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PARTITIONING BEHAVIOR OF PORPHYRIN DYES IN AQUEOUS BIPHASIC SYSTEMS

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ABSTRACT

The partition of protoporphyrin IX and the phthallocyanine dye, propyl astra blue iodide, in aqueous biphasic systems (ABS) and onto aqueous biphasic extraction chromatographic (ABEC™) resins has been examined. Solubility of protoporphyrin IX was found to be too low for recovery by ABS other than by use of thermoseparating surfactants. Partitioning behavior of the phthallocyanine dye was found to depend on the salting-out strength of the salt. As a result of the partition of this dye to the interface of ABS, the adoption of ABEC for recovery of this dye is more favorable.

INTRODUCTION

Solvent extraction is an established technology for the recovery of metal ions and small organic molecules from aqueous solution (1, 2). The application of different diluents and extractants and the ability to operate in aqueous-phase conditions enable application of the technology to the extraction of a wide variety of solutes. Extraction kinetics are rapid, and the unit operation is readily scalable and may be engineered for high selectivity and efficiency through the use of multistage contactors without the requirement for extreme distribution ratios. However, many solvent extraction schemes employ toxic and flammable organic diluents, which add significantly to design costs and which are increasingly regulated because of their environmental impact.

Despite their 40-year history (3), little attention has been paid by the chemical engineering community to a whole class of solvent extraction systems whose nature is wholly aqueous. Aqueous biphasic systems (ABS) retain all the advantages of solvent extraction and additionally are nontoxic and nonflammable and have components that are available as inexpensive bulk commodities. The physical properties of ABS remain close to those of many traditional liquid/liquid extraction systems, and a common plant may be adapted for their use (4). ABS have been shown to be effective for the extraction of biomolecules and particles (5, 6) and, more recently, for the extraction of metal ions and small organic molecules (7-9).

ABS are formed by the phase separation of immiscible polymer pairs or when solutions of PEG are salted out by specific salt solutions (see Table 1). A typical ABS phase diagram is shown in Figure 1. ABEC^{TM} is a solid-phase chromatographic resin bearing covalently linked methyl-PEG-5000 chains which has been demonstrated to effect separations similar to those of ABS (10).

Porphyrins form the chemical basis of electron-transport and light-harvesting pigments in biochemical systems (12) and are also a minor component of fossil fuels (13). The structure of a typical porphyrin is shown in Figure 2. Potential applications for porphyrins exist in the fabrication of photonic and electronic devices (14). The related pthallocyanine dyes are important industrial products because of their chemical stability, being used principally in blue and green printing inks and paints (15). Since the weakly aromatic tetrapyrrole ring structure may coordinate with a guest cation, there are potential applications in metal ion recovery. Application of ABS technology may benefit many of these areas through efficient extractive recovery of these pigments.

EXPERIMENTAL

Phase systems were prepared from reagent grades of PEG and salts either as w/w % or molar solutions. Protoporphyrin IX and propyl astra blue iodide (PABI) were purchased from Aldrich. Pigments were added to phase systems as solutions of the dye in water (PABI, 5 mg/mL). Pigment concentrations were determined by

TABLE 1
TYPICAL AQUEOUS BIPHASIC SYSTEMS[a]

POLYMER		**POLYMER**
Polyethylene glycol		Polyvinyl alcohol
		Polyvinyl pyrrolidone
		Dextran (polyglucose)
		Ficoll (polysucrose)
		Hyroxypropyl starch
POLYMER	**SALTS**	
Polyethylene glycol	NaOH	Sodium formate
	KSCN	Sodium succinate
	$(NH_4)_2SO_4$	Sodium tartrate
	$NH_2CO_2NH_4$	Sodium citrate
	Na_2HPO_4	K_3PO_4
	K_2CO_3	

[a] From reference 11.

spectrophotometry (λmax of PABI = 603 nm, protoporphyrin IX in H_2O = 471 nm). Distribution ratios (D) were calculated as in eq. 1 using suitable dilutions of samples withdrawn from the separated phases of the ABS.

$$D = \frac{[c]\,\text{pigment in the upper PEG - rich phase}}{[c]\,\text{pigment in the lower salt - rich phase}} \quad (1)$$

Solid-phase distribution studies were also performed on ABEC^{TM} resin (Eichrom Industries, Darien, IL) by suspension of suitable quantities of resin in solutions of varied salt concentration. The amount bound to the solid phase was determined from the equilibrium concentration of the pigment in the supernatant and expressed relative to the wet weight of the ABEC resin. Detailed methods utilizing ABS and ABEC may be found in reference 8.

