂O₂ and FeCl₃ accelerated the surface reaction at the pyrite/water interface; therefore, the conditioning step was not necessary in the presence of these additives.

FIGURE 2.12. Effect of pH on pyrite partition in the PEG-2000/Na₂SO₄/H₂O system in the presence of 0.1M H₂O₂; no conditioning.

TABLE 2.3. Effect of FeCl₃ on pyrite partition in the PEG-2000/Na₂SO₄/H₂O system.

pH	FeCl ₃ concentration (M)	Y _t *	Y _b *
2.7	3×10 ⁻³	81.4	1.8
2.7	0	96.5	1.6
7.7	3×10 ⁻³	82.6	2.2
8.1	0	6.6	92.5

*Y_t: yield of pyrite in top (polymer-rich) phase;

Y_b: yield of pyrite in bottom (salt-rich) phase;

No conditioning.

2.3.5 Effects of Surfactants on Pyrite Partition in the PEG/Na₂SO₄/H₂O System

SDS and Oleate. Figure 2.13 shows the partitioning behavior of pyrite in the PEG-2000/Na₂SO₄/H₂O system in the presence of sodium dodecylsulfate (SDS, 3.5×10^{-4} M), oleate (1×10^{-4} M), and xanthate (1×10^{-3} M). Comparing Figures 2.5 and 2.8, it can be seen that the addition of SDS or oleate had no effect on partitioning behavior. This result suggests that these surfactants do not adsorb significantly on pyrite in the aqueous biphasic system.

In a polymer/surfactant system, it is possible to form both polymer-surfactant complexes and surfactant micelles. Like the critical micelle concentration (CMC), there is also a critical surfactant concentration when the polymer-surfactant complex begins to form. Generally, this critical concentration is lower than the CMC (28). After the polymer sites are saturated, the micelle begins to form. It is also found that the presence of salts promotes the formation of polymer-surfactant aggregates (28, 29). Therefore, in an aqueous biphasic system containing a surfactant and solid particles, there are four possible dispositions of the added surfactant, i.e., the surfactant may exist as soluble monomeric species, soluble micelles, polymer (PEG)-surfactant complexes, or surfactants adsorbed on the solid surface. The dominant form of the surfactant in the PEG/Na₂SO₄/H₂O system depends upon many factors. These include the concentrations of the polymer and the salt, the dissociation of surfactants, the interaction between polymer and surfactants, and the affinity of the surfactants for the surface species on the particles.

It appears from the present results that there is only a weak interaction between pyrite and the surfactants SDS and oleate in the studied systems. At high pH, pyrite oxidizes to form a surface oxide layer (Equation 2.4). This ferric oxide/hydroxide coating

FIGURE 2.13. Effects of pH, oleate, SDS, and xanthate on pyrite partition to the polymer-rich phase of the PEG-2000/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ system (oleate: 1×10^{-4} M, SDS: 3.5×10^{-4} M, xanthate: 1×10^{-3} M); conditioning time = 2 hours.

is expected to be negatively charged, given the fact that the pzc of FeOOH is about 7-8 (30). Because both the pyrite surface and the surfactants are negatively charged, there is electrostatic repulsion. Therefore, it is most likely that SDS and oleate existed mainly as their complexes with PEG (because of the high concentration of PEG in this system), and the adsorption of the surfactants on the solid particles was negligible. Without adsorption, the particle surface remained unmodified, resulting in unchanged partitioning behavior.

Xanthate. The partitioning results of pyrite in the PEG-2000/Na₂SO₄/H₂O system in the presence of xanthate are shown in Table 2.4 and Figure 2.13. As indicated in Table 2.4, when the concentration of xanthate was 1×10^{-5} M, the yield in the polymer-rich phase was still relatively low. Actually, the particles mainly stayed at the interface. As mentioned above, however, for the purpose of mass balance, particles at the interface were combined with particles in the salt-rich phase. When the xanthate concentration increased to 1×10^{-3} M, almost all the particles preferred the polymer-rich phase. From Figure 2.13, it can be seen that when the concentration of xanthate was 1×10^{-3} M, the surfactant did not improve partitioning of pyrite into the polymer-rich phase for acidic conditions. However, under neutral and alkaline environments, pyrite partition in the polymer-rich phase was significantly increased.

These results indicate that, unlike SDS and oleate, xanthate adsorbs strongly on pyrite surface. It is well established that xanthate adsorbs on pyrite surface to form Fe(III) xanthate or Fe(III) dixanthate compounds which are responsible for the flotation of this metal sulfide (20, 31-33). The hydrophilic thio groups of xanthate bond to the Fe atoms on the pyrite surface, and the hydrophobic ethyl groups extend into the surrounding

TABLE 2.4. Effect of xanthate on pyrite partition to the polymer-rich phase of the PEG-2000/Na₂SO₄/H₂O system; conditioning time = 2 hours.

Expt. No.	pH	Xanthate conc. (M)	Y (wt%)
1	8.1	0	6.6
2	8.6	1×10^{-5}	14.3
3	11.5	0	1.0
4	11.4	1×10^{-5}	3.9
5	11.5	1×10^{-3}	73.8

solution. In this way, the pyrite surface acquires a hydrophobic layer that promotes the distribution of the particles into the polymer-rich phase.

2.4 Conclusions

Phase diagrams for PEG/Na₂CO₃/H₂O systems (PEG-2000, 3400, 4600, 8000) were determined and the effect of the molecular weight of PEG on the phase equilibria was studied. The binodal curves shifted in the direction of lower polymer and salt concentrations with increasing polymer molecular weight. The observed trends were consistent with previous work based on other aqueous biphasic systems (5, 17).

The work in this chapter clearly indicates that the partitioning behavior of pyrite in PEG/salt/water systems depends significantly on the surface chemistry of the solid. The surface of pyrite is easily oxidized in aqueous solution and many factors, such as conditioning time and pH, can modify the surface chemistry, leading to changes in pyrite partition. In PEG/salt/H₂O systems, pyrite initially stayed at the interface of the aqueous biphasic systems. With increase in the conditioning time, however, the solid particles transferred increasingly into the bottom salt-rich phase. Because the extent of pyrite surface oxidation is pH-dependent, the partitioning behavior of pyrite changed with pH. At high pH, pyrite transferred into the bottom salt-rich phase, while pyrite preferred the top polymer-rich phase at low pH. This behavior was attributed to the different oxidation products obtained under different pH conditions: formation of hydrophilic FeOOH in alkaline solution, and a hydrophobic iron-deficient product (Fe_{1-x}S₂) in acidic environment.

Because aqueous biphasic extraction is dependent upon the surface property of the solid, depressants such as those used in flotation and oil agglomeration can also affect the partitioning behavior. Addition of H_2O_2 removed the requirement of conditioning, although it did not change the partitioning behavior of pyrite. With FeCl_3 , pyrite stayed in the polymer-rich phase in both acidic and neutral media.

Surfactant addition also offers an important way to change the surface chemistry of a solid. The results showed that only certain flotation collectors could significantly affect the behavior of pyrite in biphasic systems. Xanthate was found to be effective in changing the partition behavior in neutral and alkaline solutions; the sulfide particles preferred the polymer-rich phase instead of the salt-rich phase or the interface. This effect was attributed to the chemisorption of xanthate on the sulfide surface (31-33). In contrast, in the case where surfactant adsorption is predominantly electrostatic (physical), i.e., SDS or oleate on pyrite, surfactant addition had no effect on partitioning behavior.

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Chapter 3

PARTITIONING BEHAVIOR OF OXIDE PARTICLES IN THE PEG/Na₂SO₄/H₂O SYSTEM

3.1 Introduction

As mentioned in Chapter 1, the objective of this research is to study the feasibility of applying aqueous biphasic systems in removing mineral matter from fine coal. As shown in Chapter 2, pyrite partition in polymer/salt/water biphasic systems is highly dependent upon pH, and addition of xanthate can significantly change the distribution of this sulfide mineral. The results demonstrate that pH can be used to change the surface chemistry of pyrite (e.g., from FeS₂ to Fe_{1-x}S₂ or FeOOH), and consequently, the partitioning behavior of pyrite in aqueous biphasic systems. Therefore, it is of interest to compare the behavior of pyrite and iron oxide in aqueous biphasic systems. In coal ash, oxide and silicate particles are important components (1-3). Therefore, in order to understand the experimental data and control the separation process for coal ash, it is necessary to investigate the partition of simple model particles in these two-phase solutions. Using alumina, hematite, silica, and titania as model oxide materials, this chapter reports on experiments designed to investigate the partition of oxide particles in the polyethylene glycol (PEG)/Na₂SO₄/H₂O system.

Although a lot of research has been conducted on the application of aqueous biphasic extraction in biological science and technology (4-8), only a few results (9-17) are available in the literature about the partition of solids in aqueous biphasic systems. Ananthapadmanabhan and Goddard (9) were among the first to study the selective partition of oxide particles, e.g., iron oxide, silica, titanium dioxide, and other minerals in the PEG/Na₂SO₄/H₂O system. The metal oxides were found to prefer the bottom salt-rich phase, while silica concentrated in the top polymer-rich layer. Chaiko et al. (10-12) investigated the possibility of applying aqueous biphasic extraction to separate radioactive Pu oxide from silicate. They (10) obtained the same partitioning behavior of the oxide particles in the PEG/Na₂SO₄/H₂O systems as Ananthapadmanabhan and Goddard (9): Al₂O₃, Fe₂O₃, PuO₂ and TiO₂ stayed in the bottom phase, and SiO₂ migrated to the top layer. The exceptional behavior of silica was attributed to the adsorption of PEG on the solid surface. These results show that, as in conventional oil-based liquid-liquid extraction (18-20), the basic principle behind the selective partition of solids in aqueous biphasic systems is the physicochemical interaction between the solid surface and the liquid solution, rather than the bulk properties of the solid (4-8). In the polymer/salt/water systems, the top phase is enriched in polymer and is hydrophobic, while the bottom salt-rich layer is more hydrophilic. Therefore, the hydrophilic oxide particles prefer the bottom solution. However, for the case of silica, the polymer-solid specific interaction dominates the partition of particles.

In conventional flotation technology, surfactants are used to modify the surface hydrophobicity and an extensive literature exists on the flotation-related surface chemical effects (21, 22). In contrast, the effects of surfactants on solid partitioning in aqueous

biphase systems have been little explored (9-12). Ananthapadmanabhan and Goddard (9) investigated the effect of surfactants (e.g., alkylbenzene sulfonate, oleic acid, and cetyl trimethyl ammonium bromide) on the partitioning behavior of solid particles in the PEG/Na₂SO₄/H₂O system. For oxide particles, they found that in many cases, surfactants were not able to change the solid partition. The only exceptions they encountered were alkylbenzene sulfonate/iron oxide and cetyl trimethyl ammonium bromide/silica. In the work of Chaiko et al (10-12), only the surfactants that chemically adsorbed at the solid/liquid interface were effective in significantly influencing the partitioning behavior of oxide particles in polymer/salt/water two-phase systems. It was concluded from the above previous explorations (9-12) that it would be profitable to further investigate the influence of flotation collectors on solid partitioning in aqueous biphase system. In the work reported here, sodium dodecyl sulfate (SDS), potassium oleate, and potassium ethyl xanthate were chosen as model surfactants, and their effects on the partition of hematite particles were investigated.

3.2 Experimental Procedures

3.2.1 Materials

Hematite (< 5 µm), alumina (-200+325 mesh, or 44 – 74 µm), titania (< 5 µm), and silica (-325 mesh, or < 44 µm) were all purchased from Aldrich. Polyethylene glycol (PEG) with molecular weights of 2000 and 4600 (PEG-2000 and PEG-4600 respectively) were also obtained from Aldrich and used as received. Sodium sulfate, sodium

hydroxide, hydrochloric acid, and oleate sodium salt were reagent grade (Aldrich). Distilled water was used in all experiments and all experiments were conducted at room temperature ($\sim 23^\circ\text{C}$)

3.2.2 Partition Experiments

The aqueous biphasic systems were prepared by weighing fixed amounts of PEG and Na_2SO_4 in a known volume of water. The composition of the total aqueous solution was 15 wt% PEG, 10 wt% Na_2SO_4 and 75 wt% water. The top phase was enriched in PEG, and sulfate was concentrated in the bottom phase. Solutions of NaOH or HCl were used to control the pH.

