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Naphthol- and resorcinol-based azo dyes as metal ion complexants in aqueous biphasic systems

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Abstract

Aqueous biphasic systems (ABS) are comprised of both a polymer-rich phase (e.g., polyethylene glycol, PEG) and a salt-rich phase [e.g., $(NH_4)_2SO_4$] such that both phases are 80% water on a molar basis. ABS have demonstrated applications as environmentally-friendly methods to separate relatively hydrophobic anionic species, such as pertechnetate and mercury halide anionic complexes, from high ionic strength solutions although partitioning of hydrated metal ions, such as Fe^{3+} and actinides, to the PEG-rich phase is negligible without the addition of a metal ion complexant to the system. Four naphthol- or resorcinol-based dyes; 1-(2-pyridylazo)-2-naphthol (PAN), 1-(thiazolylazo)-2-naphthol (TAN), 4-(2-pyridylazo)-resorcinol (PAR) and 4-(2-thiazolylazo)-resorcinol (TAR), each incorporating a naphthol or resorcinol with an *ortho* azo functional group, have been studied as metal ion extractants in ABS as a function of pH. In the PEG-2000/$(NH_4)_2SO_4$ ABS, the distribution ratios of Fe^{3+}, Co^{2+} and Ni^{2+} were enhanced by several orders of magnitude at high pH in contrast to the behavior of Cs^+, Cd^{2+} and Eu^{3+} whose partitioning behavior was largely unaffected by the presence of these extractants at any pH. The three extracted metal ions, Fe^{3+}, Co^{2+} and Ni^{2+}, could be stripped by contact with a fresh salt phase at low pH. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Aqueous two-phase systems; Azo dyes; Naphthol; Resorcinol

1. Introduction

In light of increasingly stringent environmental regulations and efforts to eliminate known sources of pollution, several initiatives from industry and academia are underway to develop alternative industrial technologies that are intrinsically less polluting, yet economically viable and user-friendly [1–3]. A particular focus of these efforts is the replacement of volatile organic compounds (VOCs), the class of organic solvents commonly used in liquid–liquid extraction. For example, a major goal expressed in the National Mining Association's report *The Future Begins with Mining – A Vision of the Mining Industry of the Future* [2] is ‘‘safe and efficient extraction and processing’’, a goal for which new, more environmentally-sound technologies are ideally suited.

Aqueous biphasic systems (ABS) form upon the admixture of certain water-soluble polymers or polymers and salts above a critical concentration, and thus represent liquid–liquid extraction systems whose nature is entirely aqueous. These liquid–liquid systems retain all the practical advantages of traditional solvent extraction, and also possess a number of unique advantages, due, in large, to their

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wholly aqueous nature. For example, ABS based on polyethylene glycol (PEG) are virtually non-toxic and the components are inexpensive bulk commodities.

Although ABS have traditionally found application in bioseparations as a gentle, nondenaturing medium for the separation of biomass or proteins [4–8], we have demonstrated that ABS are also suitable for the extraction and separation of metal ion species [9–13] and for the liquid–liquid separations of organic molecules [14,15]. These systems warrant consideration for the development of environmentally-benign wet extraction processes, a role which is well outside, and rather different from, their current application in biotechnological separations. Since ABS represent alternatives to traditional solvent extraction techniques employing VOCs, the range for potential applications of these novel systems in separations science is broad.

Although metals in the form of hydrophobic anions (e.g., TcO_4^-) partition to the PEG-rich phase, metal ion extractants are necessary to increase the affinity of hard, hydrated metal cations for this phase of any ABS. A variety of metal ion extractants are available for these systems [16–20], although for their optimal performance in ABS, they must be water soluble and quantitatively partition to the PEG-rich phase regardless of pH. Previous work [14,21] indicates that molecules with an aryl ring are likely to have a high affinity for the PEG-rich phase. This structural feature is characteristic of many dyes and pigments (e.g., amaranth, carminic acid, indigo carmine and tartrazine) and the partitioning of those molecules in ABS bears that out [14].