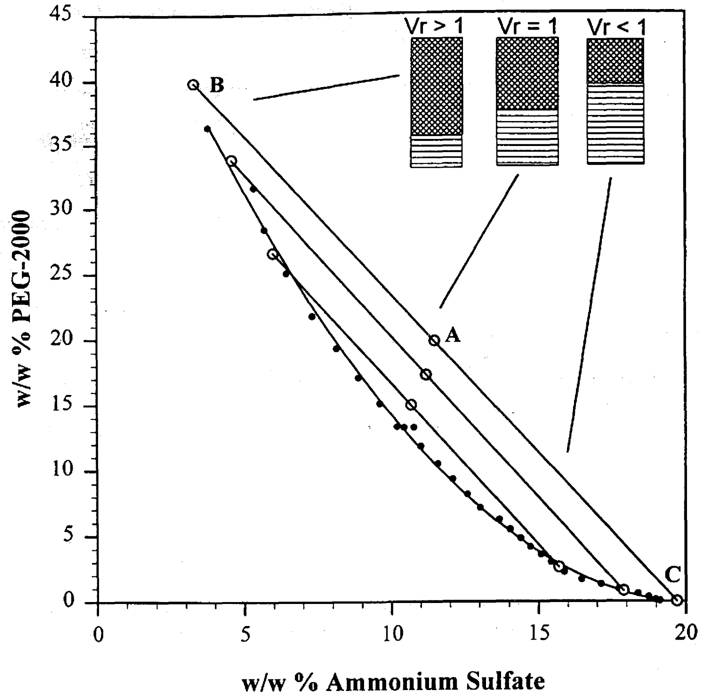

FIGURE 1. Phase diagram of a PEG-2000/$(NH_4)_2SO_4$ ABS showing the binodal curve and some representative tie lines (BAC) and illustrating the way in which the volume ratio (Vr) changes with overall composition on a single tie line.

RESULTS

Protoporphyrin IX was found to be poorly soluble in ABS. Its water solubility is also very low. However, it was found to be soluble (>0.5 mg/mL) in solutions of 1% Triton X-100 (*t*-octylphenoxypolyethyleneglycol). Since Triton is a phase-forming polymer, the phase of which separates either by increase in temperature or by increase in salt concentration (16), there is potential for the application of Triton ABS to porphyrin extractions.

Propyl astra blue iodide (PABI) is a cationic phthallocyanine with a porphyrin-like structure, shown in Figure 2. Preliminary studies showed that PABI quantitatively

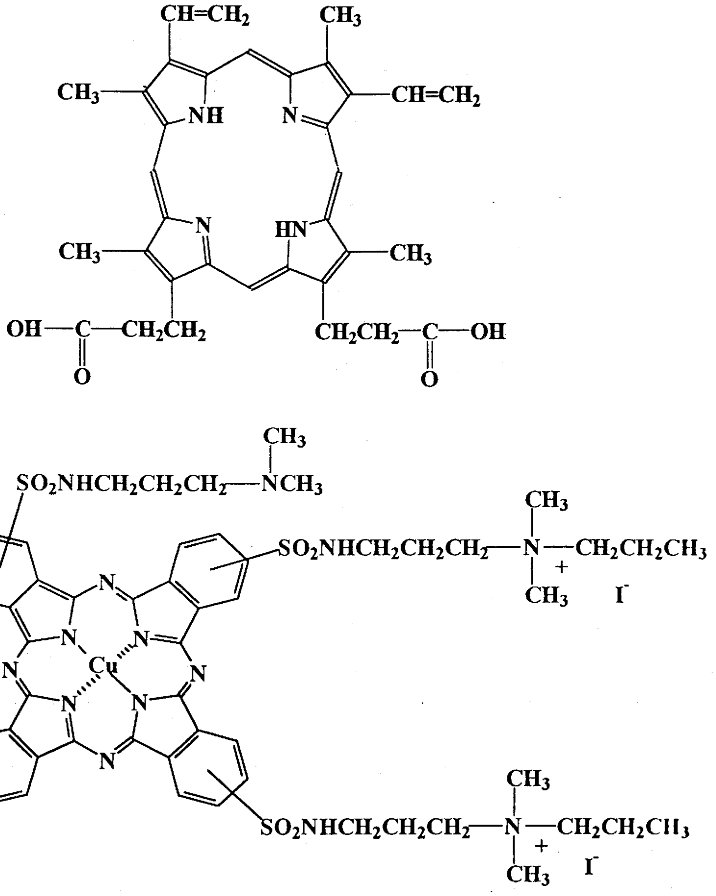

FIGURE 2. Molecular structures of protoporphyrin IX (porphine -2,18 dipropionic acid, Top) and propyl astra blue iodide (PABI, Bottom).

