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Separation and recovery of food coloring dyes using aqueous biphasic extraction chromatographic resins

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Abstract

Aqueous biphasic systems (ABS) and aqueous biphasic extraction chromatographic (ABEC) resins are currently under investigation for their utility in the removal of color from textile plant wastes. The structures of several widely used food colorings, suggest that these dyes would also be retained on the resins. In work currently in progress, we have begun to investigate the retention and resolution of several common food colorings including indigo carmine, amaranth, carminic acid, erythrosin B, tartrazine and quinoline yellow. The relationship between the uptake of these dyes on ABEC resins in terms of the binding strengths and capacities of the resins and their partitioning behavior in ABS is illustrated. Some possible theoretical and practical approaches to the prediction of the partitioning and retention behavior is discussed.

Keywords: Partitioning; Aqueous biphasic systems; Food coloring dyes

1. Introduction

Observations on the partitioning of pigmented materials have a long history in aqueous two-phase partitioning, yet specific application to this end has been rather infrequent. In 1954, Albertsson noticed the partitioning of chloroplasts in a poly(ethylene glycol) (PEG)–salt aqueous biphasic system (ABS) on elution of the bound material from hydroxyapatite [1]. In the 1970s and 1980s, the work of Hustedt et al., [2] on protein extractions demonstrated the strong preference for certain intracellular pigmented materials for the PEG-rich phase of PEG–salt ABS. Observations by Diamond et al. [3] of the strong preference of tryptophan, almost alone among the common amino acids, for the PEG-rich phase led to the development of 'affinity handles' by Köhler et al. [4] which exploit the strong tendency of tryptophan to partition to the PEG phase. Tryptophan is not usually considered a pigment but it has in common with pigments a highly conjugated aryl ring structure, which gives it a characteristic UV absorbance at 280 nm. This feature is also characteristic of the vast majority of man-made and natural pigments, which can, therefore, with some confidence, be predicted to show high preference for the PEG-rich phase in ABS. This is confirmed by our recent work on the recovery of textile dyes and metal dye complexes [5,6]. The fact that ABS seem not to have been exploited previously for the separation, recovery, and analysis of pigments is thus somewhat surprising.

Dyes and pigments, including colorless dyes in the form of fluorescent brighteners, are a major industrial commodity [7] throughout the world. Concern over the discharge, the environmental fate, and the fate of their ultimate breakdown products, makes

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Table 1
Currently permitted US and EC food coloring dyes [9]

Dye	EEC number	FDA number	Water solubility (g/100 ml)
Erythrosin	E123	FD&C Red No. 3	9[b]
Brilliant blue FCF	–	FD&C Blue No. 1	20[b]
Indigotine	E132	FD&C Blue No. 2	1.6[b]
Tartrazine	E102	FD&C Yellow No. 5	20[b]
Quinoline yellow	E104	FD&C Yellow No. 6	14[a]
Allura red	–	FD&C Red No. 40	22[b]
Yellow 2G	E107		
Ponceau 4R	E124		30[a]
Carmoisine	E122		8[a]
Amaranth	E123	FD&C Red No. 2	5[a]
Red 2G	E128		
Patent blue	E131		6[a]
Green S	E142		5[a]
Brown FK	E154		
Chocolate brown HT	E156		20[a]
Brilliant black PN	E151		5[a]

[a] 16°C
[b] 25°C.

the improved waste management of these products an urgent concern [8]. Food dyes form a small subgroup of this large class of industrial chemicals [9]. A number of the currently permitted dyes are listed in Table 1 and some of their structures are presented in Fig. 1. Because these dyes are relatively water soluble and nontoxic, they form a convenient experimental vehicle with which to address aspects of the theoretical and predictive modeling associated with the recovery of organic chemicals utilizing ABS. Such studies will be of considerable value in extending our attempts to apply aqueous biphasic extraction technology [10–12] to important industrial separations problems including, inter alia, the recovery of textile dyes and other industrial and naturally occurring pigments, porphyrins, PCBs and metal ions through complexation with small organic molecules.