The azo functionality coupled with an *ortho*-hydroxyl substituted aromatic group can form extractable complexes with transition metals [22–27]. Extractants that fit into this category include 1-(2-pyridylazo)-2-naphthol (PAN), 1-(2-thiazolylazo)-2-naphthol (TAN), and their resorcinol analogs, PAR and TAR (Fig. 1). The attempted utilization of these molecules as extractants in ABS is based on their similar use as extractants in traditional organic solvents for the extraction of various metals [22–25,28]. PAN forms complexes with over 45 metals, including Cd^{2+}, Zn^{2+}, Mn^{2+}, Bi^{3+} and Ti^{4+} [29], although the pH of the system has a profound effect on the chelation of these molecules with the metal ions. Extraction of lanthanide metal ions with PAN exhibits a pH dependence that would enable separation of the heavier Ln from the lighter Ln through careful pH control from 7.46 to 8.10 [25]. Other examples show that as the pH of the aqueous phase becomes more basic, the extraction to the organic phase increases and can be as high as 80–100% for certain metal ions [22,23,29,30].

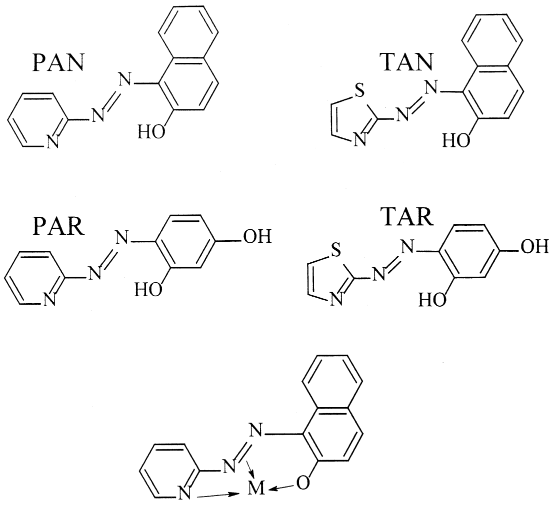

Fig. 1. Structures of PAN, TAN, PAR and TAR and proposed metal ion chelation for an ionized PAN molecule [31].

In this report we discuss the investigation of the partitioning of PAN, TAN, PAR and TAR in ABS formed by mixing equal aliquots of 40% PEG-2000 and 3.5 M $(NH_4)_2SO_4$. In addition, we report the use of these molecules as metal ion extractants as a function of pH.

2. Experimental

All salts, PEG (average molecular mass 2000), and extractants used in these experiments were of reagent grade, obtained from Aldrich (Milwaukee, WI, USA), and used without further purification. The radiotracers $^{59}FeC1_3$, $^{63}NiC1_2$, $^{109}CdCl_2$, $^{137}CsCl$ and $^{152}EuCl_3$ were obtained from Amersham (Arlington Heights, IL, USA). $^{60}CoCl_2$ was obtained from DuPont–New England Nuclear Research Products (Boston, MA, USA).

Liquid scintillation analyses were performed for

^{63}Ni using Ultima Gold Scintillation cocktail (Packard Instrument, Downers Grove, IL, USA) and a Packard Tri-Carb 1900 TR Liquid Scintillation Analyzer (Packard Instrument Company). Gamma ray emission analyses were used for the remaining isotopes and carried out on a Packard Cobra II Auto-Gamma Spectrometer (Packard Instrument Company).

All aqueous solutions were prepared in deionized water that was purified with a Barnsted deionization system (Dubuque, IA, USA) and polished to 18.3 MΩ cm. Each stock solution of PAN, TAN, PAR or TAR was prepared by weighing out a known amount of the selected material and transferring it to a volumetric flask followed by dilution to the specified volume with the 40% (w/w) PEG-2000 stock solution.