The extraction experiments were conducted in 125 mL Pyrex separatory funnels; for a given experiment, the volume of aqueous biphasic solution was 100 mL and 0.5 g of particles was added. The dispersion was subjected to a Wrist Action Shaker (Burrell Co.) for 1 hour and then allowed to phase separate. The solid in each phase was filtered through Whatman membrane filters ($0.2\ \mu\text{m}$). The recovered solids were rinsed with distilled water at least six times, dried in an oven at 100°C , and weighed. The solid yield (Y) in the polymer-rich phase was calculated as:

$$Y = W/W_0 \quad [3.1]$$

where W and W_0 respectively represent the mass of solid in the polymer-rich phase and the total mass of solids.

3.3 Results and Discussion

3.3.1 Partitioning Behavior of Oxide Particles in the PEG/Na₂SO₄/H₂O System

The partitioning behavior of alumina, titania, and silica in the PEG-2000/Na₂SO₄/H₂O system is shown in Figure 3.1; also included is the result for hematite in the PEG-4600/Na₂SO₄/H₂O system. In the pH range of 2 to 12, alumina, hematite and titania were confined to the bottom phase; however, almost all silica particles transferred into the top phase.

The surfaces of metal oxide particles are covered by hydrophilic metal hydroxide groups (-MOH). Below the pH values of their point of zero charge (pzc), e.g., ~8.5 for hematite (23), these -MOH groups combine with protons in solution to form protonated -MOH₂⁺ groups. On the other hand, the surface hydroxyls deprotonate into -MO⁻ groups when the pH is higher than the pzc. All these surface groups are hydrophilic. As mentioned above, in the polymer/salt/water two-phase system, the top polymer-rich phase is more hydrophobic, and the bottom layer enriched in salt is more hydrophilic. In the absence of specific polymer-solid interactions, the surface hydrophilic/hydrophobic properties determine the partitioning behavior of solid particles in these biphasic systems. The hydrophilic particles would prefer the bottom phase, while the hydrophobic solids would choose the top layer. It is reported that the adsorption of PEG on hematite, alumina, and titania is negligible (24-27); therefore, the polymer-solid interaction in these mixtures is not important. Thus, it is not surprising that all these hydrophilic solids stayed in the bottom salt-rich phase.

FIGURE 3.1. Effect of pH on partition of alumina, hematite, silica, and titania to the top phase to the PEG/Na₂SO₄/H₂O system.

It is somewhat surprising, however, that silica partitioned into the top phase, although the Si atoms on silica also can be hydrolyzed to form Si-OH groups. The difference in behavior of silica compared with the other oxide solids can be attributed to differences in their interactions with PEG. It is reported that PEG adsorbs on silica surface, with an adsorption density of about 0.6 mg/m^2 (27). In contrast, PEG adsorbs negligibly on hematite, alumina and titania (24-27). This polymer adsorbs on silica surface through hydrogen bonding between the H atom of the Si-OH group and the O atom in the PEG chain (27, 28). The enthalpy change for PEG displacement of water on silica surface is about 9.9 kcal/mol, a value that is typical for the formation energy of a hydrogen bond (29, 30). Therefore, in the PEG/Na₂SO₄/H₂O system, it can be said that the PEG-silica interaction dominates the partition. As a result, SiO₂ particles prefer the top PEG-rich phase, not like other oxide solids that stay in the bottom salt-rich layer.

It is believed that the neutral Si-OH sites favor the formation of hydrogen bonding between the polymer and solid surface (29). When Si-OH deprotonates to Si-O⁻, the resulting negative site does not form a hydrogen bond with PEG. Also, the adsorption of the polymer on the solid is not favored partially because of the electrostatic repulsion between these negatively charged sites and the partial negative charge on the O atoms in the polymer chains. It is reported that the flotation efficiency of silica with PEG decreased above about pH 6 because of the desorption of PEG from silica surface (31). This desorption process was due to the electrostatic repulsion between the polymer and the solid. From the above discussion, it can be seen that increase in pH will result in decrease of polymer adsorption on silica surface. This accounts for the decline in the yield of silica particles in the top phase of the PEG/Na₂SO₄/H₂O system above pH 10.

3.3.2 Effects of Surfactants on Hematite Partition in the PEG/Na₂SO₄/H₂O System

SDS and Xanthate. Figure 3.2 shows the effects of the model surfactants on the partitioning behavior of hematite in the PEG-4600/Na₂SO₄/H₂O system. The presence of SDS (3.5×10^{-4} M) or xanthate (1×10^{-3} M) had no effect on the behavior of hematite (see the surfactant-free system in Figure 3.1). These results suggest that there is no strong interaction between SDS or xanthate and hematite. It is known that SDS adsorbs on the ferric oxide surface predominantly through electrostatic interaction (32, 33). Chaiko et al. (10) also found that the presence of sodium dodecyl sulfate and sodium dodecyl benzene sulfonate had no effect on the partition of oxide particles (Al₂O₃, Fe₂O₃, and TiO₂) in the PEG/Na₂SO₄/H₂O system. They interpreted this result by referring to the fact that both these anionic surfactants adsorb on oxide surfaces through electrostatic interaction. In the highly ionic environment of this two-phase system, the surfactant adsorption was suppressed by the high concentration of electrolyte ions (10). The present results can also be rationalized in a similar manner.

Oleate. Figure 3.2 also shows the effect of oleate on the partitioning behavior of hematite particles in the PEG-4600/Na₂SO₄/H₂O system. For pH values less than 5.5, all particles stayed in the salt-rich phase, irrespective of the oleate concentration. At about pH 6, the particles transferred into the polymer-rich phase, and the yield approached the maximum of almost 100%. When the pH was increased further (especially above pH 10), the yield decreased. It is interesting to note that above pH 6, the yield was enhanced with increase in oleate concentration up to 2×10^{-4} M; above this concentration, a drop in yield was observed.

Oleate is used as a collector for hematite flotation (34-44) and it is reported that this surfactant adsorbs chemically on the surface of ferric oxide (45, 46). The trends in hematite distribution observed in aqueous biphasic systems (Figure 3.2) are similar to the situation found in the conventional flotation process (40, 43). It is reasonable, therefore, to assume that the adsorption behavior of oleate on hematite in biphasic systems is similar to that in flotation systems. Combining these experimental results (Figure 3.2) with the findings for the xanthate/pyrite system in Chapter 2 (Figure 2.13), it can be concluded that collectors can be used to modify solid partitioning in aqueous biphasic systems if they can adsorb chemically on the solid surface. In contrast, if the surfactant/solid interaction is predominantly electrostatic (i.e., SDS/hematite, and xanthate/hematite), then the partitioning behavior of particles cannot be affected significantly by surfactant addition.

At low pH, the undissociated oleate predominates in the solution and it can only physically adsorb on the hematite surface (34). Because of the high ionic strength in the aqueous biphasic system, the adsorption density of undissociated oleate is expected to be low, with a resulting minimal effect on the partitioning behavior of ferric oxide. A similar trend is observed in the flotation process, where the recovery of hematite with oleate decreases at low pH values (35). On the other hand, at relatively high pH, dissociated oleate predominates and the subsequent chemisorption of the surfactant gives the hematite surface a hydrophobic layer (21). The hydrophobic layer decreases the interfacial energy between the solid and the polymer-rich phase; the result is enhanced transfer of particles into the polymer-rich phase. Chaiko et al. (10) also found that oleate was effective to promote hematite particles from the salt-rich phase to the polymer-rich phase in the PEG/Na₂SO₄/H₂O system, and a similar rationalization was provided.

FIGURE 3.2. Effect of pH on hematite partition to the top phase of the PEG-4600/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ system in the presence of surfactants (oleate: 5×10^{-5} , 1×10^{-4} , 2×10^{-4} , 5×10^{-4} M; SDS: 3.5×10^{-4} M; xanthate: 1×10^{-3} M).

When the pH exceeds the pzc of ferric oxide, the solid surface becomes negatively charged. There is then electrostatic repulsion between the particles and the oleate ions. A similar pH effect of oleate adsorption on hematite was observed by Ofor (37). It was found that the adsorption density showed a peak at about pH 7. Above pH 7, the adsorption density first decreased slowly up to pH 9 and then sharply above pH 9.

At relatively high concentrations, adsorbed surfactant molecules tend to form bilayers on particle surfaces (47). Because of the favorable hydrophobic interaction among the hydrocarbon chains in these two layers, the polar groups in the second layer become oriented towards the liquid phase. The decrease in yield at 5×10^{-4} M oleate (Figure 3.2) suggests that, at this concentration, a similar two-layer oleate structure exists on hematite surface in the aqueous biphasic system. The outer layer of polar groups renders the surface hydrophilic, resulting in a decrease in the yield in the polymer-rich phase, as shown in Figure 3.2.

3.4 Conclusions

The partitioning behavior of particles in aqueous biphasic systems mainly depends on the surface properties of the solid materials. Therefore, physicochemical treatments that change the surface chemistry of a solid can be used to control material partitioning. The work here demonstrated that, in the absence of polymer-solid interaction, as is the case for alumina, hematite, and titania, the surface hydrophilic/hydrophobic properties determined the partitioning behavior of particles. In the pH range of 2 to 12, almost all of the alumina, hematite, and titania particles preferred the bottom phase because of the

hydrophilic surfaces of these oxides. In contrast, silica particles stayed in the top phase, a result that is attributed to PEG adsorption on silica particles. The implication is that, if the polymer can adsorb on the solid surface, then the polymer-solid interaction will dominate the distribution of solid particles in the aqueous biphasic systems.

Addition of surfactant also offers an important way to change the surface chemistry of solids. The results presented here showed that only certain flotation collectors could significantly modify the behavior of particles in biphasic systems, e.g., oleate for hematite. At about pH 6, the presence of oleate caused the transfer of the solid into the polymer-rich phase, and the yield in this phase reached the maximum. Combined with the results in Chapter 2 (i.e., pyrite/xanthate), it can be concluded that the surfactants that adsorb chemically on the solid surfaces have a significant influence on solid distribution. In contrast, in the case where surfactant adsorption is predominantly electrostatic (physical), i.e., SDS/hematite, and xanthate/ hematite, surfactant addition had no effect on partitioning behavior.

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Chapter 4

PARTITIONING BEHAVIOR OF HEMATITE IN POLYMER/POLYMER AND POLYMER/SURFACTANT SYSTEMS

4.1 Introduction

In Chapters 2, and 3, the partitioning behavior of pyrite and oxide particles was investigated in polymer/salt aqueous biphasic systems (polyethylene glycol (PEG)/ $\text{Na}_2\text{CO}_3/\text{H}_2\text{O}$ and PEG/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ systems). The results show that as in conventional liquid-liquid extraction (1-3), the partition relies on the surface properties of the solids and the interfacial interactions between the particles and the surrounding liquid solution (4-8). Many factors, such as the surface hydrophilic/hydrophobic properties, solution pH, the nature and concentration of collectors (surfactants), and specific interaction between the polymer and the oxides, can influence the distribution of solid materials in aqueous biphasic systems. The hydrophilic particles, e.g., hematite, alumina, and titania, prefer the bottom salt-rich phase; while natural hydrophobic materials, e.g., coal, migrate to the top polymer-rich layer. The distribution of pyrite greatly depends upon pH, but pH has no effect on oxide particles. Addition of surfactants significantly affects the results in some cases (pyrite/xanthate and hematite/oleate) because there are strong interactions between the solid surface and collectors. On the other hand, polymer-solid interaction is also an

important factor. The distribution of silica in the top polymer-rich phase of PEG/Na₂SO₄/H₂O was due to the adsorption of the polymer on the solid surface.