2. Experimental

2.1. Materials

Poly(ethylene glycol) and ammonium sulfate were of reagent grade and obtained from Aldrich (Milwaukee, WI, USA). The dyes indigo carmine, amaranth, carminic acid and quinoline yellow were also obtained from Aldrich. Tartrazine and erythrosin B were obtained from Sigma (St. Louis, MO, USA). All solutions were prepared in distilled and deionized water (Barnstead, Dubuque, IA, USA).

2.2. Dye concentration assay

Concentration of the dyes was determined by spectrophotometric adsorption following the preparation of suitable standard curves at the wavelength of maximal adsorption of the dye in the visible region. This wavelength was determined by wavelength scanning over the region 200 to 900 nm using a Cary 3 spectrophotometer. Single wavelength determinations of absorbance were performed using the Cary 3 or a Milton Roy Spec 21 spectrophotometer. There was no detectable difference between the concentrations of dye solutions determined on the two instruments.

2.3. Determination of dye solubility and partitioning behavior

Solubility of the dyes was determined by direct addition of 40% w/w $(NH_4)_2SO_4$–water and concentrated dye solution in water to the final desired concentration between 0 and 32% w/w $(NH_4)_2SO_4$.

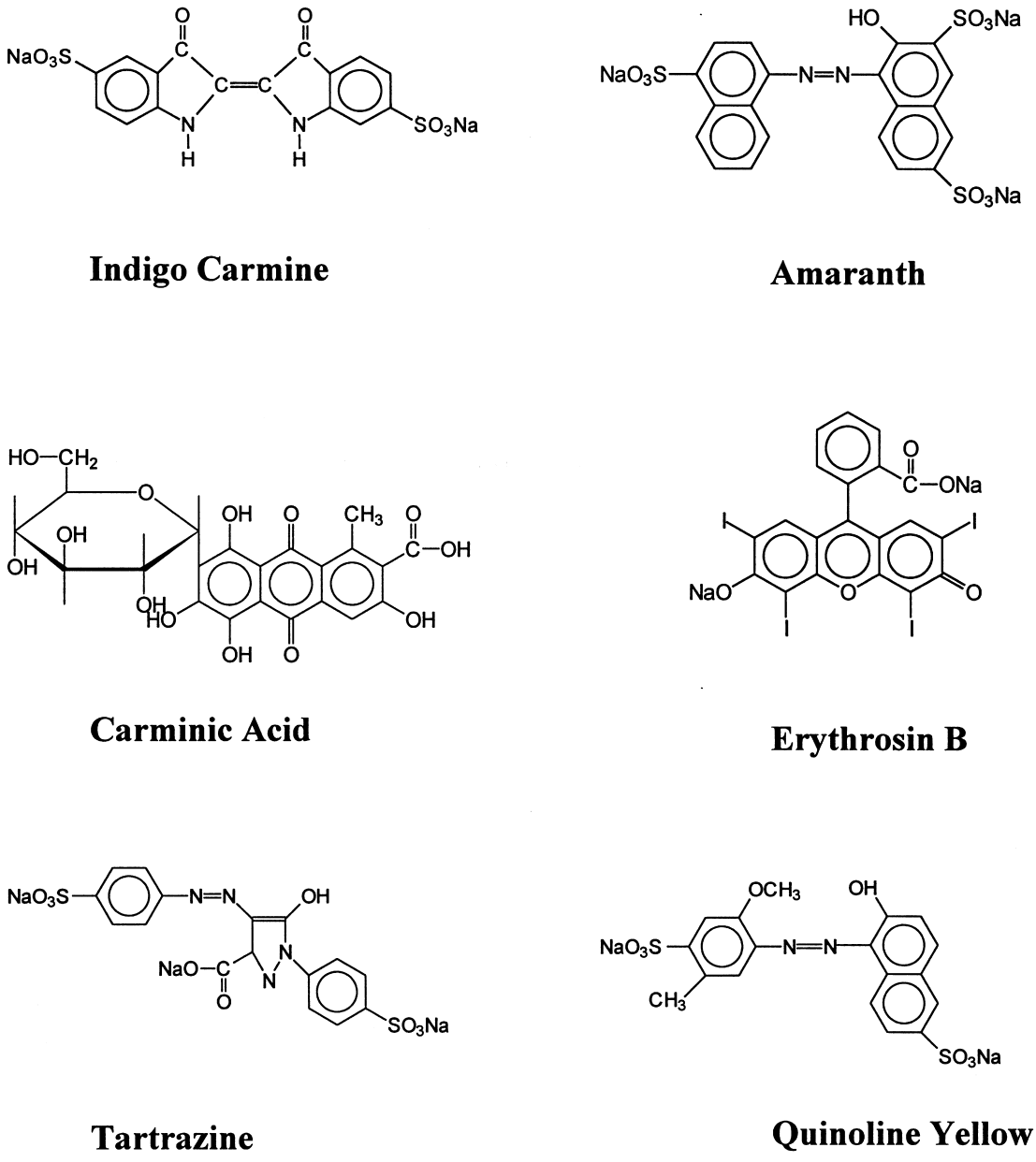

Fig. 1. Structures of some common food colorings.

The dyes were partitioned in PEG-2000–$(NH_4)_2SO_4$ ABS at increasing tie line length and the concentration in each separated phase determined as noted above. A phase diagram was prepared and the tie lines fixed from knowledge of the relationship between volume ratio and the overall composition of the system [13]. Particular systems were mixed by volume from 40% w/w solutions of $(NH_4)_2SO_4$ and PEG by taking into account the density of these solutions. Total system volumes were always 10 ml and the equilibrium temperature was kept at 25°C by means of a thermostatically controlled water bath.

2.4. Solid-phase adsorption of dyes