A series 3.5 *M* $(NH_4)_2SO_4$ stock solutions was prepared by weighing out a known amount of salt and adding it to a volumetric flask followed by dilution to the appropriate volume with DI water. The pH of the individual $(NH_4)_2SO_4$ solutions was adjusted to 1, 2 or 5 by adding a small volume of 1 *M* H_2SO_4 or adjusted to pH 8.2 with 1.5 *M* NaOH. The pH of the solutions was measured using a Corning pH meter 220 (Corning Incorporated Science Products Division, Corning, NY, USA).

To determine the distribution ratios of the metal ions, 1 ml of a 40% (w/w) PEG-2000 stock solution (with or without extractant) was contacted with 1 ml of 3.5 *M* $(NH_4)_2SO_4$ stock solution (at a specific pH) followed by vortexing (2 min) and centrifuging (2000 *g*, 2 min) to equilibrate the phases. The temperature of the systems was maintained at 25°C by equilibration in a Neslab RTE-110 water bath (Neslab Instruments, Newington, NH, USA). Each ABS was then spiked with 0.005 μCi (~5 μl) of the metal ion tracer in water, vortex-mixed (2 min), centrifuged (2000 *g*, 2 min), mixed again, and, finally, centrifuged to disengage the phases. The phases were separated and placed into shell vials from which 100-μl aliquots were removed for radiometric analysis. Since the volumes of the phases analyzed were equal, the distribution ratios (*D*) were calculated as in Eq. (1):

$$D = \frac{\text{Activity in the PEG-rich (upper) phase}}{\text{Activity in the salt-rich (lower) phase}} \tag{1}$$

Each experiment was performed in duplicate and the results agreed to within 5%.

In all experiments, the distribution ratios are reported at pH values that correspond to the pH of the salt-rich phase after contact with the PEG-rich phase. The pH of the aqueous phase was obtained by carrying out an experiment as detailed above, but without the addition of the radiotracers. After centrifuging, an aliquot of the salt-rich phase was removed, placed in shell vial, and the final pH was measured.

To quantitate the partitioning of PAN, TAN, PAR and TAR between the PEG-rich and salt-rich phases (Fig. 3), a series of solutions (0.001–0.1 m*M*) of each ligand in 40% (w/w) PEG-2000 was prepared from which 2-ml aliquots were taken and contacted with 2-ml aliquots of 3.5 *M* $(NH_4)_2SO_4$ at each pH. The systems were vortex-mixed (2 min), centrifuged (2000 *g*, 2 min), mixed again and, finally, centrifuged to disengage the phases. A 1-ml aliquot of each phase was added to a 1-ml quartz cuvette for UV–Vis analysis. The absorbance values for each ligand were measured with a Cary 3C UV–visible spectrophotometer (Varian Optical Spectroscopy, Mulgrave, Australia) at 470 nm (PAN), 485 nm (TAN), 480 nm (PAR), or 475 nm (TAR). Absorption due to the background was automatically subtracted. Absorbance values for the solutions conformed to Beer's law over the range of 0.001–0.1 m*M* for each ligand. The concentrations of the ligands in each phase were calculated using the standard curve equations obtained for each. The distribution ratios for each ligand were determined as their concentrations from Eq. (2):

$$D = \frac{\text{Concentration in the PEG-rich (upper) phase}}{\text{Concentration in the salt-rich (lower) phase}} \tag{2}$$

3. Results and discussion

In polymer–salt ABS, the partitioning of solutes between the two phases has been correlated to the Gibbs free energy of hydration of the species [32,33]. Chaotropic moieties with small negative ΔG_{hyd} values prefer the PEG-rich phase, while cosmotropic, water-structuring ions with large negative ΔG_{hyd} are highly hydrated and remain in the salt-rich phase. The metal ions in this study are cosmotropes with relatively large, negative values for ΔG_{hyd}, and all prefer the salt-rich phase (Table 1).