Previous work in the literature (9-15) has mainly focused on the partition of solids in polymer/salt aqueous biphasic systems; little research has been reported for other types of biphasic systems. Prior to our research, Baxter et al. (15) reported the only available result on solid partition in polymer/polymer biphasic systems. They studied the partition of latices and TiO₂ colloids with different surface functional groups in polymer/polymer two-phase systems (such as PEG/dextran and PEG/poly(N-vinylpyrrolidone) (PVP)). In the PEG/dextran system, the hydrophilic latices went into the bottom more hydrophilic dextran-rich phase, while the hydrophobic latices stayed in the top PEG-rich phase. The partitioning behavior was also found to be greatly dependent upon the surface chemistry of the particles, i.e., the functional group on the particle surfaces. At pH 6.5, the latex particles with carboxyl groups on their surfaces preferred the PEG-rich phase of the PEG/dextran system; this result was attributed to the protonation of the surface COO⁻ groups. When pH was increased to 9.6, most of the carboxyl groups were deprotonated; then, the particles transferred to the dextran-rich phase. In the PEG/PVP system, the particles (both latices and TiO₂) with surface OH groups concentrated in the bottom PVP-rich phase, while those with COOH groups dispersed in the top PEG-rich phase. These results were attributed to the specific interaction between the functional groups on the solid surface and the molecular chain of polymers in solution. Also, the separation of a mixture of latices with different surface groups was demonstrated for polymer/polymer biphasic systems (15).

In the available published literature, no research has been reported yet on the partition of inorganic particles in polymer/surfactant systems, although these systems have been used in bioseparation (16-18). This chapter presents the results of the partitioning behavior of hematite in polymer/polymer (PEG/dextran) and polymer/nonionic surfactant (Triton X-100/dextran) systems. First, the partitioning behavior at various pH values is presented; then, the feasibility of applying electrostatic interaction to modify particle partition is explored. In polymer/nonionic surfactant systems, electrostatic interactions have significant effects on the distribution of biological materials. In these systems, added ionic surfactants concentrate in the top surfactant-rich phase and form mixed micelles with the nonionic surfactant. Thus, it has been demonstrated that coulombic attractions or repulsions develop between the mixed micelles and charged proteins. Addition of anionic surfactants moved negatively charged proteins into the bottom polymer-rich phase, and transferred positively charged biological materials into the top surfactant-rich layer. The solutes showed opposite behaviors in the presence of cationic surfactants (16-18).

4.2 Experimental Procedures

4.2.1 Materials

Dextran (Dex, average molecular weight 24,500), polyethylene glycol (molecular weight 8000), Triton X-100 (t-octylphenoxypolyethoxyethanol), ferric oxide ($< 5 \mu\text{m}$ size), were purchased from Sigma-Aldrich Co. Sodium dodecylsulfate (SDS), potassium

oleate, dodecyltrimethylammonium bromide (DTAB), sodium hydroxide, and nitric acid were all reagent grade (Aldrich). Distilled water was used in all experiments. The structures of the polymers and surfactants are shown in Figure 4.1.

4.2.2 Partition Experiments

The aqueous biphasic systems were prepared by dissolving the polymers and/or nonionic surfactant in known volumes of water. The total composition of the TX100/Dex system was 9.0 wt% polymer, 11.0 wt% surfactant, and 80.0 wt% water. The PEG/Dex system was composed of 7.0 wt% PEG, 16.8 wt% dextran, and 76.2 wt% water. In both systems, the bottom phase was enriched in dextran, the other components were concentrated in the top phase (16-18). The relevant phase diagrams are shown in Figures 5.2 and 5.3, respectively (17, 19).

The extraction experiments were conducted in 60 mL glass bottles; for a given experiment, the volume of aqueous biphasic solution was 50 mL and 0.1 g of particles was added. Sufficient ionic surfactant was added to achieve the desired concentration, and pH was adjusted with NaOH or HNO₃ solution. The dispersions were magnetically stirred for 0.5 hr. The mixtures were then transferred to 125 mL separatory funnels, and allowed to separate into two phases. The solids in each phase were separated with Whatman membrane filters (0.45 µm). The recovered solids were rinsed with distilled water at least six times, dried in an oven at 100 °C, and weighed. The solids yield (Y_i) in each phase was calculated as:

$$Y_i = W_i/W_0 \quad [4.1]$$

Polyethylene Glycol

t-octylphenoxypolyethoxyethanol

PEG

Triton X-100

Sodium Dodecylsulfate

Dodecyltrimethylammonium Bromide

SDS

DTAB

Dextran

FIGURE 4.1. Chemical structures of polymers and surfactants.

FIGURE 4.2. Phase diagram for the Triton X-100/dextran T500/water system at 4 °C

From: U. Sivars, and F. Tjerneld, *Biochim Biophys Acta*, **2000**, 1474: 133. (17)

FIGURE 4.3. Phase diagram for the PEG-8000/dextran-40/water system at 22 °C

From: A. D. Diamond, and J. Hsu, *Biotechnol. Techniques*, **1989**, 3: 119. (19)

where W_i and W_0 respectively represent the mass of solid in that phase and the total mass of solids. All experiments are conducted at room temperature ($\sim 23^\circ\text{C}$).

4.3 Results and Discussion

4.3.1 Effect of pH on Hematite Partition in the Triton X-100/Dextran/H₂O System

Table 4.1 shows the partitioning behavior of hematite in the TX100/dextran system at pH 3, 7, and 11. Under all the pH conditions, hematite stayed in the bottom polymer-rich phase.

Like other metal oxides, the hematite surface is covered by metal hydroxyl groups (Fe-OH), which make the surface hydrophilic. According to Albertsson's scale of relative hydrophilic/hydrophobic character, PEG is at the more hydrophobic end than dextran (1). Triton X-100 is a surfactant composed of a hydrocarbon chain and a chain of about 10 oxyethylene units which is the repeating unit of PEG, as shown in Figure 4.1. It is expected that the solution of Triton X-100 is more hydrophobic than that of PEG. Hence, it is reasonable to deduce that the bottom dextran-rich phase is more hydrophilic than the top surfactant-rich layer. When solid particles are dispersed in aqueous biphasic systems, the surface hydrophilic/hydrophobic properties play a dominant role in the partitioning behavior if there is no specific interaction between the phase components and the solids. Therefore, if one considers only the hydrophilic/hydrophobic properties, then hematite particles preferred the more hydrophilic bottom phase, not the more hydrophobic top one.

TABLE 4.1. Effect of ionic surfactants on hematite partition in the Triton X-100/dextran system (Dex: 9.0 wt%, TX100: 11.0 wt%, hematite: 2.0 g/L).

Ionic Surfactant	pH 3	pH 7	pH 11
No surfactant	Bottom phase	Bottom phase	Bottom phase
1.0 g/L SDS	Bottom phase	Bottom phase	Bottom phase
1.0 g/L Oleate	Bottom phase	Bottom phase	Bottom phase
0.2 g/L DTAB	-	-	Bottom phase
0.4 g/L DTAB	-	-	Bottom phase
0.8 g/L DTAB	-	-	Bottom phase
1.0 g/L DTAB	Bottom phase	-	Mainly top phase, some at interface

It is known that dextran interacts strongly with ferric oxide in aqueous solution and can even solubilize the oxide to form iron-dextran complexes (20-24). The complexes are pharmaceutically important as synthetic substitutes for the iron storage protein ferritin, and it is used in the treatment of iron deficiency anaemias (20). Research shows that the ferric oxide-dextran complexes are composed of an iron-based core surrounded by a dextran-covered layer (20-24). At the same time, the adsorption of nonionic surfactants on metal oxides is believed to be a physical process through hydrogen bonding and van der Waals attraction (25). Thus, it is reasonable to conclude that dextran has stronger interaction with hematite than TX100; hence, the particles preferred to stay in the bottom dextran-rich phase. From the above discussion, it can be seen that both hydrophilic/hydrophobic properties and specific polymer-solid interaction favor the distribution of hematite into the bottom dextran-rich phase.

4.3.2 Effects of Surfactants on Hematite Partition in the Triton X-100/Dextran/H₂O System

Table 4.1 lists the experimental results obtained for hematite partition in the Triton X-100/dextran system at pH 3, 7, and 11 in the presence of SDS, potassium oleate, and DTAB. Figure 4.4 shows the partitioning behavior of ferric oxide from pH 2 to 12 in the presence of DTAB (1.0 g/L). From Table 4.1, it can be seen that at all the pH values, SDS and oleate had no effect on hematite partition, A similar result was obtained with low concentrations of DTAB (0.2-0.8 g/L). However, at high concentrations (1.0 g/L), DTAB could modify the distribution of hematite particles (as shown in Figure 4.4). At high pH (pH 5, 8-11), the solids mainly stayed in the top TX100-rich phase, although

there were some particles at the interface. In these cases, it was very difficult to accurately separate this material from the solid in either the top phase or the bottom phase. For convenience, this portion of solids was generally combined with the solid in the top phase. At pH 4, the oxide particles mainly concentrated at the interface. In acidic solution (pH 2 and 3), the particles resided in the bottom phase, similar to the DTAB-free system. It needs to be noted that at pH 6, 7, and 12, the system formed only one phase, not two phases. At these three pH values, no meaningful partition results could be obtained.

The pH_{PZC} of ferric oxides is known to occur in the pH range from 5 to 8.6 (26). Below this pH, the hematite surface is positively charged; the surface acquires negative charges above this pH. In the TX100/dextran system, ionic surfactants concentrate in the top phase and form mixed micelles with TX100 (16-18). It is known that cationic surfactants can adsorb on oxide surfaces above the pzc, through electrostatic attraction (27-29). Therefore, at high pH values, DTAB adsorbs on hematite surface through electrostatic attraction and transfers the particles from the bottom to the top phase. In acidic solution, DTAB cannot adsorb on the surface of ferric oxide due to coulombic repulsion, because both surfactant and solid surface are positively charged. Thus, the oxide surface is still covered with dextran layer. Hence, the oxide remained in the bottom phase.

The uptake of SDS by hematite is believed to be a physical adsorption process (30, 31), while oleate can chemically adsorb on the surface (32-35). Although both of these surfactants can modify the surface chemistry of ferric oxide at certain pH values in conventional solutions, neither one changed the partitioning behavior of hematite in this

FIGURE 4.4. Effect of pH on hematite partition to the top phase of the Triton X-100/dextran/H₂O system in the presence of DTAB. (Dextran: 9.0 wt%; Triton X-100: 11.0 wt%; silica: 2.0 g/L; DTAB: 1.0 g/L).

polymer/surfactant system. Since dextran strongly interacts with ferric oxide (20-24), it is speculated that SDS or oleate is not able to replace the strongly adsorbed dextran layer on the hematite surface. Therefore, the particles continued to stay in the bottom phase.

4.3.3 Effect of pH on Hematite Partition in the PEG/Dextran/H₂O System

Table 4.2 shows the partitioning behavior of hematite in the PEG/dextran system at pH 3, 7, and 11. The solids stayed in the bottom dextran-rich phase under all the pH conditions. This result was the same as that observed in the TX100/dextran system and it can be explained by similar reasoning. From Albertsson's scale of relative hydrophilic/hydrophobic character, the bottom dextran-rich phase is more hydrophilic than the top PEG-rich layer (1). Therefore, the hydrophilic hematite particles preferred the bottom phase. At the same time, as discussed above in Section 4.3.1, dextran interacts strongly with ferric oxide in aqueous solution (20-24). In contrast, there is negligible adsorption of PEG on hematite (36-39). It is obvious that there is stronger interaction between dextran and hematite than between PEG and hematite; this leads the particles to prefer the bottom dextran-rich phase. Thus, on the basis of both hydrophilic/ hydrophobic properties of the solid surface and specific interaction between the polymers and the particles, hematite was likely to stay in the bottom dextran-rich phase.

4.3.4 Effects of Surfactants on Partitioning Behavior of Hematite in the PEG/Dextran/H₂O System

Table 4.2 lists the results of hematite partition in the polyethylene glycol/dextran/H₂O system at pH 3, 7, and 11 in the presence of SDS and DTAB. In all the experiments, the

particles stayed in the bottom phase. The effect of SDS on the hematite partition in the PEG/dextran was the same as that in the Triton X-100/dextran system. Like the polymer/surfactant system, it was difficult for SDS to replace the adsorbed dextran layer because dextran interacts with ferric oxide strongly (20-24) and SDS only adsorbs on the solid surface physically (30, 31).