Adsorption studies on aqueous biphasic extraction chromatographic (ABEC) resin [10–12] followed a variation of the methodology of Chase [14]. Here the amount of adsorbent added, rather than the concentration of adsorbate, was varied because of the limited solubility of the dyes in $(NH_4)_2SO_4$ solution. A 20-ml sample of the dye at a concentration which varied between 0.1 mg/ml and 1 mg/ml depending on the solubility of the dye, was used. The adsorbent concentration was varied between 5 and 50 mg in 2.5 or 20 ml of solution based upon the affinity of the dye for the adsorbent. The concentration of dye in the supernatant, following mixing for 1 h, was determined by removal of the adsorbent by filtration using a 0.45-μm pipette tip filter. (Prior to use, the ABEC resin was extensively washed with 30% w/w $(NH_4)_2SO_4$ on a Whatman qualitative filter paper, since it was found that a subfraction of the particles was able to pass this filter, despite the fact that the bulk of the particles were found to have a nominal diameter between 70 and 150 μm, as determined visually by microscopy.) The resin was then pressed dry with filter paper and its dry mass subsequently obtained thermogravimetrically by drying to constant mass at 100°C [12]. From the supernatant concentration, the amount bound at equilibrium could be found. The equilibrium time was established using a time course of Amaranth binding and was found to be essentially complete in under 10 min. Adsorption isotherms were constructed from which capacities and binding constants could be obtained [14].

3. Results and discussion

The solubility of a number of common food dyes in concentrated $(NH_4)_2SO_4$ solutions is shown in Fig. 2 as the log of the initial concentration over the final concentration of the dye. The starting concentration was in all cases close to 1 mg/ml except for indigo carmine where the initial concentration was 0.4 mg/ml due to its limited solubility even in pure water. It can be seen that only tartrazine and amaranth are soluble over the whole range of $(NH_4)_2SO_4$ concentrations. Erythrosin B and quinoline yellow show reduced solubility above 10% w/w $(NH_4)_2SO_4$ and the solubility of indigo carmine is extremely low over the whole range.

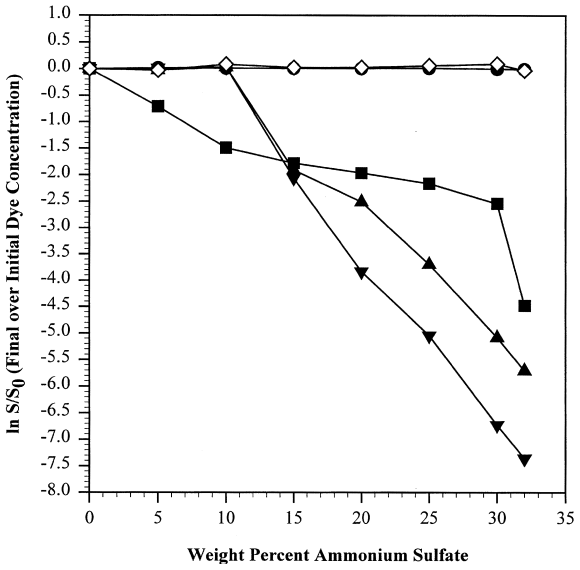

Fig. 2. Solubility of some food colorings in ammonium sulfate: (■) indigo carmine; (●) amaranth; (▲) erythrosin B; (▼) quinoline yellow; (◇) tartrazine.