To increase the PEG-rich phase affinity for these metal ions, it is necessary to change the hydration sphere around the ion to increase their hydrophobicity (as in traditional solvent extraction). What is unique to ABS extraction, however, is that the extractants must still be water soluble to some degree, since even the PEG-rich phase is over 80% water on a molar basis. This added constraint suggests one must find extractants that not only have high complexation constants for the metal ions of interest, but also prefer one type of aqueous phase over another.

Adding one or more sulfonic acid groups to water soluble polyaromatic chelating dyes results in quantitative partitioning of those molecules to the PEG-rich phase [14] and suggests their use as metal ion extractants. Dyes such as the mono-sulfonated acid alizarin violet can complex metal ions and increase their partitioning to the PEG-rich phase [19]. Similar results were observed for the partitioning of calixarenes in ABS; the addition of four sulfonic acid groups for each calix molecule increases both the water solubility and the affinity of calix-4 and calix-6 for the PEG-rich phase [20]. When selecting a sulfonated extractant, however, attention has to be paid to the degree of sulfonation which can negatively affect the retention of the molecules in the PEG-rich phase [19]. Thus, finding a class of extractants that has a clear affinity for the PEG-rich phase can be difficult since many molecules that are water soluble may be soluble in both phases.

Table 1
Distribution ratios for metal ions in the PEG-2000/$(NH_4)_2SO_4$ ABS as a function of salt-rich phase pH

Cation	ΔG_{hyd} (kJ/mol)[a]	pH 1.2	pH 2.5	pH 5.6	pH 8
Cs^+	−245	0.054	0.023	0.026	0.041
Co^{2+}	−1880	0.063	0.044	0.030	0.034
Ni^{2+}	−2005	0.025	0.034	0.031	0.039
Cd^{2+}	−1575	0.026	0.030	0.019	0.022
Eu^{3+}	−3550	0.074	0.066	0.078	0.084
Fe^{3+}	−4580	0.064	0.059	0.053	0.079

[a] Values of ΔG_{hyd} (calc.) from Ref. [33].

The four extractants studied here (PAN, TAN, PAR and TAR) all appear to have an affinity for the PEG-rich phase in PEG-2000/$(NH_4)_2SO_4$ ABS in the pH range 1–8. Fig. 2 illustrates distribution ratios ranging from 40 (PAR, pH 1) to 67 (PAN, pH 8). The distribution ratios increase in the order PAR~TAR<TAN<PAN. While there is little affect of pH on the partitioning of PAR and TAR, PAN and TAN exhibit an increase in *D* as pH is increased. (PAN and TAN are more hydrophobic and less water soluble than PAR and TAR which may explain the higher affinity of PAN and TAN for the PEG-rich phase). The distribution of these molecules, especially PAN and TAN, displays the type of phase affinity that is desired for extractant molecules in ABS; they remain in the PEG-rich phase over the pH range of interest, indicating that the ionization of the molecules does not affect their partitioning.

The ionization constants for these molecules are summarized in Table 2 [29,31]. These molecules act as tridentate ligands and form complexes through the *ortho*-hydroxyl groups, commonly in a 2:1 ratio with the metal ions [25,26,31], although 1:1 ratios also form [28].