However, compared to the results in the Triton X-100/dextran system, the presence of DTAB in the PEG/Dex system has an opposite effect on solid partition. In the polymer/polymer system, the distribution of particles remained unchanged, i.e., the solids still occupied the bottom dextran-rich phase. The phenomenon can be explained with the different distributing behavior of cationic surfactant in the polymer/polymer systems and in the polymer/nonionic surfactant systems. As discussed above, DTAB concentrates in the top surfactant-rich phase of the polymer/nonionic surfactant system (TX100/dextran system). However, the results from Save and Pangarkar (40) showed that in the PEG/dextran system, cationic surfactants preferred the dextran-rich phase, and anionic surfactants went into the PEG-rich phase. As discussed above, at high pH, DTAB adsorbs on the oxide surface through attractive coulombic interaction. However, unlike the case of the Dex/TX100 system in which the particles transferred to the top phase, the solids still stayed in the dextran-rich phase because DTAB also preferred the bottom phase of the polymer/polymer system. At low pH, there is no adsorption of DTAB on the hematite surfaces due to electrostatic repulsion, and the surfaces were still surrounded with a polysaccharide layer. As a result, the particles continued to stay in the dextran-rich phase.

TABLE 4.2. Effect of ionic surfactants on hematite partition in the PEG/dextran system.

(PEG: 7.0 wt%, dextran: 16.8 wt%, hematite: 2.0 g/L).

Surfactant	pH 3	pH 7	pH 11
No surfactant	Bottom phase	Bottom phase	Bottom phase
1.0 g/L SDS	Bottom phase	Bottom phase	Bottom phase
1.0 g/L DTAB	Bottom phase	Bottom phase	Bottom phase

4.4 Conclusions

The principle behind the partition of inorganic particles in aqueous biphasic systems is the physicochemical interaction between the solid surface and the surrounding liquid solution. In this chapter it is demonstrated that many factors, such as hydrophilic/hydrophobic properties, polymer-solid specific interaction, adsorption of surfactant on the solid surface, and surfactant distribution could influence hematite partition in aqueous biphasic systems.

The experimental results showed that in both the Triton X-100/dextran and PEG/dextran systems, hematite stayed in the bottom dextran-rich phase under all pH conditions. In both systems, the bottom phase is more hydrophilic than the top layer; hence, the hydrophilic oxide particles preferred the dextran-rich phase. Also, the strong interaction between dextran and ferric oxide favored the dispersion of the solids in the polysaccharide-rich phase.

In the TX100/Dex system, addition of SDS or oleate had no effect on the solid partition; on the other hand, DTAB transferred the particles to the top phase or interface at high pH values. In the PEG/Dex system, hematite remained in the bottom phase in the presence of either SDS or DTAB. The effects of SDS or oleate on the partition behavior in both systems are attributable to the fact that they are not able to replace the strongly adsorbed polysaccharide layer on the solid surface. The results obtained with DTAB are due to electrostatic interaction between the cationic surfactant and the negatively charged surface of hematite. The different effects of DTAB in the TX100/Dex and PEG/Dex systems (i.e., particle transfer to the top phase in the TX100/Dex system versus particle

transfer to the bottom phase in the PEG/Dex system) was the result of the different distribution of DTAB in these systems. In the Dex/TX100 system, DTAB prefers the top surfactant-rich phase, while it concentrates in the bottom phase in the PEG/dextran system.

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Chapter 5

PARTITIONING BEHAVIOR OF SILICA IN POLYMER/POLYMER AND POLYMER/SURFACTANT SYSTEMS

5.1 Introduction

The objective of this research is to investigate the feasibility of employing aqueous biphasic extraction as a new separation technology for fine coal processing. As in liquid-liquid extraction (1-3), the basic principle behind the selective partition of particles in aqueous biphasic systems (4-8) is the physicochemical interaction between the solid surface and the liquid solution, rather than the bulk properties of the solid or solution such as density. Accordingly, differences in the surface chemistry of particles, e.g., hydrophobic/ hydrophilic property, can be exploited to achieve selective separations according to differences in this property for the two conjugate aqueous phases. In the published literature (9-15) and in Chapters 2-4, attempts have been made to control the partitioning behavior of inorganic particles in aqueous biphasic systems.

In the polymer/inorganic salt two-phase system, the top polymer-rich phase is more hydrophobic, and the bottom salt-rich one is more hydrophilic. Therefore, a naturally hydrophilic material, like hematite, would prefer the bottom phase (9, 10, Chapter 3). In contrast, a hydrophobic particle, e.g., graphite, will be concentrated in the top phase (10).

It has also been found that pH adjustment is effective in controlling the partitioning behavior of sulfide particles, e.g., pyrite (as shown in Chapter 2). The surface of pyrite was oxidized in aqueous solution to form different products, whose relative concentrations were determined by the solution pH. Below pH 5, pyrite particles transferred into the top polymer-rich phase of the polyethylene glycol (PEG)/Na₂SO₄/H₂O systems, a result attributable to the fact that, under these relatively acidic conditions, the surface reacted to form a hydrophobic metal-depleted product (Fe_{1-x}S₂). Above pH 9, all particles transferred into the bottom salt-rich phase; under the prevailing alkaline conditions, the metal sulfide surface was oxidized to hydrophilic iron oxide. These trends demonstrate that pH can be used to change the surface chemistry of pyrite (e.g., from FeS₂ to Fe_{1-x}S₂ or FeOOH), and, consequently, the partitioning behavior of pyrite in aqueous biphasic systems.

Aside from the hydrophilic/hydrophobic properties, specific interaction between the particle surface and the polymer molecules in solution can also play an important role in selective partition of solids (10). As shown in Chapter 3, unlike other hydrophilic oxides (e.g., alumina, hematite, and titania), silica particles stayed in the top polymer-rich phase in the PEG/Na₂SO₄/H₂O system. This behavior was attributed to hydrogen bonding between the ether oxygen atoms in the PEG backbone and the neutral hydroxyl groups on the silica surface. This explanation was supported by the adsorption results in the literature (16-26). On silica surface, the adsorption of PEG showed a high affinity type, while the adsorption of PEG on other oxide materials, e.g., hematite, alumina, and titania, was negligible (16-26). In polymer/polymer/water biphasic systems too, selective partition

of polymeric latex particles was achieved because of the specific interaction between the dissolved polymers and the functional groups on the particle surfaces (15).

Approaches that change the solid surface chemistry through surfactant adsorption can also be used to control the partitioning behavior (9, 10). In conventional flotation technology, surfactants are used to modify the surface hydrophobicity (27-29). Previous work in Chapter 2 showed that for pyrite, the presence of xanthate markedly changed the partition behavior in neutral and alkaline solution; the sulfide particles preferred the top phase instead of the bottom phase or the interface. It was reported that xanthate also affected the partition of other metal sulfides (e.g., copper sulfide, lead sulfide, zinc sulfide, and nickel sulfide) in the PEG/Na₂SO₄/H₂O system (9). In the case of hematite, as shown in Chapter 3, oleate effectively modified the partition behavior. Above pH 6, the presence of oleate caused the transfer of the solid from the bottom salt-rich phase to the top polymer-rich layer, and the yield in this phase reached the maximum at about pH 6.

In addition to the factors mentioned above, electrostatic forces can also play an important role in the behavior of colloids in aqueous solution. However, nothing is mentioned about this interaction in the limited literature of particle partition in aqueous biphasic systems (9-15). In the polymer/nonionic surfactant aqueous biphasic systems, electrostatic interaction can be applied to control the partitioning behavior of proteins in the presence of ionic surfactants (30-32). The ionic surfactants concentrate in the top surfactant-rich phase and form mixed micelles with the nonionic surfactants. Thus, it has been demonstrated that a coulombic attraction or repulsion was created between the mixed micelles and charged proteins (30-32). Addition of anionic surfactant moved

negatively charged proteins into the bottom dextran-rich phase, and transferred positively charged ones into the top phase. The proteins showed opposite behavior in the presence of cationic surfactant (30-32). In Chapter 4, it was shown that electrostatic interaction influenced hematite partition in the Triton X-100 (TX100)/dextran/water system in the presence of DTAB.

Chapter 3 presented the partitioning behavior of silica in the PEG/Na₂SO₄ system. The particles preferred the top PEG-rich phase under all pH conditions, a behavior which is attributable to the specific polymer-solid interaction through hydrogen bonding between the surface silanol groups and oxygen atoms in the polymer chains. No report has been found in the literature about the partition of silica in the polymer/polymer and polymer/surfactant aqueous biphasic systems (9-15). For comparison with the results in Chapter 3, this chapter investigated the partitioning behavior of silica in the PEG/dextran and TX100/dextran aqueous biphasic systems. This work also investigated whether electrostatic effects could modify silica partition in the presence of ionic surfactants.

5.2 Experimental Procedures

5.2.1 Materials

Dextran (Dex, average molecular weight 24,500), polyethylene glycol (PEG, molecular weight 8,000), Triton X-100 (TX100, t-octylphenoxypolyethoxyethanol), and silicon dioxide (-325 mesh or < 44 μ m) were purchased from Sigma-Aldrich. Sodium dodecyl sulfate (SDS), dodecyl trimethyl ammonium bromide (DTAB), sodium

hydroxide, and nitric acid were all of reagent grade (Aldrich). Distilled water was used in all experiments and all experiments were conducted at room temperature (~ 23 °C). The chemical structures of polymers and surfactants are given in Figure 5.1.

5.2.2 Partition Experiments

The aqueous biphasic systems were prepared by dissolving the polymers and/or nonionic surfactant in known volumes of water. The total composition of the TX100/Dex system was 9.0 wt% polymer, 11.0 wt% surfactant, and 80.0 wt% water. The PEG/Dex system was composed of 7.0 wt% PEG, 16.8 wt% TX, and 76.2 wt% water. In both systems, the bottom phase was enriched in dextran, the other components were concentrated in the top phase. The relevant phase diagrams were presented previously in Chapter 4.

The extraction experiments were conducted in 60 mL glass bottles; for a given experiment, the volume of aqueous biphasic solution was 50 mL and 0.1 g of particles was added. A given amount of ionic surfactant was introduced, and the pH was adjusted with NaOH or HNO₃ solution. The dispersion was magnetically stirred for 0.5 hours. The mixture was then transferred to 125 mL separatory funnels to allow phase separation to occur. In some cases, there were particles at the interface; it was very difficult to accurately separate this material from the solid in either the top phase or the bottom phase. At the same time, because the liquid/liquid interface area in the separatory funnel was too small to support all particles at the interface, many of the particles settled down along the glass wall and went into the bottom phase. Therefore, for the mass balance, the particles at the interface were generally combined with the solids in the bottom phase.

Polyethylene Glycol

t-octylphenoxypolyethoxyethanol

PEG

Triton X-100

Sodium Dodecylsulfate

Dodecyltrimethylammonium Bromide

SDS

DTAB

Dextran

FIGURE 5.1. Chemical structures of polymers and surfactants.

The solid in each phase was recovered by filtering the mixtures through Whatman membrane filters (0.45 μm). The recovered solids were rinsed with distilled water at least six times, dried in an oven at 100 $^{\circ}\text{C}$, and weighed. The solid yield (Y_i) in each phase was calculated as:

$$Y_i = W_i/W_0 \quad [5.1]$$

where W_i and W_0 respectively represent the mass of solid in that phase and the total mass of solids.

5.3 Results and Discussion

5.3.1 Effects of pH on Silica Partition in the Triton X-100/Dextran/ H_2O System

Figure 5.2 shows the partitioning behavior of silica in the TX100/dextran/ H_2O system. Below pH 3.5, almost all the silica particles went into the top surfactant-rich phase. When the pH increased from 4.0 to 8.0, the particles began to concentrate at the interface, and the yields in the top phase decreased with increase in pH. Between pH 9.0 and 11.3, the solids preferred the bottom polymer-rich phase. At pH 11.5 and 11.7, the oxide particles mainly stayed at the interface. With further increase in pH from 11.8 to 12.5, the solids transferred to the top phase again. As mentioned above, for the cases where the solid accumulated at the interface, for purposes of mass balance, the particles were combined with the silica in the bottom polymer-rich phase.

FIGURE 5.2. Effect of pH on silica partition in the Triton X-100/dextran/H₂O system.

(Dextran: 9 wt%; Triton X-100, 11 wt%; silica: 2 g/L).