partitioned to the lower, salt-rich phase of a PEG-2000/$(NH_4)_2SO_4$ ABS. Other dyes examined (17), containing aryl hydrophobic structures, partition strongly to the PEG-rich phase, suggesting that the charge state of PABI might be responsible for this behavior. However, in a 19% w/w PEG-2000/11% $(NH_4)_2SO_4$ system buffered to pH values of 2.5, 5.6, and 9.25, no substantial change in PABI partitioning was observed.

At elevated pH (pH >13) in a PEG-2000/K_3PO_4 ABS, PABI was observed to partition to the upper, PEG-rich phase. Partition of PABI is shown in Table 2 in relation

TABLE 2
PARTITION OF PABI IN PEG-2000/K_3PO_4 WITH INCREASING SALT CONCENTRATION

[K_3PO_4], M	Phase	Phase vol., mL	A_{603}, nm	D	Interfacial dye from 550 μg, μg
0.75	PEG	5.5	0.981	1.1	368
	Salt	2.5	0.876		
1.0	PEG	4.4	2.212	92.2	353
	Salt	3.6	0.024		
1.5	PEG	3.6	4.026	1342.3	384
	Salt	4.4	0.003		
2.0	PEG	3.1	4.416	200.7	269
	Salt	4.9	0.022		
2.5	PEG	3.0	1.920	80.1	465
	Salt	5.0	0.024		
3.0	PEG	2.8	3.084	171.3	448
	Salt	5.2	0.018		

to the concentration (M) of phosphate stock solution in contact with a 40% w/w PEG-2000 solution. Under these circumstances a proportion of the solute in the system is recovered at the interface on phase separation. No material is found at the interface when PABI partitions to the lower phase. At high pH, an increase in salt concentration causes an increase in partition to the PEG-rich phase.

By combination of monobasic and tribasic phosphate salts, a range of ABS differing in pH (and also in ionic strength) can be constructed. Under these conditions (pH 7.8 – 13.6), PABI increasingly partitions to the PEG-rich phase with increasing pH as shown in Table 3. This contrasts with the finding that PABI preferred the salt-rich phase in the PEG 2000/$(NH_4)_2SO_4$ ABS at pH 9.25, suggesting that increase in salting-out strength is the determining factor controlling PABI partition, rather than pH.

Partition of PABI in PEG-2000/phosphate systems consisting of different w/w % of a 7:18 mixture of monobasic and dibasic potassium phosphate (pH 7.5) is shown in

TABLE 3
PARTITION OF PABI IN PEG-2000 ABS COMPOSED OF DIFFERENT RATIOS OF K_3PO_4:KH_2PO_4 SALTS

K_3PO_4, w %	KH_2PO_4, w %	Phase	Vol., mL	A_{603}, nm	pH	D	Interfacial dye from 550 µg, µg
42.5 (2 M)	0	PEG	2.5	2.150	13.57	358	351
		Salt	5.5	0.006			
37.2	5.3	PEG	2.8	2.591	12.36	216	280
		Salt	5.3	0.012			
31.9	10.6	PEG	3.2	2.041	11.53	120	306
		Salt	4.8	0.017			
26.6	15.9	PEG	2.7	1.458	9.77	27	395
		Salt	5.0	0.053			
21.2	21.2	PEG	2.8	1.491	7.78	71	392
		Salt	5.2	0.021			

Figure 3. The salt concentration at which the plot of ln D crosses the ln D = 0 boundary is the minimum concentration required to bring about a change in phase preference.

Partition of PABI to ABEC resins from phosphate solutions was also studied. Increase in salt concentration leads to increased uptake as shown in Figure 4. The greater salting-out strength of the dibasic over the monobasic salt leads to higher capacity at lower salt concentrations. Comparison with Figure 3 shows that the behavior of ABEC parallels that of the ABS. However, in the liquid/liquid system, there appears to be a threshold salt concentration below which there is no significant partition of PABI to the PEG-phase. No such threshold is apparent for ABEC. It has previously been reported (18) that the distribution of solutes to ABEC is higher than for ABS. In addition, it is often possible to bring about adsorption to ABEC at salt concentrations below which no