Tracer-scale extraction of Ni^{2+} and Fe^{3+} is

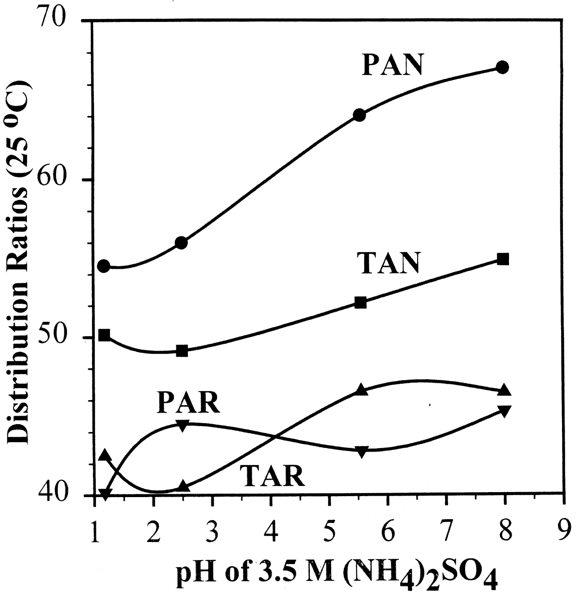

Fig. 2. Distribution ratios of PAN, TAN, PAR and TAR measured in an ABS prepared by mixing 1 ml of 0.1 m*M* extractant in 40% (w/w) PEG-2000 with 1 ml 3.5 *M* $(NH_4)_2SO_4$.

Table 2
Dissociation constants for PAN, TAN, PAR and TAR[a]

Ligand	pK_{NH}	pK_{OH} (*para*)	pK_{OH} (*ortho*)
PAN	1.9	–	12.2
TAN	2.3	–	8.5
PAR	3.1	5.6	11.9
TAR	1.0	6.2	9.5

[a] Data from Ref. [31].

achieved using PAN as an extractant (Fig. 3). Distribution ratios for these metal ions at pH 8 increase from $2.0 \cdot 10^{-3}$ at 10^{-6} *M* PAN to a distribution ratio of 10 at 10^{-4} *M* PAN. The slopes of the *D* vs. [PAN] profile are 1.89 for Ni^{2+} and 1.92 for Fe^{3+} indicating formation of the expected 2:1 PAN–metal ion complex. PAN is an ineffective complexant for the hard alkali metal cation Cs^+ and does not extract this cation.

Figs. 4–7 present the data for extraction of Fe^{3+}, Ni^{2+}, Co^{2+}, Eu^{3+}, Cd^{2+} and Cs^+ from ABS prepared by mixing equal aliquots of 40% (w/w) PEG-2000 (0.1 m*M* in extractant) and 3.5 *M* $(NH_4)_2SO_4$ with PAN (Fig. 4), TAN (Fig. 5), PAR (Fig. 6) and

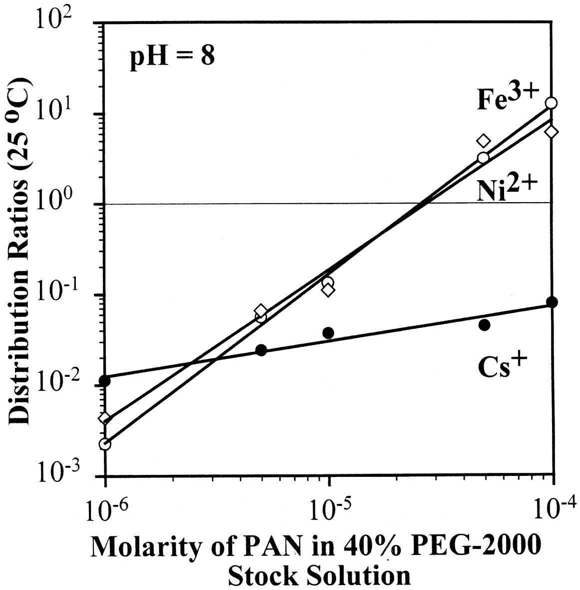

Fig. 3. Distribution ratios for Cs^+, Ni^{2+} and Fe^{3+} measured in an ABS prepared by mixing 1 ml of 0.1 m*M* PAN in 40% PEG-2000 with 1 ml of 3.5 *M* $(NH_4)_2SO_4$ to give a salt-rich phase pH of 8. PAN concentrations refer to those prior to contact with the salt stock solution.