It is known that nonionic surfactants, such as Triton X-100, can adsorb on silica surface in aqueous solution (33-41). The oxyethylene groups of TX100 molecules attach onto silica surface through hydrogen bonding with the neutral silanol surface groups. More surfactant molecules concentrate at the solid/liquid interface and form surface micelles around anchored molecules through hydrophobic interactions among the tail groups of the surfactant (33-41). On the other hand, dextran can also adsorb on silica, a result of hydrogen bonding between the surface silanol groups and the glycosidic and hydroxylic acceptor sites in the repeating glucose units of the polysaccharide (42-45). However, it appears that the polymer is weakly bound to silica surface; the adsorbed polymers could be partially removed by diluting the supernatant solution (46). Jucker et al (43) found that the adsorption of polysaccharides on SiO_2 was much less than on TiO_2 and Al_2O_3 . All these reports show that dextran has weak interaction with silica surface.

In principle, both dextran and Triton X-100 can adsorb on silica (33-45). Therefore, when silica particles are dispersed in the TX100/Dex system, a competitive adsorption process involving the polymer and the surfactant molecules occurs at the solid/liquid interface. The partition behavior of silicon dioxide is determined by the relative strength of the Dex/ SiO_2 and TX100/ SiO_2 interactions. At the pH_{PZC} of silica ($\sim\text{pH } 2$) (47), most of the silanol groups on the surface remain undissociated. Thus, these surface groups will provide sites for adsorption of Triton X-100 on the silica surface. The TX100/ SiO_2 interaction may be stronger than the Dex/ SiO_2 interaction, given the documented poor affinity of dextran for the solid surface (42, 43). Therefore, the particles are expected to prefer the top surfactant-rich phase. With increase in pH, the surface acquires negative charges through deprotonation of silanol groups, the amount of neutral sites decreases

and the adsorption of TX100 on SiO₂ is expected to decrease accordingly. Moreover, since the oxygen atom in the oxyethylene unit of Triton X-100 carries a partial negative charge, a certain amount of electrostatic repulsion between the surfactant and the oxide surface is also expected; this repulsion will result in decreased adsorption of nonionic surfactant. This pH effect is also demonstrated by results in the literature which show that the uptake of TX100 by silica decreases with increase in pH (33, 39). It follows then that with increase in pH, the TX100/SiO₂ interaction becomes weak, and as a result, the particles begin to transfer from the surfactant-rich phase to the interface, then to the polymer-rich phase. This explains the experimental trend in the pH range of 3.5 to 11.3, i.e., the steady decrease in yield in the top phase with pH increase.

The result obtained above pH 11.5 is very interesting; the particles moved into the top phase again. This behavior is difficult to explain from the current literature on the adsorption of dextran and TX100 on silica. It is likely that future polymer adsorption experiments will help to uncover the physico-chemical origins of this trend.

5.3.2 Effects of Surfactants on Silica Partition in the Triton X-100/Dextran/H₂O System

SDS. Table 5.1 presents some data for the partition of silica in the Triton X-100/dextran system in the presence of SDS at pH 3, 8, and 10. From this table, it can be seen that at low concentration (0.1 g/L), SDS had no effect on silica partition under all pH conditions. With increase in SDS concentration from 0.2 to 1.0 g/L at pH 8, silica particles transferred from the interface to the bottom phase. At pH 3, 0.4 g/L of SDS was able to move the solids from the top surfactant-rich phase to the interface. However, at

pH 10, silica remained in the bottom phase irrespective of the SDS concentration. Figure 5.3 presents data for silica partition in the presence of 0.4 g/L or 1 g/L SDS in the pH range from 2 to 12. With 0.4 g/L SDS, silica particles stayed in the top phase at pH 2; at the interface from pH 3 to 5, and at pH 12; and in the bottom phase from pH 7 to 10. At high SDS concentration (1.0 g/L), silica particles transferred to the bottom dextran-rich phase from pH 8 to 12. However, below pH 7, this amount of SDS caused the whole system to form only one phase. These results show that for pH conditions (except pH 2) where silica stayed in the top phase or at the interface in the TX100/dextran system, addition of anionic surfactant (SDS) transferred the solid from the top layer to the interface, or from the interface to the bottom phase.

In polymer/nonionic surfactant aqueous biphasic systems, ionic surfactants mainly concentrate in the top surfactant-rich phase and form mixed micelles with the nonionic surfactant (30-32). Therefore, an electrostatic interaction is developed between the mixed micelles and the charged solid surface (30-32). In the TX100/Dex/H₂O system, as discussed above, the partition of silica in the top phase at certain pH values is due to hydrogen bonding between the oxyethylene groups of the nonionic surfactants and silanol groups on the solid surface. Addition of SDS makes the micelles in the top phase negatively charged (30-32). Since silica surface is negatively charged above its pH_{PZC} (about pH 2), it is expected that there would be coulombic repulsion between the mixed micelles and solid particles. Thus, the adsorption of nonionic surfactant should be suppressed due to this repulsive force. This effect of SDS on TX100 adsorption on silica has been demonstrated experimentally (48). Therefore, the particles are expected to transfer from the top phase to the interface or the bottom phase. The experimental results

TABLE 5.1. Effect of SDS concentration on silica partition in the Triton X-100/dextran/H₂O system (Dextran: 9 wt%; Triton X-100: 11 wt%; silica: 2 g/L).

SDS conc. (g/L)	Experimental results		
	pH 3	pH 8	pH 10
0	In the top phase	Mainly at the interface, some in the top phase	In the bottom phase
0.1	In the top phase	Mainly at the interface, some in the top phase	In the bottom phase
0.2	-	At the interface	-
0.3	-	At the interface	-
0.4	Mainly at the interface	Mainly in the bottom phase, some at the interface	In the bottom phase
1.0	-	In the bottom phase	In the bottom phase

FIGURE 5.3. Effect of pH on silica partition to the top phase of the Triton X-100/dextran/H₂O system in the presence of SDS and DTAB. (Dextran: 9 wt%; Triton X-100: 11 wt%; silica: 2 g/L; SDS & DTAB: as indicated in the figure).

show that this really happens. As can be seen from Figure 5.3, at pH 12 silica stayed in the top phase in the absence of ionic surfactant; however, the oxide particles moved to the interface with 0.4 g/L SDS and then to the bottom phase with further increase in anionic surfactant concentration to 1.0 g/L. From pH 3 to 5, the yields of solid in the top phase decreased in the presence of SDS. In the pH range in which silica particles initially stayed in the bottom phase, the presence of SDS had no effects on solid partition. At pH 2, since silica surface was almost neutrally charged, the particles still preferred the surfactant-rich phase after SDS was added.

DTAB. Table 5.2 and Figure 5.3 present data for the partition of silica in the Triton X-100/dextran system in the presence of DTAB. From Table 5.2, it can be seen that 0.2 g/L DTAB was enough to transfer the silica from the bottom polymer-rich phase to the top phase. As shown in Figure 5.3, in the presence of 0.4 g/L DTAB, silica particles always preferred the top phase of the TX100/Dex system in the pH range from 4 to 11.

In the TX100/Dex system DTAB, like SDS, also prefers the top surfactant-rich phase and forms mixed micelles with TX100; therefore, the mixed micelles are positively charged (30-32). Thus, an electrostatic attraction is expected to develop between the mixed micelles in the top phase and the oppositely charged silica surface. The adsorption of cationic surfactant on silica surface neutralizes the surface charge, and as a result that the repulsion between the nonionic surfactant and the solid surface, as discussed above (Section 5.3.1), will decrease. Moreover, these adsorbed DTAB molecules provide hydrophobic sites for adsorption of nonionic surfactant. Hence, adsorption of nonionic surfactant is expected to increase in the presence of the cationic surfactant. This has been

TABLE 5.2. Effect of DTAB concentration on silica partition in the Triton X-100/dextran/H₂O system. (Dextran: 9 wt%; Triton X-100, 11 wt%; silica: 2 g/L).

DTAB conc. (g/L)	Experimental results (at pH 10)
0	In the bottom phase
0.1	Mainly at the interface, some in the top phase
0.2	Mainly in the top phase, some at interface
0.4	In the top phase

demonstrated with adsorption experiments in mixed cationic and nonionic surfactants solutions (49). It follows that in the Triton X-100/dextran system, the presence of DTAB may enhance the adsorption of nonionic surfactant on silica surface and the particles are expected to prefer the top phase. The experimental results demonstrated this expectation. From pH 4 to 11, silica particles stayed in the top surfactant-rich phase with 0.4 g/L of DTAB, irrespective of whether they were at the interface or in the bottom phase in the absence of DTAB.

5.3.3 Effects of pH on Partitioning Behavior of Silica in the PEG/Dextran/H₂O System

Figure 5.4 shows the partitioning behavior of silica in the PEG/dextran system. From pH 2 to 7, silica particles mainly stayed in the top PEG-rich phase while there were increasing solids concentrated at the interface with increase in pH. At pH 8, the particles mainly transferred to the interface, with some in the top phase. In the pH range from 9 to 11, most of the solids transferred to the bottom dextran-rich phase, the amount of silicon dioxide at the interface decreased with increase in pH. At pH 12, the solids transferred to the top phase again. As mentioned above, for purposes of mass balance, the particles at the interface were combined with the silica in the PEG-rich phase.

It is known that PEG adsorbs on silica surface through hydrogen bonding between the H atom of the Si-OH group and the O atom in the PEG chain (16-23). The enthalpy change for PEG displacement of water on silica surface is about 9.9 kcal/mol, a typical value for the formation energy of a hydrogen bond (18). The neutral Si-OH sites favor the adsorption of PEG (20-23). When Si-OH deprotonates to form Si-O⁻ above the p*H*_{PZC} of

FIGURE 5.4. Effect of pH on silica partition in the PEG/dextran/H₂O system. (PEG: 7.0 wt%; dextran: 16.8 wt%; silica: 2.0 g/L).

silica, the formation of hydrogen bonds is not favored because of the electrostatic repulsion between the negatively charged SiO^- sites and the partially negatively charged oxygen atoms in the PEG chain.

On the other hand, as discussed above, dextran can also adsorb on the silica/water interface through hydrogen bonding between silanol groups and glycosidic and hydroxylic acceptor sites in the repeating glucose units of the polysaccharide. However, it is believed that this polymer has only poor affinity for the solid surface (42-45).

It can be concluded, therefore, that PEG interacts more strongly with silica surface than does dextran. This is the reason why silica prefers the PEG-rich phase at low pH values. With increase in pH, more and more surface silanol groups begin to deprotonate and the surface acquires negative charges. The hydrogen bonding between PEG and SiO_2 becomes limited because of the electrostatic repulsion between the negatively charged solid surface and the partial negative charges on the oxygen atoms in the polymer chains. This repulsion was demonstrated by the observed decrease in PEG adsorption on SiO_2 with increase in pH (24-26). Thus, the PEG/ SiO_2 interaction becomes weak. Accordingly, as pH increases, the particles begin to transfer from the PEG-rich phase to the interface (at pH 8), then to the dextran-rich phase (at pH 10 and 11).

The result at pH at 12 is very interesting and is similar to that previously reported above for the Triton X-100/dextran system in the same pH range. This behavior is difficult to explain from our current understanding of PEG and dextran adsorption on silica. Further work (e.g. adsorption experiments) is needed in order to unravel the physico-chemical origins of this behavior.

5.3.4 Effects of Surfactants on Silica Partition in the PEG/Dextran/H₂O System

SDS. In Figure 5.5, the partitioning behavior of silica in the PEG/dextran/H₂O system in the presence of 1.0 g/L SDS is presented. In the pH range from 3 to 12, the particles mainly stayed in the bottom dextran-rich phase. At pH 2, there were solids in both the top and bottom phases.

In the PEG/dextran/H₂O system, SDS partitions preferentially into the top PEG-rich phase; this is due to the formation of a polymer/surfactant complex in the top phase (50). This kind of complex is known to have a “necklace” structure: the polymer chain penetrates into the surfactant micelle, and usually several micelles are connected to one macromolecular chain (51). At the silica surface the adsorption of PEG will attract SDS to the surface and a complex with the polymer is formed. Since silica is negatively charged above its pH_{PZC} (about pH 2) (47), there is electrostatic repulsion between the SDS and the solid particles. It is expected, therefore, that the adsorption of PEG on silica will be suppressed in the presence of SDS in the PEG/dextran system. Maltesh and Somasundaran (52) reported that PEG adsorption on silica decreased with addition of SDS. Therefore, the partition of oxides in the top phase is not favored in the presence of SDS. The results in Figure 6.7 show that from pH 3 to 12, silica particles mainly stayed in the bottom dextran-rich phase. At pH 2, the silica surface is almost neutrally charged because of the coincidence with the pH_{PZC} (about pH 2). Therefore, the repulsion between SDS and silica surface is reduced, and the particles dispersed in both the top and bottom phases.