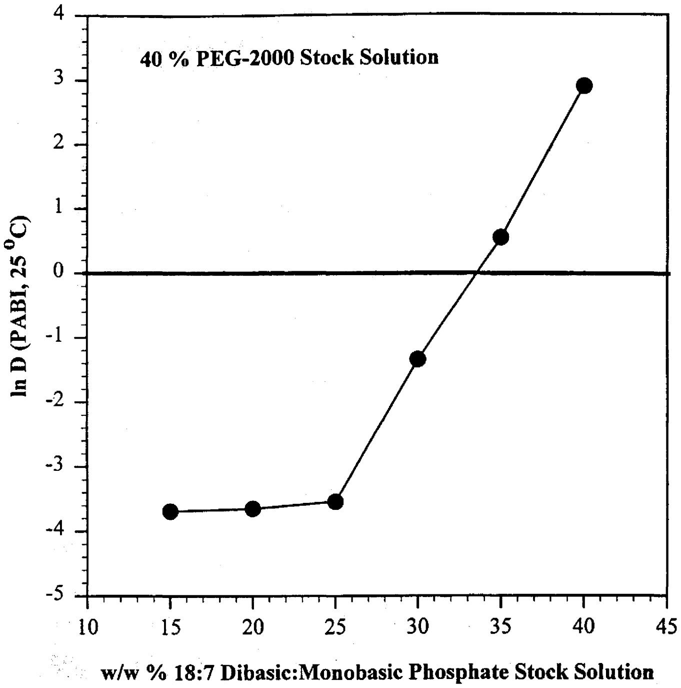

FIGURE 3. Partition coefficient of PABI in ABS composed of 40% w/w PEG-2000 in contact with the indicated concentrations of an 18:7 mixture of dibasic and monobasic potassium phosphate.

significant distribution would take place to PEG-rich phases, or even outside the biphasic region altogether (vide infra). This may reflect the fact that due to the covalent attachment of the PEG ligands to the solid phase, at high density, the effective salt concentration experienced by the solutes at the resin surface is higher than in an apparently similar ABS.

CONCLUSIONS

ABS and ABEC resins may be used for the recovery of some pthallocyanine dyes from aqueous solution. The partitioning behavior of propyl astra blue iodide is governed

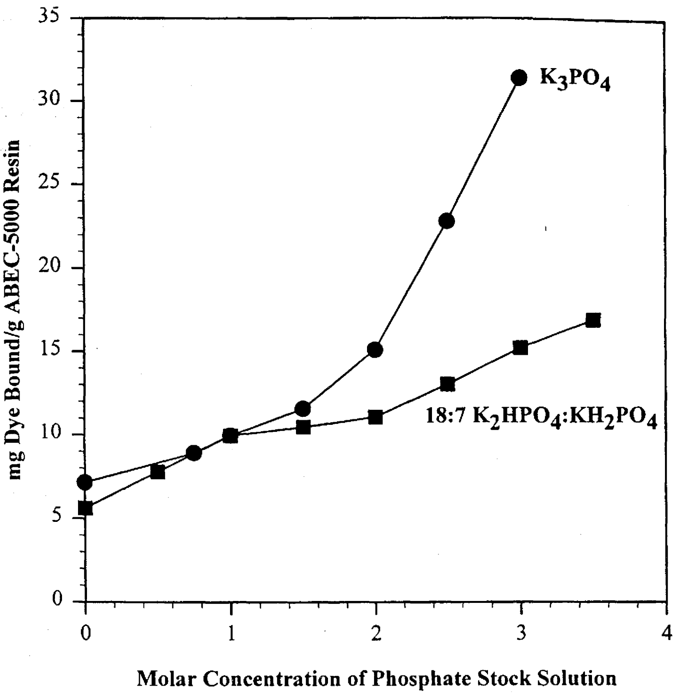

FIGURE 4. Binding of PABI to ABEC resin in the presence of the indicated concentration of K_3PO_4 (●) or an 18:7 mixture of dibasic and monobasic potassium phosphate salts (■).

by the salting-out strength of the salt, which is unusual among the dyes that have been examined by ABS partition (17). Significant precipitation of the dye at the interface compromises application of ABS to its recovery. This can be overcome by application of ABEC processes where the lower salt concentration required to bring about binding can be used advantageously.

The solubility of porphyrins in aqueous solution, as exemplified by protoporphyrin IX, is too low for the direct application of ABS or ABEC processes. However, we have determined that porphyrins may be extracted utilizing Triton-based thermoseparating ABS. Developments based on the use of surfactant-containing ABS and solid phases are currently being pursued.

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