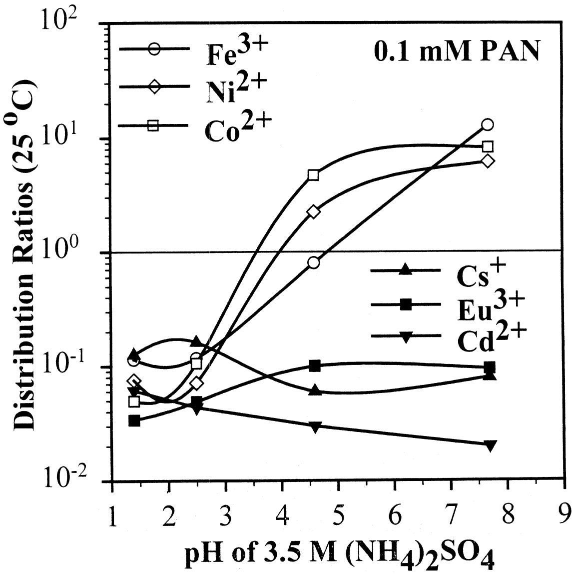

Fig. 4. Metal ion distribution ratios measured in an ABS prepared by mixing 1 ml of 0.1 m*M* PAN in 40% PEG-2000 with 1 ml of 3.5 *M* $(NH_4)_2SO_4$ ABS. The pH values indicated were measured after for the salt-rich phases after the ABS had been formed.

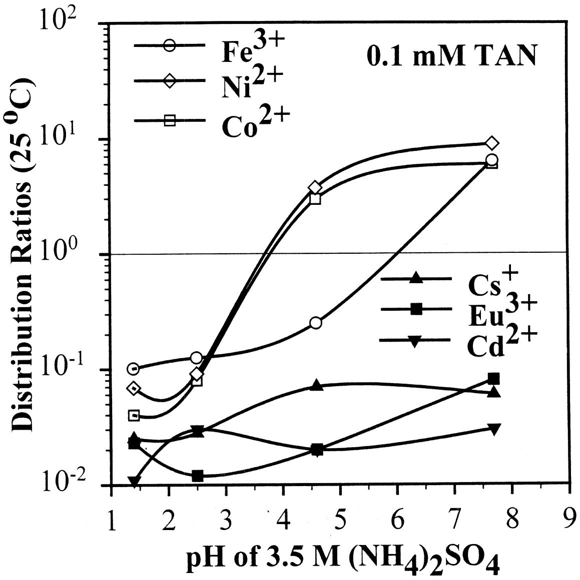

Fig. 5. Metal ion distribution ratios measured in an ABS prepared by mixing 1 ml of 0.1 m*M* TAN in 40% PEG-2000 with 1 ml of 3.5 *M* $(NH_4)_2SO_4$ ABS. The pH values indicated were measured for the salt-rich phases after the ABS had been formed.

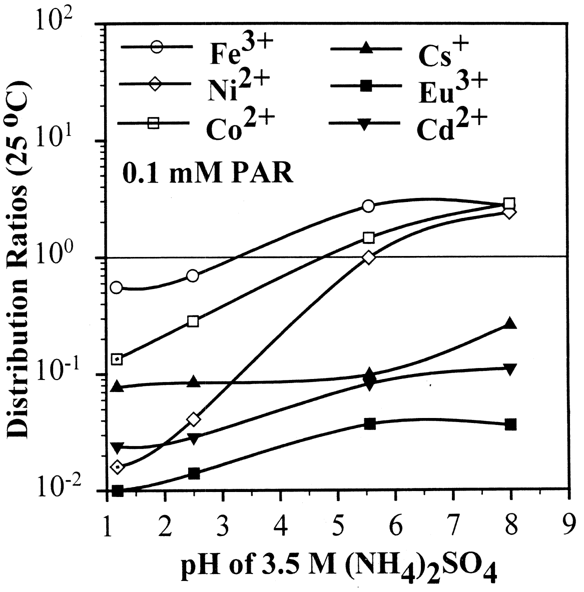

Fig. 6. Metal ion distribution ratios measured in an ABS prepared by mixing 1 ml of 0.1 m*M* PAR in 40% PEG-2000 with 1 ml of 3.5 *M* $(NH_4)_2SO_4$ ABS. The pH values indicated were measured for the salt-rich phases after the ABS had been formed.