DTAB. The effect of DTAB (0.1 g/L) on the partition of silica in the PEG/dextran/H₂O system was also investigated, as shown in Figure 5.5. From pH 2 to 6,

the particles mainly stayed in the top PEG-rich phase, with some at the interface. In the pH range of 7 to 10, the oxides transferred to the bottom dextran-rich phase, and the amount of solids at the interface decreased with increase in pH. At pH 11 and 12, almost all the silicon dioxide particles moved to the dextran-rich phase.

In the PEG/Dex/H₂O system, unlike SDS, DTAB prefers the bottom dextran-rich phase (50). Above pH_{PZC} of silica, the adsorption of cationic surfactants on SiO₂ is believed to compose of two steps: at low concentration, individual surfactant adsorbs on negatively charged surface site mainly by coulombic attraction; then, with increase in concentration, more surfactants migrate to the surface and form hemimicelles at the solid/liquid interface through the hydrophobic interactions between alkyl chains of the surfactants molecules (53-58). Therefore, the interaction between DTAB and the particles favors the partition of silica particles into the dextran-rich phase. At the same time, PEG can adsorb on the silica surface through hydrogen bonding (16-23), which transfers the solids into the top phase. Thus, a competitive adsorption process occurs in this system when the particles are dispersed in the solution. Since dextran has only a poor affinity for SiO₂ (42-45), the adsorption of the polysaccharide is not so important. Therefore, the solid partition is determined by the relative strengths of the PEG/SiO₂ and DTAB/SiO₂ interactions. At low pH, most of silanol groups on the surface remain neutral so that the hydrogen bonding is relatively stronger than the electrostatic attraction. Therefore, silica particles prefer the PEG-rich phase. As pH increases, the surface becomes increasingly negatively charged, and then the electrostatic attraction between the cationic surfactant and the solid begins to dominate in the system. Thus, with increase in pH, the oxide

FIGURE 5.5. Effect of pH on silica partition to the top phase of the PEG/dextran/H₂O system in the presence of SDS and DTAB.

(PEG: 7.0 wt%; dextran: 16.8 wt%; silica: 2.0 g/L; SDS and DTAB: 1.0 g/L).

particles begin to transfer from the top phase to the interface, and then to the bottom phase. At high pH (pH 11 and 12), almost all the particles stay in the dextran-rich phase.

5.4 Conclusions

The partition of solid particles in aqueous biphasic systems depends on the physicochemical interaction between the solid surface and liquid phase, rather than the bulk properties of the solid particles. In this chapter it is shown that in the polymer/surfactant and polymer/polymer two-phase systems, the interaction between phase-component compound and solid surface plays an important role in determining the solid partitioning behavior. In the Triton X-100/dextran system, silica particles stayed in the top surfactant-rich phase at either very low pH (<3.5) or very high pH (>11.7). From pH 9 to 11.3, the particles preferred the bottom dextran-rich phase. The oxide particles concentrated at the interface in the pH range of 4 and 8. In the PEG/dextran system, a similar partitioning trend was observed for silica particles. The solids migrated to the top surfactant-rich phase at either low pH (< 7) or very high pH (pH 12). From pH 9 to 11, the particles transferred to the bottom dextran-rich phase, and concentrated at the interface at pH 8. These trends are attributed to the competition between dextran/SiO₂ and TX100/SiO₂ interactions in the TX100/dextran system, or dextran/SiO₂ and PEG/SiO₂ interactions in the PEG/dextran system.

In this chapter, it is also shown that electrostatic forces can play an important role in the partition of silica particles when ionic surfactants are introduced into these two

biphasic systems. In the TX100/dextran system, ionic surfactants concentrate in the top phase and form mixed micelles with the nonionic surfactant (30-32). Therefore, electrostatic attractive or repulsive interactions develop between the mixed micelles and the solid surface. Addition of an anionic surfactant, SDS, moves the silica particles from top phase to the interface or bottom phase. On the other hand, DTAB, a cationic surfactant, attracts the particles to the top phase in the pH range from 4 to 11, where in the absence of DTAB the solids either stay at the interface or in the bottom phase. In the PEG/dextran system, anionic surfactants (e.g. SDS) concentrate in the top PEG-rich phase, and cationic surfactants (e.g. DTAB) prefer the bottom dextran-rich phase (50). Therefore, in the presence of SDS, SiO_2 prefers the bottom dextran-rich phase above the pH_{PZC} because of the electrostatic repulsion between the anionic surfactant in the top phase and the negatively charged solid surface. After addition of DTAB, the silica particles move from the top phase to the interface, and then to the bottom phase, with increase in pH. This behavior is attributable to the competing coulombic attraction of DTAB on SiO_2 and adsorption of PEG on the solid surface. From the results, it is also interesting to notice that even though SDS and DTAB have opposite charges, they can have the same effect on silica partition in the PEG/dextran system because the two surfactants transfer to the opposite phases. But in the TX100/dextran system, these two surfactants had opposite effects on the distribution of silica particles since they both preferred the top nonionic surfactant-rich phase.

5.5 References

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Chapter 6

PARTITION OF FINE COAL AND FLY ASH IN AQUEOUS BIPHASE SYSTEMS

6.1 Introduction

As mentioned in Chapter 1, the overall objective of this research project is to develop an aqueous biphasic extraction process for the treatment of fine coals. In order to successfully remove the mineral matter from coal, it is important to know the partitioning behavior of real fine coal and its inorganic mineral components in aqueous biphasic systems. In Chapter 2 pyrite partition was investigated in polymer/salt/water systems. Chapters 3, 4, and 5 studied the partitioning behavior of model oxide materials in aqueous biphasic systems of the type polymer/salt, polymer/polymer, and polymer/surfactant. Although aqueous biphasic extraction has been used in biological science and technology for a long time (1-5) and some attempts have been made to extend this technique to inorganic particles (6-14), no reports are available in the literature concerning the distribution of fine coal in aqueous biphasic systems. In this Chapter, the partition of fine coal in the polymer/salt aqueous biphasic system is reported for the first time.

As a potential new separation technology for fine coal processing, aqueous biphasic extraction is not only limited to removing mineral matter from fine coal. The applicability of this technique to other challenging coal-related fine particle separation problems is worth exploring. Therefore, this chapter includes a report of the first efforts to apply aqueous biphasic extraction in fly ash processing.

Fly ash, as a major coal combustion byproduct (CCB), is produced in the amount of 50 million tons/year in the USA (15). The utilization of fly ash is about 20%, and most of it is used in the cement industry, as a road base, and as structural fills (16). In response to the Clean Air Act Amendment of 1990, low temperature combustion of coal is being carried out in order to reduce the emission levels of NO_x and SO_x . However, as a side effect of this new technology, the carbon content in fly ash is increased significantly. This limits the utility of fly ash as a construction material in the cement industry (17, 18). High amounts of carbon in fly ash that is used in concrete promote the undesirable adsorption of air-entraining admixtures in concrete (these admixtures are added in order to prevent cracking). It is, therefore, necessary to separate the high carbon component from ash in fly ash. Also, beneficiated fly ash has potential application as a raw material for the synthesis of mullite (15, 19), as a filler in the plastic industry (20), and as an adsorbent (17, 21). Several beneficiation methods have been developed, such as froth flotation (22-27), density gradient centrifugation (28), and triboelectrostatic processes (29-31). This chapter reports experiments conducted to investigate the feasibility of applying aqueous biphasic systems as new separation media for the beneficiation of fly ash. The partitioning behavior of fly ash in polyethylene glycol (PEG)/salt/water biphasic systems was studied, and characterization of the solid fraction in each phase was carried out.

6.2 Experimental Procedures

6.2.1 Materials

The coal sample (Illinois #6) was kindly provided by Dr. Chander (Penn State University) as lumps. It was ground, sieved through ASTM certified screens, and the –400 mesh fraction was used in all the experiments. Fly ash was obtained from the Coal Utilization Laboratory, Penn State University. It was classified with ASTM certified screens, and the –400 mesh fraction was collected for all the experiments. Polyethylene glycol (PEG-2000 (molecular weight 2000)) was supplied by Aldrich. Sodium sulfate, hydrogen peroxide, ferric chloride, sodium hydroxide, and hydrochloric acid were all of reagent grade (Aldrich). Distilled water was used in all experiments and all experiments were conducted at room temperature ($\sim 23^{\circ}\text{C}$).

6.2.2 Partition Experiments

The aqueous biphasic systems were prepared by weighing fixed amounts of PEG and salt in a known volume of water. The composition of the total aqueous solution was 15 wt% PEG, 10 wt% inorganic salt and 75 wt% water. Solutions of NaOH or HCl were used to control the pH.

The extraction experiments were conducted in 125 mL Pyrex separatory funnels; for a given experiment, the volume of aqueous biphasic solution was 100 mL and 0.5 g of particles was added. For the fine coal samples, the dispersions were mixed thoroughly with magnetic stirring and then allowed to separate into the polymer-rich and salt-rich phases. For the fly ash samples, the mixtures were subjected to a Wrist Action Shaker

(Burrell Co.) for 1 hour and then allowed to separate into the polymer-rich and salt-rich phases. The dispersion in each phase was filtered through Whatman membrane filters (0.2 μm). The recovered solids were rinsed with distilled water at least six times, dried in an oven at 100 $^{\circ}\text{C}$, and weighed. The solid yield (Y) in the each phase was calculated as:

$$Y = W/W_0 \quad [6.1]$$

where W and W_0 respectively represent the mass of solid in the corresponding phase and the total mass of solids.

6.2.3 Characterization of Fly Ash

After partition experiments, the fly ash fractions in each phase of the aqueous biphasic system were collected as mentioned above. After drying at 100 $^{\circ}\text{C}$ for at least 24 hrs, the chemical composition of the solids was determined (carbon content and elemental composition in the ash), and the crystalline minerals in the ash were identified using X-ray powder diffraction (XRD). The carbon content in the samples was determined with a CHN-600 Carbon-Hydrogen-Nitrogen Determinator (Leco Corporation) by combusting the solids at 950 $^{\circ}\text{C}$ under pure O_2 . Two coal samples were used to calibrate the equipment: one was 501-531 with 88.42 wt% of carbon, and the other was AR2782 with C content of 64.95 wt%. The elemental composition of the ashes was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The fly ash samples were heat-treated at 750 $^{\circ}\text{C}$ overnight to remove the organic matter. The residues were ground, melted with lithium metaborate at 900 $^{\circ}\text{C}$, and dissolved with 5% nitric acid

TABLE 6.1. The elemental compositions of standard samples in ICP-AES measurement.

Samples	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO ₂	CaO	MgO	Na ₂ O	K ₂ O	BaO	SrO
AB-1	65.6	20.8	0	0.04	0	1.93	0	9.06	2.39	0	0
AGV-1	58.8	17.1	1.05	6.76	0.092	4.94	1.53	4.26	2.91	0.14	0.08
BCR-1	54.1	13.6	2.24	13.41	0.18	6.95	3.48	3.27	1.69	0.08	0.04
BR	38.2	10.2	2.6	12.9	0.2	13.8	13.3	3.05	1.4	0.12	0.16
BR/76A	46.6	24.5	2.32	7.24	0.1	7.01	6.9	1.56	1.37	0.06	0.1
FE-MICA	34.4	19.5	2.5	25.7	0.35	0.43	4.55	0.3	8.75	0.02	0
GH	75.8	12.5	0.08	1.34	0.05	0.69	0.03	3.85	4.76	0	0
GSP-1	67.2	15.1	0.65	4.29	0.04	2.07	0.96	2.81	5.51	0.15	0.03
MRG-1	39.1	8.46	3.77	17.9	0.17	14.7	13.6	0.74	0.18	0.01	0.03
NIM-S	63.6	17.3	0.04	1.4	0.01	0.68	0.46	0.43	15.35	0.27	0.01
NS-1	53.2	21.31	1.05	4.1	0.18	1.7	0.64	9.85	6.52	0	0
OR-1	64.4	18.6	0	0.03	0	0	0	1.14	14.9	0.82	0.04
NBS278	73.0	14.15	0.25	2.04	0.052	0.98	0.23	4.84	4.16	0.13	0.01
GFS403	1.81	0.43	0.03	0.31	0.018	38.0	13.8	0.03	0.14	0.01	0.04
NBS76A	54.9	38.7	2.03	1.6	0	0.22	0.52	0.07	1.33	0	0.04
NBS77A	35	60.2	2.66	1	0	0.05	0.38	0.04	0.09	0	0.01
NBS78A	19.4	71.7	3.22	1.2	0	0.11	0.7	0.08	1.22	0	0.25

in Teflon beaks. The elemental contents in the solutions were measured on Leeman Labs PS3000UV inductively coupled plasma spectrophotometer, and a series of standard rock samples were used as calibration (as shown in Table 6.1). The XRD measurements were carried out in a Rigaku Geigerflex with a Dmax-B controller. The crystalline phases were identified with the JCPDS database as reference data.