The solubility of the solute in salt is important for a number of reasons. In particular, it may strongly affect its partitioning behavior [15] and in the context of adsorption systems, such as ABEC, may determine the mode of operation since the presence of precipitated material would recommend batch contacting or expanded bed modes of operation over packed beds.

The partitioning behavior of erythrosin B in a PEG-2000–$(NH_4)_2SO_4$ ABS is shown in Fig. 3. The almost wholly quantitative partitioning of this dye into the PEG-rich phase is immediately apparent. Even at the shortest tie line length (15% w/w) the partition is extremely one-sided. While from an extractive point of view this is very favorable, from a modeling perspective this is inconvenient. Table 2 shows the partition coefficients obtained at a tie line length of 15% w/w in the PEG-2000–$(NH_4)_2SO_4$ system for a number of the common food dyes. The absolute values are difficult to reproduce and considerable uncertainty is attached to them. In large part, this is due to the sensitivity of the partition at short tie line length to external factors such as temperature, coupled to the great disparity in the concen-

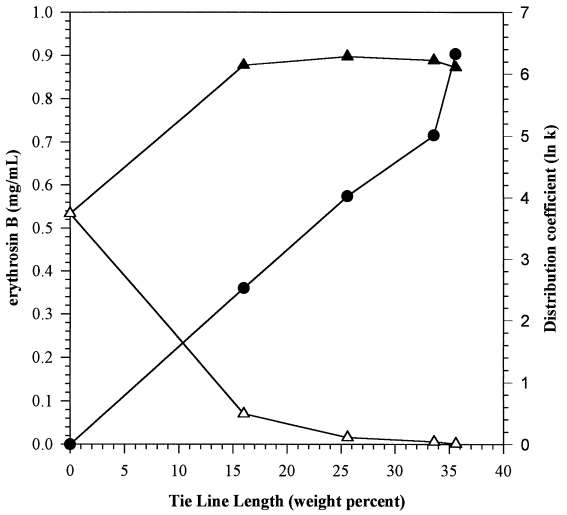

Fig. 3. Partition of erythrosin B in PEG-2000–$(NH_4)_2SO_4$ ABS: (▲) [c] mg/ml top phase; (Δ) [c] mg/ml bottom phase; (●) ln *k*.

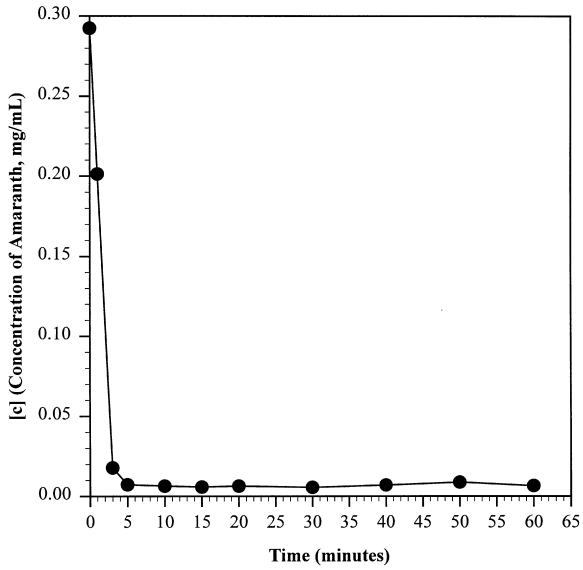

Fig. 4. Time course of binding of amaranth to ABEC resin. Initial conditions: 0.041 g ABEC resin in contact with 2.5 ml amaranth (0.29 mg/ml) in 20% w/w $(NH_4)_2SO_4$.

tration found in each phase. In effect, all the solutes are found to have a similar partition coefficient and it is difficult to relate the results to molecular structure as may be judged by comparison of Table 2 with Fig. 1.