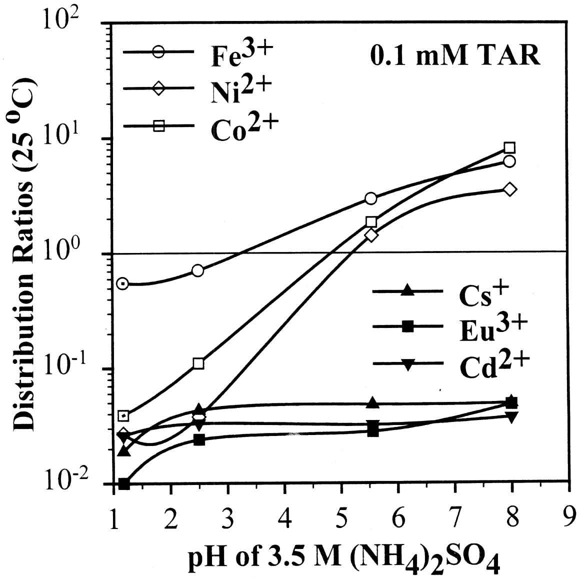

Fig. 7. Metal ion distribution ratios measured in an ABS prepared by mixing 1 ml of 0.1 m*M* TAR in 40% PEG-2000 with 1 ml of 3.5 *M* $(NH_4)_2SO_4$ ABS. The pH values indicated were measured for the salt-rich phases after the ABS had been formed.

TAR (Fig. 7) in the PEG stock solutions. The data show little difference in the extractants used, we will thus focus on one of these, PAN. PAN effectively extracts Fe^{3+}, Ni^{2+} and Co^{2+} at high pH, but with little selectivity. The larger ion Cs^{+}, Eu^{3+} and Cd^{2+} are not extracted at any pH. For the metal ions extracted, the similarity to traditional solvent extraction technology is striking. The metal ions can be loaded to the PEG-rich phase at high pH and stripped at low pH.

The most marked difference between the results in ABS and what has been reported in the literature for traditional solvent extraction is the poor extraction of lanthanides (exhibited by Eu^{3+}) observed in ABS with these extractants. Gao et al. [25] report the solid–liquid extraction of lanthanides at pH 7.8 with 0.005 *M* PAN in paraffin with cresin and *D* values of ~4 for Sm^{3+} although the heavier Ln^{3+} had better extraction than the lighter lanthanides. Other studies [23] have reported quantitative extraction of rare earth elements with PAN at pH values higher than 8.

Facchin and Pasquini [24] utilized a monosegmented flow system to perform liquid–liquid separation with 75% extraction of Cd^{2+} with 0.25% PAN in chloroform at an aqueous pH of 9.9. Other work [22] has shown 100% uptake of Ni^{2+} as a PAN complex at pH~7. TAN, at a concentration of 0.2%, has been shown to quantitatively extract Ni^{2+} from pH 4–10 [30]. PAR has been reported to be a good complexing agent for Ni^{2+} and Co^{2+} in alkaline solutions [26] where the maximum pH for extraction is 6–8. The traditional liquid–liquid results and ABS extraction are similar in that the most efficient extractions occur at a pH where the molecule is sufficiently ionized.

It is particularly interesting to note that for Fe^{3+}, Co^{2+}, and Ni^{2+}, the distribution ratios increase as the extractant molecules become more ionized, showing the role of the nitrogen and oxygen heteroatoms in the metal ion chelation and attests to the strong interactions of those molecules with the small, highly charged cations. Stripping of the metal ions from the PEG-rich phase may be facilitated in these systems simply via a change in the salt-rich phase pH.