6.3 Results and Discussion

6.3.1 Partitioning Behavior of Coal in the PEG/Salt/Water System

The partitioning results of coal in polymer/salt/water systems are shown in Table 6.2 (solids concentration: 0.5 wt%). In the PEG/Na₂SO₄/H₂O system, almost all the coal samples stayed in the top polymer-rich phase because of its naturally hydrophobic surface. Some additives, such as hydrogen peroxide, ferric chloride, sodium sulfide, etc, have been reported to be effective in suppressing the agglomeration of pyrite in oil agglomeration of fine coal (32). In order to effectively separate the mineral matter from fine coal with aqueous biphasic extraction, it is worthwhile to study the effects of these additives on the partitioning behavior of coal in the aqueous biphasic systems. From Table 6.2, it can be seen that H₂O₂ had no effect on the coal partition in both the PEG/Na₂SO₄/H₂O and PEG/Na₂CO₃/H₂O systems; neither did FeCl₃ in the PEG/Na₂CO₃/H₂O system.

TABLE 6.2. Effect of additives on coal partition of in PEG-2000/salt/H₂O system
(solid content: 0.5 wt%).

Salt	pH	Additive	Additive conc. (M)	Y _t *	Y _b *
Na ₂ SO ₄	7.8	-	-	91.5	1.3
Na ₂ SO ₄	11.7	H ₂ O ₂	0.1	96.1	0.5
Na ₂ SO ₄ **	11.8	H ₂ O ₂	0.1	95.9	0.9
Na ₂ CO ₃	11.6	H ₂ O ₂	0.1	93.4	0.5
Na ₂ CO ₃	11.6	FeCl ₃	3×10 ⁻³	93.4	6.6

* Y_t: yield of pyrite in the top phase; Y_b: yield of pyrite in the bottom phase

** conditioning for 2 hours

6.3.2 Partitioning Behavior of Fly Ash in the PEG/Na₂SO₄/H₂O System

Figure 6.1 shows the effect of pH on the partitioning behavior of fly ash in the PEG-2000/Na₂SO₄/H₂O system (solids concentration: 1 wt%). In the pH range from 2 to 5, two solid fractions were obtained. The particles in the bottom salt-rich phase were brown, while the particles in the top polymer-rich phase were black. However, above pH 5, the particles in the polymer-rich phase separated into two zones. The upper zone was still black, while the newly formed lower zone was grayish. At pH 12, most of the fly ash was concentrated in the lower zone of the polymer-rich phase. With decrease in pH, the yield in the lower zone of the polymer-rich phase decreased; while the solid content in the upper zone increased simultaneously. However, the fraction of the solids that partitioned into the salt-rich phase was very low for the entire pH range investigated, from almost 0 wt% at pH 2 to ~6 wt% at pH 12.

When the amount of the added fly ash increased to 2 wt%, this 3-fraction phenomenon only happened above pH 10 (Table 6.3). Comparing the data in Figure 6.1 and Table 6.3, it can be seen that, the yields obtained at pH 12 with 2 wt% solids (i.e., 9.4 wt% for the upper zone of the polymer-rich phase, 81.4 wt% for the lower zone of the polymer-rich phase, and 9.3 wt% for the salt-rich phase) are similar to those obtained for the experiments conducted with 1 wt% solids. At pH 11, the yield in the upper zone of the polymer-rich phase increased to 39.6 wt%, while the yield in the lower zone of the polymer-rich phase decreased to 52.1 wt%. These two values were similar to the results at pH 7 when the amount of added fly ash was only 1 wt%. At pH 10, only two fractions of solids were obtained after phase separation. The yields in the salt-rich phase (6.2 – 9.3

FIGURE 6.1 Effect of pH on fly ash partition of in the PEG-2000/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ system (solids content: 1 wt%).

wt%) was comparable to those obtained in the same pH range (pH 10 - 12) for the experiments with 1 wt% solids.

6.3.3 Characterization of the Fly Ash Fractions after Partitioning Experiments

Carbon Content. Figure 6.2 shows the carbon content in each of the fractions obtained in the above partition experiments. The particles in the salt-rich phase had a low carbon content, which satisfies the requirement for application in cement manufacture. Because the amounts of the samples in the salt-rich phase at pH 2 and 3 were too small for the carbon content measurement, data for these two pH values could not be included in Figure 6.2. However, from the trend shown in this diagram, these samples are also expected to have low-carbon contents. In all the cases of 3-fraction partitioning, the solids in the upper zone of the polymer-rich phase had a carbon content of 80 wt%. This value was much higher than the C-content in the parent fly ash (63.2 wt%). In the case of the 2-fraction partition systems ($\text{pH} < 5$, Figure 2), the carbon content of the solids in the upper zone of the polymer-rich phase was almost the same as that in the parent fly ash. In terms of the mass balance, this was easy to understand because almost all the solid materials stayed in the polymer-rich phase, while the yield in the salt-rich phase was very small. For the 3-fraction partition systems ($\text{pH} > 5$), the carbon content of the solids in the lower zone of the polymer-rich phase was intermediate between that of the upper zone and the salt-rich phase. With decrease in pH, the carbon content decreased from 66 wt% at pH 12 (almost the same as that in the parent fly ash) to 41 wt% at pH 6. Comparing Figure 2 with the yield results in Figure 1, it can be seen that the largest

TABLE 6.3. Effect of pH on fly ash partition of in the PEG-2000/Na₂SO₄/H₂O system
(solids content: 2 wt%).

pH	Yield (wt%)			Ash Content (wt%)		
	Upper zone*	Lower zone*	Salt-rich phase	Upper zone*	Lower zone*	Salt-rich phase
12.0	9.4	81.4	9.3	11.8	27.7	91.5
11.1	39.6	52.1	8.3	14.3	35.4	97.5
9.9	96.6	-	6.2	29.1	-	92.7

*: In the polymer-rich phase.

FIGURE 6.2. The carbon contents in each liquid fraction (solids content: 1 wt%). The dashed line indicates the carbon content in the original fly ash.

amount of product (~60% yield) with the highest carbon content (~80 wt% C) was obtained in the range pH 6 - 9.

XRD Results. The XRD results are shown in Figures 6.3-6.6. The diffractograms show that in the parent fly ash, quartz, mullite, and hematite are the main crystalline components (Figure 6.3). The intensities of the peaks coming from quartz and mullite are much stronger than those associated with hematite. The strong, broad peak may come from amorphous carbon. The several small peaks indicate that there are other crystalline components present, but at low amounts. After beneficiation with aqueous biphasic extraction, the solid in the upper zone of the polymer-rich phase only showed several weak peaks (identified as quartz and mullite) with a strong broad peak (amorphous carbon), as shown in Figure 6.4. This result indicates that there is only a small amount of crystalline components in this solid fraction, which is consistent with the carbon content results (Figure 6.2). The diffractogram of the solids in the lower zone of the polymer-rich phase (Figure 6.5) is very similar to that of the parent fly ash (Figure 6.3). Quartz, mullite, and hematite are identified as the main crystalline components. The strong, broad peak of amorphous carbon is also apparent. However, for the solids in the salt-rich phase (Figure 6.6), the peak of amorphous carbon is relatively weak when compared to the results for the other beneficiated solid samples and the parent fly ash. Similar to the result of the parent sample, quartz, hematite, and mullite are the main crystalline phases in this solid fraction. But the relative intensity of these peaks (i.e., compared to amorphous carbon) is stronger than that of other samples.

FIGURE 6.3. XRD result of the parent sample (-400 mesh). Q = quartz, M = mullite, and H = hematite.

FIGURE 6.4. XRD result of the sample in the upper zone of the polymer-rich phase at pH 12 (solids content: 1 wt%). Q = quartz, M = mullite.

FIGURE 6.5. XRD result of the sample in the lower zone of the polymer-rich phase at pH 12 (solids content: 1 wt%). Q = quartz, M = mullite, and H = hematite.

FIGURE 6.6. XRD result of the sample in the salt-rich phase at pH 12 (solids content: 1 wt%). Q = quartz, M = mullite, and H = hematite.

Elemental Analysis. Table 6.4 lists the elemental composition of the parent fly ash, as well as the corresponding results for the beneficiated samples at pH 10, 11, and 12 (solids content: 2 wt%). The data show that in both the parent and beneficiated samples, Si, Al, and Fe are the major elements in the ash (in agreement with the XRD results). The concentrations of K, Ca, and Mg were in the range of 1 - 2 wt%, with Na, Ba, Sr, and Mn content less than 1 wt%. After the aqueous biphasic extraction, the fly ash in the salt-rich phase had more Si, with less Ca, Fe, and Mg at the same time; other elements remained almost the same as in the parent samples. In contrast, the Si content of the fraction in the upper zone of the polymer-rich phase was reduced, and the concentration of Ca increased. There was no apparent change for the other elements. The solids in the lower zone of the polymer-rich phase had the same composition as the original samples. From Table 6.4, it can be seen that there was no big difference in the elemental composition in all the fly ash fractions, including the parent samples. The reason for this trend is not very clear, and it needs further investigation, especially for the texture and morphology of the individual particles in each fraction. It is apparent, however, that the main separation effected is that involving carbon and mineral matter.

6.3.4 Preliminary Flowsheet

Based on the above results, a preliminary flowsheet is proposed for the aqueous biphasic extraction of high carbon fly ash (Figure 6.7). After contacting the fly ash and aqueous biphasic solutions, the mixture is allowed to phase separate. For the condition of 3-fraction partition (e.g., pH 11 and 2 wt% fly ash), a carbon product will be obtained from the upper zone of the polymer-rich phase, and an ash product can be produced from

TABLE 6.4. Elemental composition of ash in the parent fly ash and several beneficiated samples (solid content of 2 wt%).

Sample*	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO ₂	CaO	MgO	Na ₂ O	K ₂ O	BaO	SrO
Parent	52.2	31.3	1.34	9.17	0.0355	1.82	1.04	0.385	2.13	0.366	0.099
12-T	46.2	30.6	1.52	9.48	0.0372	2.35	0.682	2.01	1.89	0.283	0.128
11-T	48.0	31.6	1.63	10.8	0.0457	2.38	1.29	1.50	2.12	0.322	0.127
10-T	51.3	31.6	1.38	9.41	0.0377	1.68	1.04	0.823	2.05	0.369	0.106
12-M	51.0	31.7	1.40	9.28	0.0386	1.78	1.11	0.876	2.03	0.388	0.109
11-M	52.2	32.1	1.37	9.28	0.0372	1.71	1.05	0.691	2.08	0.414	0.107
12-B	56.9	30.9	1.08	7.93	0.0283	0.841	0.801	0.347	2.01	0.225	0.062
11-B	58.1	30.9	1.05	7.46	0.0259	0.726	0.733	0.277	2.02	0.219	0.056
10-B	56.4	30.5	1.01	6.63	0.0247	0.689	0.710	0.295	1.95	0.210	0.055

*: Parent: the parent fly ash;

the number means the pH value;

T: the upper zone in the polymer-rich phase,

M: the lower zone in the polymer-rich phase,

B: the salt-rich phase.

the salt-rich phase. The solid in the lower zone of the polymer-rich phase will be recycled to the mixing tank.