A simple kinetic experiment for the binding of amaranth to the ABEC resin is shown in Fig. 4. Uptake of these small organic molecules is essentially complete within about 10 min. This is a valuable result as it represents an important design parameter both for investigative experiment and practical operation.

Results of a typical adsorption experiment to determine the equilibrium capacity and the dissociation constant for the interaction between the dye and the ABEC adsorbent is shown in Fig. 5. This example shows the binding of amaranth to the ABEC resin at a concentration of 15% w/w $(NH_4)_2SO_4$. Fig. 5a shows the experimentally determined isotherm and Fig. 5b shows a rearrangement of this data which simplifies the determination of the binding capacity and the dissociation constant of this binding reaction from the slope and intercept of the plot of C^*/Q^* against C^* [14]. In Fig. 5b, Q^* and C^* are, respectively, the equilibrium concentrations on the adsorbent and in solution. This is typical of the results which may be obtained for pure soluble dyes, but differs markedly from the behavior of impure multicomponent systems as may be represented by, for instance, waste streams or streams for purity upgrading.

Table 2
Distribution of food coloring dyes in ABS and on ABEC resins

Food dye	ln D^a	Proportional uptake	log D_w^b
Carminic acid	1.40	0.282	3.09
Amaranth	2.43	0.486	3.47
Indigo carmine	2.23	0.450	3.41
Erythrosin B	2.46	0.995	5.82
Tartrazine	2.13	0.669	3.80
Quinoline yellow	2.25	0.970	5.00

[a] ABS.
[b] ABEC.

Fig. 6 shows the binding of amaranth to the ABEC resin in terms of the strength of the association (K_d) and the maximal capacity as a function of the $(NH_4)_2SO_4$ concentration of the equilibrium solution. For amaranth, it appears that the onset of significant binding occurs at very low salt concentration and that thereafter the dissociation constant and maximal capacity are a simple linear function of the salt concentration up to 32% w/w $(NH_4)_2SO_4$. Most recently, we have found that for dyes of limited solubility, uptake to the resin may be

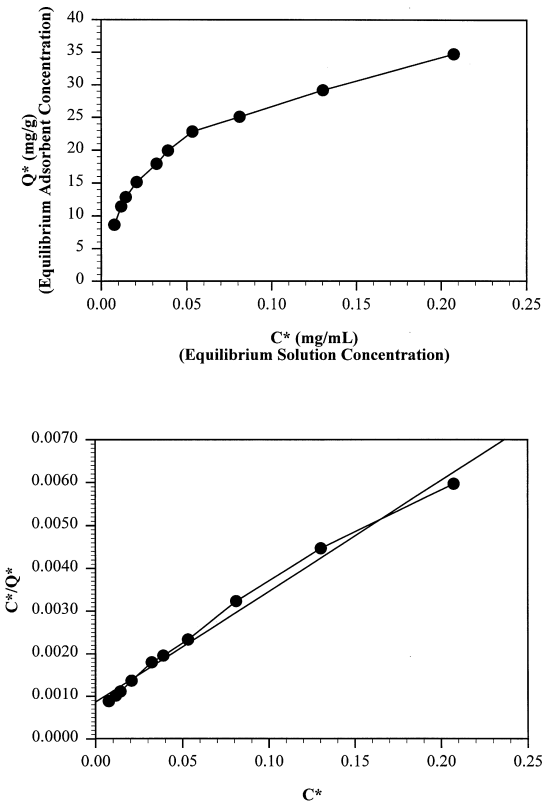

Fig. 5. (a) Adsorption of amaranth on ABEC resin from 15% w/w $(NH_4)_2SO_4$. (b) Rearrangement of the data to obtain the dissociation constant ($K_d = 1.41 \cdot 10^{-3}$ M) and maximal capacity ($Q_m =$ 30.35 mg/ml).

improved by performing adsorption in the presence of insoluble dye thereby maintaining the highest possible final equilibrium concentration. This is analogous to certain dyeing processes using dispersed dyes [16].