The distribution ratios for the other cations remain below one, indicating their preference for the salt-rich phase despite the presence of extractants. The metal ions that remain in the salt-rich phase are larger and tend towards higher coordination numbers [34]. The presence of additional water molecules that are not displaced by the coordination of the molecules around the metal ions could prohibit effective partitioning out of the salt-rich phase.

There are few differences between the extractant molecules studied here with respect to the resulting metal ion *D* values, although the chemistry of the molecules differs in a few respects. The water solubility is increased for the molecules with a resorcinol ring instead of a naphthol group [31]. As extractants, the thiazolyl group is less basic than the pyridyl group and suggests that those metal–ligand complexes would be weaker than the corresponding pyridyl analogues, although the observed *D* values are similar here. The chemistry of the ligand appears to have little influence on the maximum *D* values obtained in these systems.

The distribution ratios for the first row transition metals are much higher than those for other metal cations. The rationale for that behavior could be attributed to their complexation constants, shown in Table 3 [35,36], although several of the K_n are of the same order of magnitude regardless of whether they are extracted (e.g., $Eu^{3+} >$ vs. Ni^{2+} with PAN). This type of behavior suggests the potential for selective extraction of certain metal ions from a complicated matrix, however, more detailed information on speciation of extracted moieties is clearly needed.

Table 3
Complexation constants for the extractant and transition metal cations used in this study

Dye	Metal ion	Log K_1[a]	Log K_2[a]
PAN	Ni^{2+}	12.7	12.6
	Co^{2+}	>12	12.01
	Eu^{3+}	12.39	11.59
TAN	Ni^{2+}	8.5	8.3
	Cd^{2+}	9.18	8.70
	Co^{2+}	9.50	9.40
	Eu^{3+}	9.56	9.26
PAR	Ni^{2+}	13.2	12.8
	Cd^{2+}	10.5	
	Co^{2+}	10.0	7.1
TAR	Ni^{2+}	12.94	11.82
	Cd^{2+}	7.0	16.0
	Co^{2+}	12.05	11.23

[a] Data from Refs. [31,35,36].

4. Conclusions

ABS have established their utility in novel separation technologies and offer similar physical properties and also important differences from traditional liquid–liquid separations employing VOCs as the extracting phase. The chief distinction associated with ABS is the formation of wholly aqueous biphasic systems without the use of organic solvents. However, as in traditional liquid–liquid systems, the addition of a metal ion extractant is necessary and, as shown in this report, molecules that partition to the PEG-rich phase can simultaneously function as metal ion extractants through the incorporation of certain functional groups. In ABS formed by mixing 40% (w/w) PEG-2000 and 3.5 *M* $(NH_4)_2SO_4$, the distribution ratios of Fe^{3+}, Co^{2+} and Ni^{2+} were enhanced several orders of magnitude in the presence of PAN, TAN, PAR and TAR at a pH where the molecules were partially ionized. In contrast, the distribution ratios of Cs^{+}, Cd^{2+} and Eu^{3+} were largely unaffected by the presence of these extractants in similar systems.

The partitioning of these cations in ABS warrants further consideration and study since there are several system parameters that can be fine-tuned to increase the distribution ratios. An increase in the system temperature, PEG concentration, or salt concentration would act to increase the phase divergence and effectively enhance the partitioning such that the molecules that have an affinity for the PEG-rich phase would experience a heightened affinity for that phase [15]. Conversely, using a salt-rich phase that attains a higher pH (e.g., 4 *M* NaOH) would suffice to completely deprotonate the extractant molecules and result in higher distribution ratios for the metal ions. Thus, the selectivity of PAN and the other extractants for the small metal cations could be increased. The basis for liquid–liquid extraction can be extended to ABS, but with the important distinction and novelty associated with a purely aqueous system.

Acknowledgements

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