6.4 Conclusions

In order to remove the mineral matter successfully from coal, it is important to know the partitioning behavior of fine coal in aqueous biphasic systems. In this Chapter, the partitioning behavior of a fine coal sample (Illinois #6) in the polymer/salt/water biphasic system was studied. The results showed that the coal particles preferred the top polymer-rich phase because of the relatively high hydrophobicity of their surfaces. Additives had no major effects on the partitioning behavior.

The feasibility of processing high carbon fly ash with aqueous biphasic extraction was also studied. In order to improve the utility of fly ash, it is necessary to separate the carbon fraction from the fly ash to give a product with low carbon content. The availability of a carbon rich product is also of interest (e.g. for use as adsorbent). This report studied the partitioning behavior of fly ash in the PEG-2000/Na₂SO₄/H₂O system. The samples were also characterized for carbon content, elemental composition, and mineralogy. In the pH range from 2 to 5, the particles partitioned to give two aqueous fractions when the solid content was 1 wt%. Above pH 5, the particles in the polymer-rich phase divided into two zones. The weight percent carbon content in the upper zone was higher than that in the parent sample, and the lower zone had almost the same ash content as the original sample. The particles in the salt-rich phase were mainly composed

of ash. XRD results showed that the main crystal components in the ash included quartz, hematite, and mullite. The ICP results showed that Si, Al, and Fe were the major elements in the fly ash, with minor elements of Na, K, Ca, Mg, and Ba. The composition of the ash in the lower zone of the polymer-rich phase remained almost the same as that in the parent fly ash. Comparing Figure 2 with the yield results in Figure 1, it can be seen that the largest amount of product (~60% yield) with the highest carbon content (~80 wt% C) was obtained in the range pH 6 - 9. Based on the experimental results obtained, a flowsheet is proposed for the beneficiation of high-carbon fly ash with the aqueous biphasic extraction process.

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Chapter 7

RESEARCH SUMMARY

Ever-stringent environmental constraints dictate that future coal cleaning technologies should be compatible with micron-size particles. This research program seeks to develop an advanced coal cleaning technology suited to micron-size particles, i.e., aqueous biphasic extraction. Aqueous biphasic extraction relies on the ability to form a two-phase aqueous system, starting with an aqueous solution consisting of a water-soluble organic polymer and another component, such as another polymer, a nonionic surfactant, or an inorganic salt. The principle behind the partition of solid particles in aqueous biphasic systems is the physicochemical interaction between the solid surface and the surrounding liquid solution. Therefore, many factors, such as hydrophilic/hydrophobic properties, polymer-solid specific interaction, adsorption of surfactant on the solid surface, and electrostatic interaction, may influence the partition of solids. In order to remove sulfur and mineral matter from fine coal with aqueous biphasic extraction, it is necessary to know the partitioning behavior of coal, as well as the inorganic mineral components. Therefore, in this research emphasis was placed on the partitioning behavior of model fine particles in aqueous biphasic systems.

The partitioning behavior of pyrite, an important mineral component in coal, was investigated in the polymer/salt/water systems. The result clearly indicated that pyrite

partition in these systems depends significantly on the surface chemistry of the solid. Since pyrite surface is easily oxidized in aqueous solution, many factors, such as conditioning time and pH, can modify the surface chemistry, leading to changes in solid partition. In polyethylene glycol (PEG)/Na₂CO₃/H₂O systems, pyrite initially stayed at the interface of the aqueous biphasic systems. With increase in the conditioning time, however, the solid particles transferred into the bottom salt-rich phase. Because the oxidation of pyrite surface is pH-dependent, the partitioning behavior of pyrite changed with pH. At high pH, pyrite transferred to the bottom hydrophilic salt-rich phase, while it moved to the top hydrophobic polymer-rich phase at low pH. This behavior is attributable to the different surface oxidation products associated with the pH variations: formation of FeOOH in alkaline solution, and a hydrophobic iron-deficient product (Fe_{1-x}S₂) in acidic environment.

Because aqueous biphasic extraction is dependent upon the surface property of solids, depressants such as those used in flotation and oil agglomeration can also affect the partitioning behavior of pyrite. Addition of H₂O₂ removed the need for conditioning, although it did not change the partitioning behavior of pyrite. With the presence of FeCl₃, pyrite stayed in the polymer-rich phase.

Surfactant addition also offers an important way to change the surface chemistry of a solid. The results showed that only certain flotation collectors could significantly affect the behavior of pyrite in biphasic systems. Xanthate was found to be effective in modifying the partition behavior in neutral and alkaline solutions; the sulfide particles preferred the polymer-rich phase instead of the salt-rich phase or the interface. This behavior is attributable to the chemisorption of xanthate on the sulfide surface. In

contrast, in the case where surfactant adsorption is predominantly electrostatic (physical), i.e., sodium dodecylsulfate (SDS)/pyrite, oleate/pyrite, surfactant addition had no effect on partitioning behavior.

With the PEG/Na₂SO₄/H₂O system, the partitioning behavior of oxide particles was also studied. The results demonstrated that, in the absence of polymer-solid interaction, the surface hydrophilic/hydrophobic properties determine the partitioning behavior. In general, hydrophilic particles, e.g., alumina, hematite, and titania, preferred the bottom salt-rich phase. However, silica particles stayed in the top phase, a result of PEG adsorption on silica particles. The implication is that, if the polymer can adsorb on the solid surface, then the polymer-solid interaction will dominate the distribution of the solid particles.

The effects of surfactants on hematite partition were investigated. Similar to the case of pyrite, it was found that only certain flotation collectors (e.g., oleate) significantly affected the behavior of the particles. At about pH 6, the presence of oleate caused the transfer of hematite particles into the polymer-rich phase. Combined with the results of pyrite (i.e., pyrite/xanthate), it is apparent that surfactants which adsorb chemically on the solid surfaces have a significant influence on solid distribution. In contrast, in the case where surfactant adsorption is predominantly electrostatic (physical), i.e., SDS/hematite, and xanthate/ hematite, surfactant addition has no effect on partitioning behavior.

Aside from the polymer/salt aqueous biphasic systems, the partitioning behavior of hematite was also determined in polymer/polymer (PEG/dextran) and polymer/nonionic surfactant (Triton X-100 (TX100)/dextran) systems. In both these systems, hematite stayed in the bottom dextran-rich phase. In these systems, the bottom phase is more

hydrophilic than the top layer; hence, the hydrophilic oxide particles preferred the dextran-rich phase. Also, the strong favorable interaction between dextran and ferric oxide favored the dispersion of the solids in the polysaccharide-rich phase.

In the TX100/dextran system, addition of SDS or oleate had no effect on the solid partition; on the other hand, dodecyl trimethyl ammonium bromide (DTAB) transferred the particles to the top phase or interface at high pH values. In the PEG/dextran system, hematite remained in the bottom phase in the presence of either SDS or DTAB. The effects of SDS or oleate on the partition behavior in both systems are attributable to the fact that they were not able to replace the strongly adsorbed polysaccharide layer on the particle surface. The results obtained with DTAB were due to electrostatic interaction between the cationic surfactant and the negatively charged solid surface. The difference in the solid partition in these two systems was the result of the different location of DTAB in these systems. In the Dex/TX100 system, DTAB preferred the top surfactant-rich phase, while it concentrated in the bottom phase in the PEG/dextran system.

The partitioning behavior of silica was also investigated in the TX100/dextran and the PEG/dextran systems. The results showed that in these systems, the interaction between the phase components and the solid surface played an important role in determining the solid distribution. In the Triton X-100/dextran system, silica particles stayed in the top surfactant-rich phase at either very low pH (<3.5) or very high pH (>11.7). From pH 9 to 11.3, the particles preferred the bottom dextran-rich phase. The oxide particles concentrated at the interface in the pH range of 4 and 8. The PEG/dextran system showed a similar trend for silica particles. The solids migrated to the top surfactant-rich phase at either low pH (< 7) or very high pH (pH 12). From pH 9 to 11, the particles transferred

the bottom dextran-rich phase, and concentrated at the interface at pH 8. These trends were attributed to the competition between dextran/SiO₂ and TX100/SiO₂ or dextran/SiO₂ and PEG/SiO₂ interactions.

An interesting result was the finding that electrostatic forces generated through the addition of ionic surfactants can cause significant changes in the partition of silica particles. In the TX100/dextran system, ionic surfactants concentrated in the top surfactant-rich phase and formed mixed micelles with the nonionic surfactant. Therefore, electrostatic attractive or repulsive interactions developed between the mixed micelles in the top phase and the charged solid surface. Addition of an anionic surfactant, SDS, moved the particles from the top phase to the interface or bottom phase. On the other hand, DTAB, a cationic surfactant, attracted the solids to the top phase in the pH range from 4 to 11, where in absence of DTAB the solids either stayed at the interface or in the bottom phase. In the PEG/dextran system, anionic surfactants (e.g. SDS) concentrated in the top PEG-rich phase, and cationic surfactants (e.g. DTAB) preferred the bottom dextran-rich phase. In the presence of SDS, SiO₂ stayed the bottom dextran-rich phase above its pHPZC. With addition of DTAB, the silicon dioxide particles migrated to the top phase at low pH; then moved to the interface, and even to the bottom phase with increase in pH. This phenomenon was attributed to the competing electrostatic attraction between DTAB and SiO₂ and adsorption of PEG on the solid surface. It was also interesting to notice that even though SDS and DTAB had opposite charges, they could have the same effect on silica partition in the PEG/dextran system because the two surfactants preferred the conjugate phases. In contrast, in the TX100/dextran system, these surfactants had the opposite effects since they both concentrated in the top nonionic surfactant-rich phase.

After investigating the partitioning behavior of inorganic particles, this research also studied the partition of a fine coal sample in the polymer/salt/water systems. It was found that the coal particles preferred the top polymer-rich phase because of the naturally hydrophobic surface of this carbonaceous material. Additives (such as H_2O_2 and FeCl_3) and pH had no significant effects on the partitioning behavior.

Finally the feasibility of processing fly ash of high carbon content by aqueous biphasic extraction was investigated. In order to improve the utility of fly ash, it is necessary to separate the carbon fraction from the fly ash to give a product with low carbon content and a carbon-rich product. The partitioning behavior of fly ash was investigated in the $\text{PEG}/\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ system; the beneficiated samples were characterized for carbon content, elemental composition, and mineralogy. In the pH range from 2 to 5, the particles separated into two aqueous fraction when the solid content was 1 wt%. Above pH 5, the particles in the polymer-rich phase divided into two zones. The weight percent carbon content in the upper zone was higher than that in the parent sample, and the lower zone had almost the same ash content as the original sample. The particles in the salt-rich phase were mainly composed of ash. XRD results showed that the main crystal components in the ash included quartz, hematite, and mullite. The ICP results showed that Si, Al, and Fe were the major elements in the fly ash. The composition of the ash in the lower zone of the polymer-rich phase remained almost the same as that in the parent fly ash. It was found that the largest amount of product (~60% yield) with the highest carbon content (~80 wt% C) was obtained in the pH range of 6 - 9. Based on the experimental results obtained, a flowsheet was proposed for the beneficiation of high-carbon fly ash with the aqueous biphasic extraction process.

In the present work it was found that the partitioning behavior of fine particles in aqueous biphasic systems was mainly dependent on interfacial interaction between the solids and the surrounding liquids. Many factors, such as surface hydrophilic/hydrophobic properties, pH conditions, the presence of collectors and surfactants, the specific interaction between polymer and solid, can significantly affect solid partition. Hence, it is worthwhile to develop a more thorough understanding of the physico-chemical factors that control solids partition in aqueous biphasic systems, especially those of the type polymer/polymer/water and polymer/surfactant/water. In order to better control fine coal processing, it is also necessary to investigate partitioning behavior of fine coal samples with different size ranges, especially less than 10 μm . Future research should examine particle mixtures (i.e., coal/pyrite, coal/silica, etc.). Also useful will be scale-up experiments that will provide a critical bridge between laboratory work and eventual industrial practice.

LIST OF PUBLICATIONS

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4. X. Zeng and K. Osseo-Asare, **Liquid-Liquid Extraction in Aqueous Biphasic Systems: Partitioning Behavior of Silica and Hematite in the Dextran/Triton X-100/Water System**, in *Proceedings, International Solvent Extraction Conference (ISEC 2002)*, Cape Town, South Africa, in press.