Finally some deficiencies in the current approach are worth highlighting. Table 2 shows the results of a comparative binding experiment with the ABEC resin in which approximately 0.03 g of resin was contacted with a constant initial concentration of each dye of 0.5 mg/ml in 20% w/w $(NH_4)_2SO_4$ solution. D_w in this table is given by:

$$D_w = \frac{C_i - C_f}{C_i} \frac{\text{contact volume}}{(\text{resin mass} \cdot \text{dwcf})} \quad (1)$$

where C_i and C_f represent the initial and final

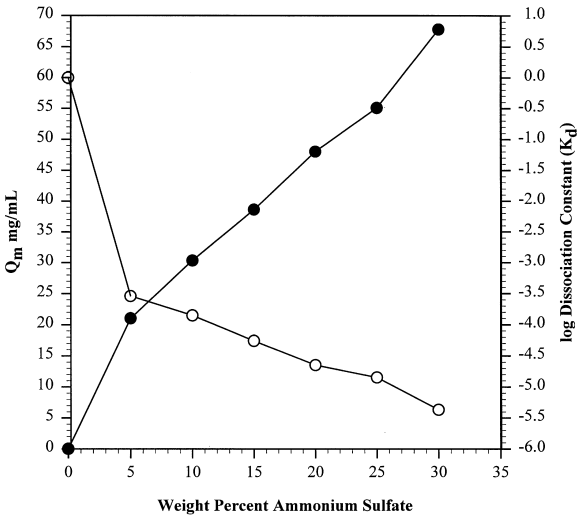

Fig. 6. Binding of amaranth to ABEC resin in $(NH_4)_2SO_4$: ● maximal capacity; ○ log K_d.

concentration of the dye and dwcf, the dry weight conversion factor, is given by:

$$\text{dwcf} = \frac{\text{mass dehydrated resin}}{\text{mass wet resin}} \quad (2)$$

D_w is, self evidently, a function of the proportion removed from the solution as shown in the table. The results are very encouraging for the application of ABEC resin to the recovery of the dyes, however, there is seemingly little connection between the adsorption efficiency of the resin and the measured partition coefficient in a liquid–liquid system. Further clarification of this unsatisfactory situation is a matter of current concern.

4. Conclusions

Quantitative partition of food coloring dyes in ABS and to ABEC resins has been demonstrated which recommends these techniques to a variety of applications including the analysis, purification, recovery, and recycling of similar small organic molecules. Currently, it is difficult to relate the observed behavior of the dyes in these systems to the details of their molecular structure. This is an important requirement, which would enable the prediction of the

behavior of other suitable small organic species of industrial and environmental importance. A number of different theoretical approaches to this problem readily suggest themselves.

Firstly, the molecular size and complexity of these dyes is sufficiently limited that their *c*log *P* values (calculated octanol–water partition coefficients) may be calculated by group contribution methods [17]. These may then be related to ABS partition by simple linear function [18]. Additionally, the thermodynamic cycle for different molecules A and B:

$$\begin{array}{ccc} A_{(aqueous)} & \xrightarrow{\Delta G_3} & B_{(aqueous)} \\ \downarrow{\scriptstyle \Delta G_1} & & \downarrow{\scriptstyle \Delta G_2} \\ A_{(organic)} & \xrightarrow{\Delta G_4} & B_{(organic)} \end{array} \quad (3)$$

may be used to obtain the difference in log *P* in aqueous–organic systems. The free energy of solvation (ΔG) may be computed by quantum mechanical calculation, for instance using AMSOL [19], then from the relationship [20]:

$$-2.303RT\Delta\log P = \Delta G_1 - \Delta G_2 = \Delta G_3 - \Delta G_4 \quad (4)$$

the difference in log *P* from that of a selected reference species may be obtained.

Finally solvatochromic approaches to LSER (linear solvent free energy relationships) [21] may be attempted in which the bathochromic shift in the UV–Vis adsorption spectra of betaine dyes should allow the direct comparison of the physicochemical properties of ABS to other solvent systems. In this way it may be possible to predict the replacement of current aqueous–organic extraction schemes by suitably tuned ABS and ABEC processes. However, it must be admitted at the outset that we can never hope to mimic the entire range of solvent systems (amphiprotic, proton donor, proton acceptor and neutral or inert) in a single wholly aqueous system [18].

Acknowledgements

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